

**CHEMICAL AND ANALYTICAL ASPECTS OF
THE EARLY ALKALI AND BLEACHING
INDUSTRIES IN BRITAIN**

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ABSTRACT

CHEMICAL AND ANALYTICAL ASPECTS OF THE EARLY BLEACHING INDUSTRIES IN BRITAIN

by

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Chemical analysis is a continuous thread in the history of chemistry. This thesis, which concentrates on the period from the mid-eighteenth century until the time of the Alkali Acts of the 1860s, assesses the role of chemical analysis in terms of developing methodology, its adoption during what has become known as the industrial revolution, and especially its contextual setting within the early alkali and bleaching industries. The thesis traces the development of volumetric analysis from its early beginnings to the time when standard solutions became the accepted means of measuring an unknown component in the process of titrimetry.

The research has focused on a range of industrial entrepreneurs (Lewis, Watt, Macintosh, Crum, Keir, Clark, Ure and Griffin) who pursued economic rewards by the application of chemical knowledge, and shows how their intuitive and innovative practical efforts created the means by which their chemically based processes could be controlled and nurtured by analytical means. Simple though some of these methods now seem, nevertheless they satisfied the technical and commercial needs of the period. One standard test, using indigo blue, has been shown to have developed into a routine method that allowed the growing demand for textiles to be met.

The thesis concludes that industrial chemists and chemical consultants were successful in their analytical methods without depending upon a knowledge of atomic weights or chemical equations. The exploitation of simple measurements, and the quantitative relationships between reactants and the products of reactions, provided information and a set of technical resources sufficiently useful for the control and management of raw materials, purchasing, and quality control of saleable products.

PREFACE

When I began this study I believed firmly that reliable quantitative analysis could only be performed when based upon the following data:

1. A theoretical understanding of the reaction(s) involved, usually represented by a chemical equation.
2. A knowledge of atomic and molecular weights. This information makes it possible to calculate the amounts of reactants and reaction products, assuming pure materials.

In the first half of the present century, many industrial laboratories used analytical methods based on the above knowledge. To many chemists of that period, an understanding of the chemical reaction and the atomic weights of the elements involved were sufficient data from which to design an analytical method. Furthermore it was almost commonly accepted that analysis depended on such data and was not possible without them. Student examination questions reinforced this perspective:

Name the elements in the following compounds, and give the amounts of each present:-
 H_2O , CaCO_3 , NaOH , NH_4OH , $\text{C}_{17}\text{H}_{33}\text{COONa}$. Calculate the percentage composition of the compounds given.¹

Therefore, to begin a research project about analytical chemistry in a period when neither of the above aspects had come into being may appear ill-conceived; it should be noted however, that the early industrial revolution did not wait for the discoveries of Lavoisier and Dalton. Neither did analytical chemistry.

ACKNOWLEDGEMENTS

I am indebted to the staff of many libraries and institutions throughout the United Kingdom and Ireland, in particular the Central Libraries of Manchester and Birmingham. The University Libraries of Leicester, Liverpool, Manchester, Edinburgh, the National Library of Scotland and Trinity College, Dublin, have also proved invaluable. Help from the many individuals on which this research depended is hereby recognised. My special thanks are given to Dr. Richard Hills (UMIST) regarding the James Watt archives and I would like to thank all those who have so kindly answered my many letters of enquiry. I shall remain indebted to Dr. David Edwards of Liverpool University for his continual encouragement and practical help and for directing me into the exceptional supervisory hands of Professor W. H. Brock of Leicester University.

¹ Jones, R. H. *Laundry Chemistry* (Manchester, 1914), p. 20.

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INTRODUCTION

This study is about chemical analysis in the period 1750 to 1860s when quantitative analytical measurement began to occur in a form recognisable by present day chemists. For over half of this period aspects of analysis such as atomic weights and formulae, which we now regard as essential, had not come into being. It was anticipated that during this period it might be possible to trace the better understanding and refinement of analysis in areas supporting industries dependent upon chemical raw materials. This has been shown to be the case. Furthermore it was hoped to show that new analytical conceptions occurred following the discoveries and ideas of Lavoisier and Dalton. There is a temptation for present day chemists to regard the period as one in which quantitative chemical analysis seemed almost impossible in the absence of reliable atomic weights and chemical formulae on which we have become dependent. This thesis shows that the development and use of analysis was usually adequate for the needs of the industries of the period.

An important aim throughout this research will be to explore the ways in which the industrial context shaped industrial analysis. This is evident throughout the entire period, beginning with some early analysts involved with alkali made from kelp, through to the influential demands of the Alkali Acts. Conversely it will be argued that analysis, to some extent, shaped industry as is evidenced by the necessity of analytical control in chlorine bleaching. In order to strengthen these arguments the difference between industrial and academic analysis will be examined. The early analysts of alkali made from kelp were both academic and industrial chemists, but it will be shown that over the period covered by this thesis industrial analysis fell more to the entrepreneurs such as Keir, Crum and Mercer and other managers of the new chemical and bleaching industries. Academics saw analysis as a means of proving chemical theory, whereas industry needed analysis in a service role. By considering the relations between industrial analysis and the conceptual context provided by the chemical theory of the time, it is hoped that the apparent adequacy of the industrial analytical techniques will be confirmed.

Many of the analyses assessed in this research have been drawn from published papers by the analyst being considered, or from original unpublished sources where these have been discovered, for example the newly acquired Watt archives at Birmingham and Dalton's analysis of Buxton water. Original laboratory notebooks from the past have clearly not been regarded as worthy of preservation, a sentiment held today particularly where developments are quickly changing; some dependence on secondary material from reliable sources and texts has therefore been necessary.

In keeping with the title of this thesis the main objective has been to identify from original sources, wherever possible, the methods of chemical analysis used in, and the analytical influences on, two important and related industries within the chosen period. An attempt has been made to trace practical chemical analysis - often in the form of volumetric analysis - through these two industries, and those chemists engaged in developing and using these methods.

No previous writer has attempted this. The only wide-ranging historical assessment of chemical analysis is in the book by Szabadváry (1966),¹ on which an essay review by Brock provides a useful commentary.² It should be noted, however, that Szabadváry was not focusing specifically on analysis in its industrial context, and his claim that 'all important new results in chemistry were preceded by the suitable development of analytical methods'³ could not be made of industrial analysis, as my thesis will clearly show.

Edmund Rancke Madsen's *The Development of Titrimetric Analysis till 1806*⁴ has been found useful within the imposed time span but his 'Experimental Testing' devoted to certain historical analytical processes must be questioned in the absence of contemporary data regarding purity of substances, accuracy of weighing etc.⁵ Madsen made no conscious attempt to relate his text with particular industrial settings, but his focus on titrimetry or volumetric analysis includes the work of Black, Geoffroy, Lewis, *et al* who are similarly considered in this thesis. The evolution of the methods and apparatus used in volumetric analysis is described by Christophe,⁶ whose article shows the useful industrial application of this form of analysis in the period 1790 to 1860.

Of the existing published texts to which frequent reference has been made, *The Chemical Revolution* of Archibald Clow and Nan Clow has been of particular value in connection with the Scottish kelp industry as a source of natural alkali.⁷ In this work there is little reference to analytical chemistry although Tennant's method of estimating barilla is given as an example of volumetric analysis.⁸ A full critical review of this book was given by Gibbs who confirmed the Clows' view that the growth of eighteenth-century chemistry paralleled a corresponding growth of chemical manufacturing.⁹

Another source of secondary material is by A. E. Musson and Eric Robinson who appreciated the value of analytical chemistry in their re-evaluation of the Industrial Revolution particularly in treating the introduction of chlorine into bleaching, and the work of chemists to produce alkali from sources other than kelp and barilla.¹⁰ Whilst they show the use and influence of 'science' on the industrial revolution there is no focus on the part played by practical analysis although space is given to William Lewis and the Society of Arts, the significance of which appears later in this thesis.¹¹

One question constantly held in view throughout this study has been, if atomic weights were not available, how did early chemists meet the analytical demands of the new chemically based industries?

¹ Szabadváry, F. *History of Analytical Chemistry* (Oxford, 1966).

² Brock, W. H. 'An Attempt to Establish the First Principles of the History of Chemistry', *History of Science*, 6 (1967), pp. 156-169.

³ Szabadváry, *op. cit.* (1), vii.

⁴ Madsen, E. Rancke, *The Development of Titrimetric Analysis till 1806* (Copenhagen, 1958).

⁵ *Ibid.* Madsen applied experimental testing to some of the analytical methods discussed but made little reference to aspects of purity and weighing.

⁶ Christophe, R. 'L'analyse volumétrique de 1790 à 1860 Caractéristiques et importance industrielle. Évolution des instruments', *Revue d'Histoire des Sciences*, 24 (1971), pp. 25-44.

⁷ Clow, A. & Clow N. L. *The Chemical Revolution* (London, 1952), chap. III, IV & IX

⁸ *Ibid.* p. 80.

⁹ Gibbs, F. W. 'Prelude to Chemistry in Industry', *Annals of Science*, 8 (1952), pp. 271-81, a review of the Clows' *The Chemical Revolution* (1952).

¹⁰ Musson, A. E. & Robinson, E. *Science and Technology in the Industrial Revolution* (Manchester, 1969).

¹¹ *Ibid.* pp. 53-4.

To answer this, the research has centred on the two main subjects of alkali and the textile industry on the assumption that these would need chemical analysis for their continuing expansion.

The few original analytical sources available have been examined and have shown that even in the absence of atomic weights and established chemical equations or formulae, analyses were carried out by intelligent and careful manipulation of simple laboratory apparatus and techniques. Indeed in a later chapter it may appear that chemical analysis evolved satisfactorily without Lavoisier and Dalton and perhaps would have continued to do so. One area of analysis which barely came into being, that of mixing volumetric and gravimetric means, was clearly overtaken by atomic quantification and is now largely forgotten.

Empirical observations such as smell, taste and appearance were taken as reliable tests of quality; the development from these to actual chemical tests was probably seen as a mere extension and confirmed a growing belief that empiricism always led to success. The development of analytical techniques shown throughout this thesis confirms only in part Musson's and Robinson's belief that practical empiricism was largely responsible for technical advancement.¹² The analytical progress shown in this study generally supports Morrell's interpretation that 'science and industry intersected from time to time but that the instances of intersection were few'.¹³

In the following chapters evidence is given that the history of chemical analysis involved both 'doing' and 'knowing' but the latter, whether arising from Lavoisier or Dalton, found no immediate application because of entrenched empiricism. The practical craftsmanship, frequently identified within this thesis, beginning with Francis Home and extending to the work of Smith and Fletcher in implementing the Alkali Acts, supports Mathias's view¹⁴ that innovations were not so much the result of applied science as the practical craftsmanship of often anonymous untrained artisans. He also argues that the contribution of science towards industrial innovation was more through its methods than formal knowledge.

The entire thesis is related to the early bleaching industry which depended upon the cleansing properties obtained from alkali solutions. Before the synthetic alkali of Leblanc the industry used 'natural' alkali from kelp and other plant origins. But it is the introduction of chlorine bleaching which lies at the centre of this dissertation and whilst primary source material is sparse I have proved that the 'indigo blue' test was generally used as a quantitative control. It was on this test that the industry depended for safe bleaching, and which allowed its continued expansion. The method, though inefficient and unreliable, was gradually improved and provided a basis for further analytical developments such as the colorimetric work of Walter Crum.¹⁵ These developments however tended to follow industrial progress whereas the

¹² Musson and Robinson, *op.cit.* (10), p.8.

¹³ Morrell, J. B. 'Bourgeois Scientific Societies and Industrial Innovation', *Journal of European Economic History*, 24 (1995), pp. 311-332, on p. 315, citing E. Ashby, *Technology and the Academics. An Essay on Universities and the Scientific Revolution* (London, 1963), D. S. Landes, *The Unbound Prometheus. Technological Change and Industrial Development in Western Europe from 1750 to the Present* (Cambridge, 1969), and G. N. Von Tunzelmann, 'Technical Progress during the Industrial Revolution' in R. Floud and D. McCloskey (eds.), *The Economic History of Britain since 1700 Volume I: 1700-1860* (Cambridge, 1981), (citations not seen).

¹⁴ Mathias, P. 'Science and Technology during the Industrial Revolution: some general problems', *Proceedings of the Sixth International Economic History Congress* (Copenhagen, 1978), pp. 104-109.

¹⁵ See Crum, W. 'On Chlorimetry, and a new mode of Testing weak Solutions of Bleaching Powder', *Proceedings of the Philosophical Society of Glasgow*, 1 (1841-2), pp. 17-23, discussed in chap. 5, sec. VII.

early 'blue test' will be shown to have occurred concurrently with the introduction of chlorine bleaching. It may be that this apparently insignificant episode in testing remains unique to the present day, insofar as without it the use of highly dangerous chlorine would have been rejected at the cost of the industry's expansion. As a general rule, analysis was secondary to industrial progress, a mere afterthought of convenience to such aspects as buying, quality control, etc. This was not so with chlorine bleaching and its dependence on the 'blue test' method of control.

This thesis confirms that useful industrial analysis existed before the introduction of atomic weights and chemical equations, and depended upon the work of analytical chemists whether of academic or industrial standing. With the growth in the early chemical industry the role of industrial chemists became better defined but only reached professional standing through government legislation and enforcement of the Alkali Acts.¹⁶

No strict chronological treatment has been adopted, although the broad thematic approach regarding bleaching before and after the discovery of the effects of chlorine, does of itself create such a structure. In researching the contextual setting of volumetric analysis in the early bleaching and alkali industry it seemed logical to begin with the very uncertain measurements given by the teaspoon of Francis Home, ending with the adoption of the finely graduated glassware of J. J. Griffin. Of course this is not to suggest that the different stages in these technical advances and their understanding always occurred in a strict order of progression. Some overlapping of the accounts of advancing methodology has been inevitable and the investigations have frequently pointed to the slow adoption of new ideas and methods amongst chemical practitioners. No attempt has been made to assign priorities.

As mentioned above, the broad division in this thesis arises through the introduction of chlorine into the bleaching industry. The first chapter considers 'natural' alkali, whether imported or obtained from Scottish kelp, and the attempts by chemists of the period to analyse these products. Chapter two shows the further development of these early analytical methods into what we now term titrimetric analysis in which colour indicators are used to show the completion of a chemical reaction. The central theme of this thesis appears in chapters three, four and five, where the analytical advances devised to measure and control the use of chlorine in bleaching are considered.

Of course, alkali continued to be an essential raw material not only in bleaching but in other industries such as glass making, and this contributed to some early attempts at synthetic alkali making that are considered in chapter six. Throughout this thesis there is constant reference to methods of analysis, laboratory apparatus and techniques. The possible effect of Dalton's atomic theory on chemical analysis has not been ignored and the final chapters consider the development of standard solutions which became regarded as essential to future volumetric analysis.

¹⁶ Russell, C. A. , Coley, N. G. and Roberts, G. K. *Chemists by Profession* (Open University, 1977), pp. 96 & 101-2.

EXPERIMENTS
ON
BLEACHING.

By FRANCIS HOME, M.D.

Fellow of the Royal College of Physicians in
Edinburgh.

Των γὰρ οὐτῶν ἀγαθῶν ἢ καλῶν ὕδεν, ἀνευ ποῦν ἢ ἐπιμελείας Θεοῦ
διδόασιν ἀνθρώποις. PROD. DE HERCUL.

To which are Added,

- I. An Experimental Essay on the Use of Leys and Sours in Bleaching. By JAMES FERGUSON, M. D.
- II. An Explanation of the Effect of Lime upon Alkaline Salts; and a Method pointed out whereby it may be used with Safety and Advantage in Bleaching. By JOSEPH BLACK, M. D.
- III. An Abstract of the foregoing Essays, containing, Practical Rules and Plain Directions for the Preparation and Use of the Sours made of Oil of Vitriol, and of the Leys made of Bleaching-ashes with the addition of Quick-lime.

D U B L I N :

PRINTED BY T. EWING, IN CAPEL-STREET..

M DCC LXXI.

Fig. 1. Title page of the 1771 edition of Home's work containing Black's paper on the effect of lime upon alkaline salts.

CHAPTER ONE

ANALYSIS AND THE EARLY ALKALI TRADE

Bleaching was of great importance in the period now called the industrial revolution. Before the introduction of chlorine and the rise of the chemical industry, the process was extremely slow and depended upon repeated washing and boiling in alkaline solutions, treatment with milk sours, and exposure to sunlight. These empirical activities were clearly without the chemical understanding we would now apply. Dr Francis Home changed this situation and his influence has been commented on in an early history of this industry by Higgins.¹ In 1952 Clow and Clow considered the importance of Joseph Black's analysis of various kelps² while Musson & Robinson³ have treated the work of Home and Black in the wider context of the association of science with industry.

Francis Home also suggested the use of sulphuric acid instead of milk sours and this may have been one reason why John Roebuck (1718-1794), and Samuel Garbett (1717-1807) set up their acid works at Prestonpans in 1749.⁴ It now seems impossible to know whether Roebuck foresaw the potential market in this new and expanding industry but according to Jardine (1796)⁵ several of Roebuck's chemical friends knew that he (Roebuck) had tried out the bleaching effect of sulphuric acid even before the publication of Home's *Experiments on Bleaching* in 1756. Durie (1979)⁶ goes so far as to suggest that it was Roebuck's partner, Samuel Garbett, who initiated early tests using acid. Certainly the availability and low cost of acid from the Prestonpans works may have stimulated interest in that product. The wider application of sulphuric acid and its effect upon industrial growth is discussed later in this work.

I. Introduction: Francis Home (1719-1813) and Joseph Black (1728-1799)

Home's publication of 1756, *Experiments on Bleaching*, was the first published work on this subject, to be followed later by a second edition in 1771 (Dublin).⁷ The latter volume contains as an appendix, a paper by Black (see figures 1. and 2.) entitled 'An Explanation of the Effect of Lime upon Alkaline Salts: and a Method pointed out whereby it may be used with Safety and Advantage in Bleaching'.⁸ Surprisingly, there appears to have been little communication between Home and Black other than perhaps in this joint compilation. Also contained in this edition is 'An Experimental Essay on the Use of Leys and Sours in Bleaching' by James Ferguson, and 'An Abstract of the foregoing Essays, containing, Practical Rules and Plain Directions for the Preparation and Use of the Sours made of Oil of Vitriol, and of the Leys made of Bleaching-ashes with the addition of Quick-lime'. The title page (opposite page 282) names David Macbride as author.

¹ Higgins, S. H. *A History of Bleaching* (London, 1924), p. 23

² Clow, A. and Clow N. L. *The Chemical Revolution* (London, 1952), p. 79.

³ Musson, A. E. & Robinson, E. *Science and Technology in the Industrial Revolution* (Manchester, 1969).

⁴ Gibbs, F. W. 'Prelude to Chemistry in Industry', *Annals of Science*, 8 (1952), pp. 271-281, a review of *The Chemical Revolution* (London, 1952), by Clow and Clow.

⁵ Jardine G. 'Account of John Roebuck', *Transactions of the Royal Society*, (Edinburgh), 4 (1796), p. 79.

⁶ Durie, A. J. *The Scottish Linen Industry in the Eighteenth Century* (Edinburgh, 1979), p. 84.

⁷ Home, F. *Experiments on Bleaching* (Edinburgh, 1756 and Dublin, 1771). See also Partington, J. R. *A History of Chemistry*, vol. 3 (London, 1962), p. 141.

⁸ *Ibid.* (1771), pp. 267-282.

A N
E, X P L A N A T I O N
O F T H E E F F E C T O F
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U P O N
A L K A L I N E S A L T S :
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B Y I T M A Y B E U S E D W I T H S A F E -
T Y A N D A D V A N T A G E
I N
B L E A C H I N G .
B y J O S E P H B L A C K , M . D .

N

Fig. 2. Title page of Black's paper on the effect of lime upon alkaline salts as Appendix II in Home's *Experiments on Bleaching*, Dublin, 1771.

In 1768 Francis Home became the first Professor of Materia Medica at the University of Edinburgh.⁹ Almost fifty years earlier he was born at Eccles in Berwickshire and after taking his MD at Edinburgh in 1750, he practised in that city. At that time the scale of bleaching operations was expanding and novel applications were being practised in efforts to improve the treatment of cotton and linen, particularly in the final stages of finishing. If the expansion of the textile industry was to continue, then a faster and more efficient method of bleaching would be necessary. The time saved by using sulphuric acid was its main advantage and accounts for its rapid adoption by the industry. A similar motivation for using chlorine will be shown later in this study.

It can be argued that the innovations introduced by the use of chemicals in bleaching during the eighteenth century arose, not from rising costs caused by uncertain availability of raw materials and shortage of land for bleach fields, but by the slowness of the field bleaching method itself.¹⁰ The Scottish Board of Trustees, Fisheries and Improvements concerned itself with the protection of the quality of manufactured cloth and in particular with the nature of prevailing bleaching processes. To this end, Francis Home was invited to provide a course of lectures on the subject and by these means his recommendation to use sulphuric acid instead of milk sours became known. The use of acid:

.... will answer to all the purposes of milk and bran sours; nay, in several respects, be much preferable to them. I am of the opinion that five hours will do as much with this sour, as five days with the common sort.¹¹

His suggestion, slow to gain interest initially, was by the 1770s ultimately adopted in the Scottish bleach fields and was supported by the Board of Trustees. In the same period sulphuric acid was becoming more freely available from the new lead chamber method of manufacture.

According to Anderson (1978)¹² Home was awarded £100 by the Board of Trustees in recognition of his recommendation. In 1775 a premium was paid to William Cullen (1712-1790) by the same Board but the minutes only show the reward as being 'for ingenious and useful experiments in the art of bleaching.' Cullen collected information regarding many aspects of the bleaching process on behalf of the Board of Trustees and set in place various trials using alkalis obtained from wood ashes.¹³ His conviction of the usefulness of chemistry to industry, like that of Home, is clearly expressed by Donovan.¹⁴ It seems reasonable to suppose that 'bucking'¹⁵ using alkaline solutions came into being in the bleaching process not because of any instantaneous property of causing colour to disappear, but rather because of observable cleansing and detergent value. The use of soda in some form has for these reasons been retained to this day. It is difficult to account for the apparent complexity of these early alkaline washes, the composition of which is discussed in a following section. Naturally, empirically influenced adjustments would be made from time to time and the reasons for these would no doubt become obscure.

⁹ DNB vol. IX (1908), (Francis Home).

¹⁰ Gittins, L. 'Innovations in Textile Bleaching in Britain in the Eighteenth Century', *Business History Review*, 53 (1979), pp. 194-201, on p. 201.

¹¹ Home, (1771) *op. cit.* (7), pp. 83-4.

¹² Anderson, R. G. W. *The Playfair Collection* (Royal Scottish Museum, 1978), p. 24.

¹³ Shaw, J. S. *The Management of Scottish Society 1707-1764* (Edinburgh, 1983).

¹⁴ Donovan, A. L. *Philosophical Chemistry in the Scottish Enlightenment* (Edinburgh, 1975), p. 107.

¹⁵ To soak or steep in alkaline solution; see Rees, A. *Manufacturing Industry*, vol. 1 (Trowbridge, 1972), p. 178.

At some time in the past, lime was included in these formulations and gave a better result; but lime was known to degrade linen fibres and so government control stepped in to protect the standard of workmanship. Indeed, 'the use of lime in bleaching was forbidden by law, although Francis Home in 1756 said it was used in Manchester and in Scotland'.¹⁶ Clearly there were divergent opinions and a general misunderstanding about its function. It was to this law regarding lime that Home applied his chemical knowledge and in so doing improved the bleaching process in general. One such Act of Parliament prohibited the use of lime in combination with ashes in the bleaching of linen. Home's realisation of the scant understanding within the industry, and perhaps also government, motivated his researches. By analysing materials in current use in 'bucking' solutions, particularly the expensively imported muscovy ashes, he showed by the newly developed method of analysis, resembling a very crude acid/alkali volumetric titration, significant differences from the more common pearl and blue ashes.

II. Home and Black: Chemists without Formulae

Our present chemical terminology expresses composition and shows the mechanism and progress of a chemical reaction by written symbols and chemical equations. Steeped in modern terminology, we may no longer have the ability to appreciate a reaction without resort to this balanced chemical reaction, and for this reason modern equations and formulae have been used in this dissertation only where it is felt this can lead to better understanding. However, such use can be misleading inasmuch as our modern language of chemistry incorporates the solutions to the very problems which so beset the 18th-century chemists.

Study of the decomposition of magnesium and calcium carbonates played an important part in chemical enlightenment particularly in Scotland and this influenced chemical analysis in ways which will be discussed later. At the time of Home's and Black's work associated with bleaching, there was in common use a very unsystematic range of terms to describe chemical substances. Some of these had been inherited from the earlier alchemical period, and yet the brilliance and deductive powers of some of the early chemists associated with the Scottish Enlightenment, overcame these obstacles. Their coherent thinking about composition and interaction had in fact to over-ride those very terms in current use describing the substances designated in their researches.

III. Discovering Analysis: The Analytical Contribution of Francis Home and Joseph Black: Aspects of the Early Bleaching Industry

It is now difficult to assess with certainty the personal familiarity and communication between Francis Home and Joseph Black. An important biographer of Black was Sir William Ramsay¹⁷ who lists Black's colleagues and friends but makes no mention of Francis Home. It seems inconceivable that there was no regular communication between them considering their parallel academic positions¹⁸. Results of their individual chemical researches overlapped and reinforced each other to the advantage of established bleaching processes and hence the early beginnings of a chemical industry.

¹⁶ Partington, J. R. *A History of Chemistry*, vol. 3 (London, 1962), p. 141.

¹⁷ Ramsay, Sir William. *The Life and Letters of Joseph Black, M.D.* (London, 1918).

¹⁸ Edelstein, S. M. 'Historical Notes on the Wet-Processing Industry IX - Two Scottish Physicians and the Bleaching Industry, The Contributions of Home and Black', *American Dyestuff Reporter*, 44 (1955), pp. 681-4, on p. 682. Reprinted in *Historical Notes on the Wet-Processing Industry* (Dexter Chemical Corporation, 1972), pp. 35-38. The absence of documented evidence regarding communications between Home and Black is discussed on pp. 35-36.

What follows are not the life stories of Home and Black, fascinating though these may be, nor is it my aim to investigate the priority of their discoveries, but rather to give an account of their contributions towards providing the bleaching industry with a better chemical understanding, so assisting its continuing expansion.

The art of bleaching, at the time of Black's now famous work involving the decomposition and synthesis of magnesium carbonate, and Home's relatively simple analytical investigations of kelp and other raw materials, dates back to Hellenistic technology. By what route this technology became common practice in Britain is uncertain¹⁹, but the Netherlands and Germany appear to have become the first in this field.²⁰ It was to these countries that Britain sent linen from its expanding textile industry to be bleached and then returned, thus establishing a seasonal export import business. Such trade is known to have occurred within the first few decades of the 1700s but it was not long before similar bleaching operations became established in Britain. The process was not simple or quick, and a typical 'bucking' (wash) solution might be made thus:

The Concentrate		
Blue ashes	30 lb	
White pearl ashes	30 lb	
Marcost ashes	200 lb	
Cashut ashes	300 lb	
Muscovy ashes	300 lb	and water to make up to 170 gallons.

2 gallons of the above slurry were taken and 2 lb of soap added, the whole was then made up to 40 gallons of usable 'bucking' liquid.²¹

The linen would be steeped in this kind of alkaline solution for some hours, followed by several water washes and repeated 'buckings', finally being 'soured' in buttermilk residues (lactic acid), washed and exposed to sunlight until some satisfactory degree of bleaching was achieved.

This was typical of bleaching operations at the time when Home and Black were considering the topic. Clearly, a cursory glance at the 'bucking' solution formula above, with its puzzling admixture of similar materials, suggests it was the outcome of an empirically based development. Home and Black were the first to show the importance of chemical knowledge as a means of improving the bleaching process. The chemical theory provided by Black reinforced Home's contribution as can be seen in the 1771 edition of *Experiments on Bleaching*, and it is important to this thesis to note that their work opened the way and encouraged further analytical progress.

IV. A Study of Home's *Experiments on Bleaching* 1771

From this second edition we read that:

- 1. Home, analysed various alkaline salts including pearl and blue ashes:

In order to discover what effect acids would have on these ashes, and what quantity of the former the latter would destroy; from which I might be able to form some judgement of

¹⁹ Higgins, *op. cit.* (1), p. 17.
²⁰ Parkes, Samuel. *Chemical Essays*, vol. 4 (London, 1815), pp. 23-26. Parkes gives a detailed technical and commercial account of bleaching practice in Holland, and in the same volume refers to the work of Dr Home.
²¹ Home, (1771) *op. cit.* (7), p. 16.

the quantity and strength of the salt they contained; I took a drachm of blue pearl ashes, and poured on it a mixture of one part spirit of nitre, and six parts water; which I shall always afterwards use, and call the *acid mixture*. An effervescence arose, and, before it was finished, 12 tea-spoonfuls of the mixture were required. This effervescence with each spoonful of the acid mixture was violent, but did not last long.²²

This is Home's method of measuring the strength of the alkali salt by neutralizing a weighed amount with a measured quantity of acid of known strength. He warned however that this measurement is not the entire truth '...as there are other bodies beside alkaline salts, that effervesce with acids' (p. 64). In a later experiment (No. 14. p. 65) the importance of purity is shown and the process of crystallization is described.

2. From experiment number 27, he showed muscovy ashes to be different from pearl and blue ashes in that the more expensive imported ashes contained an alkaline salt (potassium hydroxide) and lime, 'and the latter in much greater proportion than the former' (p. 82 and expts. 27-34).

3. Having developed a method of testing alkaline salts which bleachers could carry out for themselves, he constantly recommended experimentation as the best means to improve bleaching operations.

4. He emphasised that it was unnecessary to buy muscovy ashes, as the same result could be achieved by mixing pearl ashes with quicklime (CaO).

5. He showed that lime degrades cloth but that if mixed with ordinary pearl or blue ashes, the bleaching action (cleansing) is speeded up without damage to the cloth. This he proved by trials in the bleach fields.

6. He confirmed that muscovy ashes on their own give good whiteness but some degradation of the cloth fibres. Home then established reasons for the composition of 'bucking' solutions and the use of muscovy ashes provided they were mixed with a certain amount of pearl or blue ash. In this he showed the importance and value of chemists and of chemical knowledge in bringing about technical improvements in industrial processes.

Although early bleachers had learned, by their trial and error methods, the value of including muscovy ashes in their bucking solutions, they were unaware prior to Home's work that this arose from the lime content, and that addition of lime itself to blue and pearl ashes therefore provided a much cheaper means of achieving the same result.

Home found the explanation in terms of chemistry and analysis although, according to Edelstein,²³ he employed empirical means in determining the optimum ratio of alkaline salts (ashes, blue and pearl) to added lime. He certainly had a good empirical appreciation of the practical value of the admixture of ashes with lime in bucking solutions whereby mild alkali was converted to caustic alkali, while the lime was precipitated as chalk. He appears however to have had only limited theoretical insight into the underlying chemistry and what he did not understand, and what Black added, was the exact interpretation

²² Home, (1771) *op. cit.* (7), pt. 3, section 1, p. 64. The 1756 and 1771 account by Home is word for word the same. For convenience in referring to Black's contribution the 1771 edition has been used here.

²³ Edelstein, (1955), *op. cit.* (18), p. 683.

of this reaction, as involving the transfer of fixed air. Black had established the nature of lime and fixed air through his now well known work on magnesia alba (magnesium carbonate) and quicklime which involved accurate quantitative analysis. This showed that caustic alkalies were merely alkali salts deprived of their carbon dioxide or fixed air:

the lime is found to have attracted and detained a considerable part of the salts of the ley, or more properly to have attracted and detained a substance which before was attached to the salts.²⁴

It was this new insight which, while adding greatly to the current chemical knowledge, was also relevant to the bleaching industry.

Limestone had for many centuries provided lime, and it seems natural that the early bleaching artisans should see this material as a possible helpful additive to their process. Modern chemistry shows that by 'burning' limestone and dissolving the quicklime in water, lime water (a saturated solution of calcium hydroxide) is formed. Slaked lime (calcium hydroxide), being only slightly soluble, resulted in bleachers using solutions containing undissolved slaked lime held in suspension. It was this material which was so detrimental to the cloth, causing both yellowing and fibre degradation, but which hopefully would be removed by a later acid wash. For this reason the use of lime in bleaching was forbidden by law.²⁵ Such legislation was proved to be in error by Home and Black although confusion and misunderstanding of the processes continued, even into recent biographical accounts.²⁶ Lime water in itself had no harmful effect but undissolved slaked lime did. However, this latter constituent would have been absent so long as an excess of ashes remained.²⁷ Black showed that the reaction of limewater, or undissolved slaked lime (calcium hydroxide) with ashes, i.e. causticisation, removed the potentially harmful lime, producing very desirable strong caustic and innocuous chalk (calcium carbonate). Furthermore he noted:

that if we free the bleaching salts entirely of this air [the carbon dioxide], they will be so much the more active and powerful, and that a smaller quantity of them will serve the purpose, than when used in their present state.²⁸

Appreciating the technical advantage of the expensive Russian imported ashes, in that 'the whole, or very near the whole of the air [carbon dioxide] has been separated already',²⁹ Black makes the case for using lime with the much cheaper ashes made from kelp, in order to achieve a similar degree of bleaching. There are clear hints regarding the value of quality control and the goodness of the lime and nature of the ashes, but more importantly perhaps to future chemistry, 'that lime and Mephitic air [carbon dioxide] are capable of uniting together in one certain proportion only'.³⁰ He described a simple test to determine the required amount of lime:

²⁴ Black, 'An Explanation of the Effect of Lime upon Alkaline Salts; . . .' in Home (1771), *op. cit.* (7), p. 268, (Appendix).

²⁵ Higgins, *op. cit.* (1), p.13.

²⁶ Donovan, *op. cit.* (14), p. 79.

²⁷ Black, in Home (1771), *op. cit.* (7), para. 2, p. 268, and p. 278.

²⁸ *Ibid.* p. 277

²⁹ *Ibid.*

³⁰ *Ibid.*

a bleacher however, who generally uses the same kind of lime and the same kind of ashes, will soon learn by the help of these trials to hit the due proportion so nearly as to need no amendment.³¹

With Black's theory and Home's *Experiments on Bleaching*, the ill-founded laws forbidding the use of lime could be questioned. Whatever reasons had initiated this legislation, it was the work of Home and Black which showed it to be without foundation. Black in particular had provided chemical principles which found application in bleaching; he brought a new, chemical, understanding made available through laboratory based chemical experiment and analysis.

Of course sunlight continued to play an important part in the bleaching process and this produced seasonal limitations. The use of sulphuric acid instead of milk sours no doubt speeded up the process whereby mineral deposits on the cloth were removed which otherwise might act as mordants at a later stage of dyeing, but the process remained slow and cumbersome. Fears of the consequences of mistakes which might occur in using acid lingered although Home had shown its safe use by experiment.³² A Manchester physician Dr A. Eason, having industrial chemical interests, advocated the use of muriatic acid (hydrochloric) instead of vitriol, but there is little evidence to show if muriatic acid gained common use in the industry.³³

There is little documented evidence to show Black's involvement in the bleaching industry other than his paper in the 1771 Dublin edition of Home's *Experiments on Bleaching*. The biographical writing by Sir William Ramsay (1918) remarks on Black's letter to Dr Ferguson of Belfast, the other contributor to the appendix in Home (1771).³⁴ It is to Ferguson, according to Edelstein,³⁵ that credit must be given for promoting the work of both Black and Home as a means of procuring repeal of the existing laws regarding the use of lime. Thus it was through the intervention of chemistry and in particular, analysis, that the law was ultimately relaxed.³⁶

Black reported in his paper, that by chemical analysis and practical testing, those ashes containing 'a salt that is most free from the above mentioned aerial matter' [fixed air], can be shown to be the most effective.³⁷ This was shown by the analysis and use of muscovy ashes which contained free or caustic alkali. Black argued that there was no reason for distrusting and avoiding the use of lime in bleaching if used in the presence of excess ashes. The process of causticization was not new but Black was the first to provide its chemical understanding.

V. An Early Consultancy: Chemical Analysis by James Keir (1735-1820)

³¹ *Ibid.* p. 281.

³² *Ibid.* pp. 55-6.

³³ Eason, Dr 'Observations on the Use of Acids in Bleaching of Linen', *Memoirs and Proceedings of the Manchester Literary and Philosophical Society*, 1 (1785), pp. 240-2, read 1782.

³⁴ Ramsay, *op. cit.* (17), p. 54.

³⁵ Edelstein, *op. cit.* (18), p. 684.

³⁶ Higgins, *op. cit.* (1), pp. 13-16, cites a prosecution for using lime in 1815. See also Partington, *op. cit.* (16), p. 141. The contentious nature of this topic is illustrated by Dease. Michael *Observations on the Linen Manufacture, Particularly Bleaching Pointing out the Source of the Damage LINENS sustain in that Process, including Strictures on An Act of Parliament made Last Session Prohibiting the Admixture of LIME with POTASH and Experimentally shewing it to be founded in Error* (Dublin, 1783). This Act received Parliamentary assent in May 1782 (21, 22 Geo. III c. 35).

³⁷ Black, in Home (1771), *op. cit.* (7), p. 271.

James Keir reported his analyses of two samples of fossil alkali from Bombay³⁸ in a letter to The Society for the Encouragement of Arts, Manufactures and Commerce, London in 1786; this was six years after his first attempts to make synthetic alkali (see chap. 6). The 'refined' sample was analysed fully but Keir rejected the other material marked 'rough, unrefined alkali' since this contained eight percent of clay and was not recommended for commercial use.

The paper is of importance because a titrimetric method was used as the main analytical means to determine the quality of an industrial raw material. The analysis shows Keir's attempts to obtain full compositional results and not merely the indications given by an acid/alkali balance test. He calculated the amount of soda present from the titration results by comparison with what he regarded as pure soda.

From his visual observations he reported:

I perceived it was a mild Alkali [i.e. soda]; and from the dry powdery appearance, I knew it to be of the mineral or fossil kind.³⁹

Finding no water insoluble material Keir carried out a three-stage process of evaporation, cooling and separation of the crystals. He separated and weighed the pure soda crystals and identified the presence of common salt. The value of crystallization as a means of achieving high purity was noted but because the filtrate always contained dissolved residual alkali and other salts its quantitative value was reduced. With this knowledge Keir knew that so-called pure alkali could be prepared by this method, and on this fact based his main analytical method, the titration - the saturation of a known weight of alkali sample with sulphuric acid of known concentration. This reasoning was not only central to this particular analytical instance but has remained at the heart of acid/alkali titrimetry ever since.

The second determination showed that 100 parts of alkali sample required for complete saturation 53 parts of sulphuric acid 'whose density compared with that of water, is in the proportion of eighteen hundred to one thousand'.⁴⁰ It is difficult to comment on its accuracy without further details. For example, there is no mention of how the point of saturation was recognised, no external indicator appears to have been used; we do not know the accuracy of the weighed sample or by what means a 100 grain aliquot had been obtained assuming Keir had taken a larger initial sample. Keir may have used a hydrometer to determine the acid concentration but with what accuracy remains unknown.⁴¹ Density was often determined by weighing and Keir gave a value of 1.800 (against water of 1.000). What mattered most was the purity of the initial standard anhydrous soda:

As I knew from former repeated experiments, that one hundred parts of perfectly dry and pure mild mineral Alkali (that is crystals of Alkali dried as much as they can be, in which state they lose their form, and become an opaque white powder) require ninety parts of vitriolic acid, of the above density for their saturation; and as it appeared from the above experiment, that fifty-three parts of this acid were sufficient for the saturation of one

³⁸ Keir, J. 'On an Analysis of imported Indian Fossil Alkali sent by Mr. Hellenus Scott', *Transactions of the Society for the Encouragement of Arts, Manufactures and Commerce*, 6 (1788), pp. 133-148. The letter from Keir is dated 26 April 1786.

³⁹ *Ibid.* p. 134.

⁴⁰ *Ibid.* p. 136.

⁴¹ Similarly, Keir did not state the method of determining the many specific gravities quoted in his 'Experiments on the Congelation of Vitriolic Acid', *Philosophical Transactions*, 77 (1787), pp. 267-281. See also Coley, N. G. 'James Keir, F.R.S. (1735-1820) Soldier, Chemist and Gentleman', *West Midland Studies* (Polytechnic Wolverhampton) 4 (1970/1), pp.1-22, on p. 11.

hundred parts of the Indian refined alkali. I inferred that ninety parts of this Indian Salt contains as much Alkali as is equal to fifty-three parts of perfectly dried mineral Alkali;⁴²

As long as this statement remained valid and the same acid concentration was maintained throughout succeeding tests, the final analytical figure for alkali content would be accurate but only relative to the purity of the chosen standard. This was where the weakness (if any) lay for there could be only an incomplete appreciation of what true purity was.

Whatever the concept of pure soda might have been, its saturating value probably changed as each succeeding, more pure sample was obtained. This would explain why the saturation value varied from one analyst to another. For example, Charles Tennant (see chap. 6, sec. V), over thirty years later adopted (knowingly, as a mean, and for ease of calculation) the standard of 90 parts of acid (of the same concentration as used by Keir) as being saturated by 80 parts of pure soda.⁴³ This may appear an extreme example of an unreliable analytical method, or, a varying quality of the standard of pure soda used; it was a 20% divergence from Keir's standard. Nevertheless it carried forward practical analysis of sufficient accuracy for that time. A system based on 'unit-parts' either by weight or volume gave a good workable method but always hinged on the purity of the chosen standard compound. This obviously would vary and until such times as a better understanding arose of purity and related chemical composition (that based on chemical formulae and atomic weights), the method was not without fault. It seems fortunate that so much early analysis began with acid-alkali reactions as described above, if only because relatively pure alkali was obtainable by repeated crystallizations. And so, from what Keir knew from previous saturations (titrations) using what he believed was pure alkali, he reported a dry alkali content of 58.8 parts in 100 parts of the Indian Salt.

Hellenus Scott of Bombay had sent the alkali samples to the Society of Arts in London,⁴⁴ and had used the term *natrum* in one instance and in another *natural soda* and 'that formed without heat'. According to Eklund,⁴⁵ *natrum* corresponded to what we now term sodium sesquicarbonate, or a mixture usually 1:1 of sodium carbonate and bicarbonate, with some water of crystallization ($2\text{H}_2\text{O}$). Most naturally occurring soda, particularly that formed through some process of crystallization such as would have occurred in a dried-up lake, exists as this mixture of carbonate and bicarbonate. Keir's analytical figure would have been in error if the material he analysed had been naturally occurring *natrum*. However, he was not attempting to identify the substance, but merely to show how much acid it needed for complete neutralization and how this measurement compared with a so-called pure alkali sample.

The presence of a mixture of ordinary soda and bicarbonate would not be detected by the above analytical method without further titrimetric refinement. In choosing a standard alkali of known greatest purity, and determining the amount of acid needed for saturation, there is a major assumption that the unknown sample is of like material. Keir assumed he was titrating an alkali and could therefore compare

⁴² Keir, *op. cit.* (38), pp. 136-7.

⁴³ Tennant, Charles. 'A Table showing the Quantity of Soda (either free or combined with Sulphur or Carbonic Acid) contained in the Specimen under Trial with Sulphuric Acid containing 10 per Cent. real Acid. If the Specimen under Trial consists of 100 Grains, the Table of course shows the per Centage of Alkali', *Annals of Philosophy*, **10** (1817), pp. 114-15.

⁴⁴ Scott, Hellenus. Letters to the Society from Scott in Bombay, 1784 and 1785, *Transactions of the Society for the Encouragement of Arts, Manufactures and Commerce*, **6** (1788), p. 131, see also pp. 119-130.

⁴⁵ Eklund, Jon. 'The Incomplete Chymist' *Smithsonian Studies in History and Technology*, (1975), no. 33, pp. 1-49, on p. 32.

it against a standard of known maximum purity, like-for-like, but this assumption had arisen from his initial test by taste and appearance; surely such a human facility would be of doubtful analytical value. Keir's titration could not show that soda formed by burning seaweed or the plant barilla was chemically different from the naturally occurring material being tested, but it undoubtedly indicated alkali strength.

After determining alkali content, he could so easily have made a simple moisture determination and then taken the remainder (subtracting from 100%) soluble sodium chloride to give a complete analysis. Keir did not do this, but chose to determine water content separately followed by precipitation of chlorides. The three major constituents, alkali, chloride expressed as common salt, and moisture, added up to about 100%. However satisfactory this may appear, Keir's analysis can only have been approximately correct. Whether he was aware that his unknown sample was of natural origin and that this would invalidate the titration if reported as true soda, seems doubtful and impossible to confirm; on no occasion did he refer to the material as trona, natrum, or even natural soda in the report.

A fourth experiment reported his determination of the neutral or Marine salt content following a gravimetric procedure by Bergman.⁴⁶ Using solutions of lead acetate and silver nitrate the chloride precipitates were filtered off, dried and weighed.

The somewhat lengthy determination of water content in the third experiment (two days), must be regarded with suspicion. There was no attempt to differentiate quantitatively between water of crystallization and that of occluded moisture, both of which were thought to be present;⁴⁷ but because the drying temperature did not exceed that of boiling water it is almost certain that what Keir regarded as anhydrous alkali (after two days drying) was very probably the monohydrate ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$). On this basis a more reliable moisture content might have been given by difference, assuming the alkali and common salt figures were accurate.

The refined Alkali from Bombay was reported as:

Indian Alkali.	58 parts, eight tenths of dry mild mineral Alkali.
Water.....	24 parts.
Common salt...	17 parts two tenths.

His alkali figure, though probably wrong, named the constituent as dry mild mineral alkali; it made little difference whether it was expressed in this way or any other chemical form;⁴⁸ as he later emphasised:

However, it is to be understood, when I speak of the Strength of these Alkali's [sic], that it refers only to their power of saturating acids, not to their quantities; for it is well known that the mineral Alkali, saturates much more acid than an equal quantity of an equally pure vegetable Alkali.⁴⁹

Keir pointed out that there was no comparable alkali currently available and warned that because of its high quality and newness in the market place there might be few immediate buyers. His analyses show

⁴⁶ Szabadváry, F. *History of Analytical Chemistry* (Oxford, 1966), pp. 73-75, lists silver nitrate and lead acetate as two of Bergman's 'reagents' in *Opuscula physica et chemica*, vol. 1 (1779), (De Analysi Aquarum). Keir mentions Bergman in the above paper and may have read Bergman's text or the translation into English by Edmund Cullen (London, 1784).

⁴⁷ Keir, *op. cit.* (38), pp. 141-2.

⁴⁸ Tennant, *op. cit.* (43), pp. 114-5, makes the same point.

⁴⁹ Keir, *op. cit.* (38), p. 143.

considerable advancement on Home's method and were of value to the Society for the Encouragement of Arts and Commerce which was at that time promoting attempts to increase the alkaline content of kelp above existing levels and also the importation of alkali from colonial sources.⁵⁰ The Society's Silver Medal was awarded to Scott for having supplied these samples of Indian alkali.

VI. Understanding the Analyses of Richard Kirwan (1733-1812)

Kelp production and its practical use in bleaching was a matter of interest in Ireland as well as in Scotland. Richard Kirwan, perhaps the most eminent Irish chemist of the time, carried out researches and analyses of alkaline salts used in bleaching and his results were of importance to both the bleaching industry and the Irish Linen Board.

Kirwan has been described as the first to carry out accurate determinations of alkali in kelp,⁵¹ and his comprehensive analysis of alkaline substances in following Black's work by some thirty years, reflects the advances made in that period. His important publication on bleaching salts gives details of his analyses, results and methods, and what follows in this section is based upon its reading.⁵² It should be borne in mind that Kirwan was writing before the general acceptance and understanding of the new chemistry of Lavoisier; the mass-balanced chemical equation had not been invented and Kirwan's achievements depended upon simple apparatus and his own deductive logic. He acknowledged the earlier work of Joseph Black and indeed reiterated the beliefs expressed by Francis Home some thirty years earlier. These were that bleaching involves chemical principles which even at the time of Kirwan's own writing, remained misunderstood by those closely engaged in the industry.

Bleachers operated successfully as long as their tried and rule-of-thumb tested materials remained available and responded to their simple controls. Whilst showing respect to Black, Kirwan implied that little progress in understanding the chemical principles involved had been achieved. In his paper of 1789 he attempted to show, by chemical analysis, the effectiveness of the raw materials used in bleaching and to establish methods of analytical control leading to improved results. The motivation for such a programme of work is not very clear although there is an implication in a letter from Kirwan to Joseph Banks⁵³ suggesting a government connection. Also there was a shortage of barilla in Ireland at that time, and no certainty that the country could be self-sufficient in the alkalis so necessary to the bleaching industry. Kirwan's objective is clear from his reference in the opening chapter of his paper to 'This task which I have imposed upon myself solely with a view to the utility of the public'.⁵⁴

Kirwan appears fully aware of the coastal plants from which, by combustion, the best barilla is obtained, i.e. from Alicante, and describes the process of burning as similar to established methods of kelp making. His analytical results clearly show the loss in weight suffered by barilla when calcined or reacted with acids, reflecting the loss of fixed air (carbon dioxide).

⁵⁰ Gittins, L. 'Premiums for Vegetable Alkali - The Society and the Supply of Potash, Barilla and Kelp, 1758-1827', *Journal of the Royal Society of Arts*, 3 (1963), pp. 577- 581, on p. 580, citing *Transactions [Society for the Encouragement of Arts, Manufactures and Commerce]*, vols. I-IX (1783-93). Premiums offered by the Society.

⁵¹ Clow, *op. cit.* (2), p. 80.

⁵² Kirwan, Richard. 'Experiments on the Alkaline Substances used in Bleaching, and on the Colouring Matter of Linen-Yarn', *Transactions of the Royal Irish Academy*, 3 (1789), pp. 3-47.

⁵³ Kirwan to Banks, 10th January 1789. Ms copy in British Museum, (Natural History) Dawson Turner Copies. Vol. VI. 122-124.

⁵⁴ Kirwan, *op. cit.* (52), p. 4.

Via. The Analyses

Kirwan begins the analysis by reacting a known weight of barilla with hydrochloric acid and measuring the loss in weight due to the liberation of carbon dioxide. Of course he is writing in the old terminology, but modern names in brackets are added where this helps to elucidate his work.

To find the proportion of fixed air in this substance, having reduced a quantity of it to a fine powder, I poured on an ounce of it [480 grains] a sufficient quantity of marine acid [hydrochloric acid], and found it to lose by the action of this acid 80 grains of its weight, consequently one pound troy of this substance [5,760 grains] contains 960 grains of fixed air, (mixed with a little that had an hepatic smell) that is exactly one sixth of its weight.⁵⁵

We cannot be certain what apparatus Kirwan used in this determination but the result is very clear and definite. A possible source of inaccuracy might be due to loss of moisture through effervescing release of fixed air (carbon dioxide), depending on the reaction container; also the danger of accidental additional weight due to residual gas held within the system. A refinement of the same method was devised by Schrotter in 1871 taking into account these possible errors, but even then an accuracy greater than 1% was not easily obtained.⁵⁶

Kirwan realised that more complex chemical analysis was required based on a separation of soluble and insoluble phases on which further analyses could be performed. He understood the process of crystallization and the retention of water in this form as distinct from the moisture content of the original barilla sample which he determined. The reliability of crystallization as a quantitative means is fully appreciated by Kirwan,⁵⁷ but this provided no information about the possible presence of soluble free caustic (NaOH).

The loss of fixed air was determined on both soluble and insoluble portions, again by measuring weight loss, thus establishing the amounts of calcareous earth (chalk) and mineral soda, and even differentiating these from the magnesia present. By various separations of insoluble substances and reaction to acid treatments, the amount of argillaceous material (clay) and silica present were obtained by difference.

Having in mind that the original sample contained three sources of fixed air (carbon dioxide), i.e. from calcareous earth (chalk or lime), mineral alkali (soda ash) and charcoal resulting from the original plant burning process, Kirwan showed considerable chemical ingenuity in arriving at his final analysis.

This is how the analytical results were reported in his 1789 paper:

Fixed air	960 grains
Charcoal	861.82
Calcareous earth	542.86
Muriatic earth	127
Argillaceous	131.23
Siliceous	249.58
Mineral alkali pure	842
Mineral ditto impure	250

⁵⁵ *Ibid.* p. 6.

⁵⁶ Mellor, J. W. and Thompson, H. V. *A Treatise on Quantitative Inorganic Analysis with Special Reference to the Analysis of Clays, Silicates and Related Minerals*, (London, 1938), 2nd edit. p. 624.

⁵⁷ Kirwan, *op. cit.* (52), pp. 6-7.

Mineral ditto mixed with	
common salt	127
Glauber's salt	125
Common salt	70
Earth deposited	20
	<hr/>
	4306.49
Water	1453.51
	5760.00 (one pound Troy)

Kirwan's own comment then follows:

Hence we see that the alkaline part of barilla is nearly in a caustic state [as hydroxide], for the entire pound of barilla contained but 960 grains of fixed air, and of this quantity we have seen that 759 were contained in the earthy part [the insoluble portion]. Therefore only 201 grains were contained in the saline part [the soluble portion]. Now 960 grains of this (and the mere alkaline part did not certainly amount to less) require for their saturation at least 700 of fixed air, therefore they wanted at least $\frac{2}{3}$ of the quantity requisite to saturate them.⁵⁸

Put more simply, 759 grains of fixed air came from insoluble calcium carbonate leaving only 201 grains available for the sodium carbonate (mineral alkali). But if 960 grains of soluble sodium carbonate were present this would require 700 grains of carbon dioxide. Hence there is not enough carbon dioxide to fully 'saturate' both calcium and sodium salts (as carbonates). From this, Kirwan concludes that the 'alkaline part is nearly in a caustic state' since to be present as carbonate, some of the fixed air would be needed. Such an amount was not available and the presence of free caustic is therefore indicated.

Kirwan gives precise details of both method and deduction in obtaining his analytical results clearly marking progress in this field since Black's initial work on decomposition and synthesis of magnesia alba and limestone. However there is over-certainty in his breakdown of the soluble alkaline part since strictly speaking one could only offer a very approximate composition - say 7% of soda ash and 14% free caustic. It is also not clear how he obtained the total water content, whether by measurement or difference, or both.

On page 30 of Kirwan's report there is a table of results giving the content of 'mere' alkali in various samples assessed by a method which he named as the 'Aluminous Test'; this will be discussed later. The alkali content for sweet barilla is quoted as 24%, some 3% higher than that indicated by the method under discussion and which Kirwan calls the 'direct' analysis. It must be remembered that it was from the direct analysis (from crystallized-out alkali and determination of fixed air) that he claimed the presence of free alkali, presumably caustic alkali, thereby reducing still further the probable true mineral alkali content. Of course it is not certain it is the same sample of sweet barilla in both instances, but there is some conflict of result.

His paper was addressed to members of The Royal Irish Academy and his only comment to those actively engaged in bleaching, following this important and for that time complex analysis, is that boiling water should not be used to extract the soluble material from this kind of barilla:

⁵⁸ *Ibid* pp. 12-13.

. . . for the alkaline part being in a caustic state dissolves part of the coaly matter with which it is united, which sullies the solution, gives it a dark hue, and afterwards is deposited on the linen, and cannot be separated by acids.⁵⁹

For the bleacher, hot caustic and 'coaly' material are to be avoided. No direct comment is made that barilla of this composition would, were it not for the presence of so much 'coaly' material reported as charcoal, remove the necessity to use muscovy ashes as a means of obtaining a caustic 'bucking' solution, or addition of lime to effect caustification. Perhaps bleachers had already taken note of similar recommendations arising from the earlier work of Home and Black regarding these points. The analysis would have been of more practical use if the author had attempted to construct a 'probable composition' using easily read percentage composition. But this is to take a modern view; percentage composition implies knowledge of the whole and this Kirwan did not have. Also it will be shown that his standards of 'goodness' regarding mineral and vegetable alkali varied for he could never be absolutely certain of a chemically pure alkali, i.e. one of 100% strength. At best he could only quote against the standard of material found to be purest to that time. The concept of chemical purity was not so well defined in the 1790s as it is today, granted of course the business of assaying gold and silver implied some idea of measurable quality.

The recommendation to avoid using boiling water seems not in keeping with such a complex analysis; the same knowledge could have been gained by an observant bleacher of practical experience.⁶⁰ But this again is a modern interpretation and perhaps Kirwan's comment had more value than we can now envisage. We are apt to see the use of all science as being immediately applicable to the improvement of 'arts and manufactures' but Kirwan's analysis of barilla represents more of an advance in chemical understanding than an improvement to an industrial process.

In another analysis, Kirwan slimmed down his approach and from a sample of Dantzic Pearl Ash, produced the following results:

Fixed Air.....	1290 grains	
Moisture.....	414	
Tartar vitriolate.....	505	[potassium sulphate]
Digestive salt and ditto.....	36	[potassium chloride]
Earth.....	38	
	<u>2283</u>	
Mere Alkali (by difference).	<u>3477</u>	
	5760	(one pound troy sample.)

By calculation this weight of 'mere alkali' represents a 60% potash content and Kirwan appears to ignore his determination of fixed air content which indicates only 48% of potash. Perhaps Kirwan's following statement is self-explanatory:

Disgusted by the tediousness of these experiments, and recollecting that the alkaline part of these salts was that alone with which bleachers had any concern, I besought myself of an easy practical method of discovering the presence of this principle. . .⁶¹

⁵⁹ *Ibid.* p. 13

⁶⁰ It is suggested in Home's *Experiments on Bleaching* that higher temperatures were common in 'bucking' operations in Ireland and this may account in part for Kirwan's warning. This was not the main point of difference which marked the superiority of the Irish method, see Durie, *op. cit.* (6) p. 81.

⁶¹ Kirwan, *op. cit.* (52), p. 14.

This is an attitude often seen as partly responsible for the development of a separate branch of chemical analysis, namely volumetric analysis.

This 'easy' method, reported in the same paper of 1789, was however not volumetric. It was Kirwan's Aluminous Test,⁶² probably based on the earlier work of Marggraf. In the test, a hot solution of alum was added to a clear solution of alkali sample of known weight. This formed a precipitate, and the addition of alum continued 'until the mixed liquor, when clear, turns syrup of violets or paper tinged blue by raddishes,⁶³ or by litmus, red'.⁶⁴ The precipitate or 'precipitated earth' was filtered, washed, dried and weighed.

It certainly appears from Kirwan's paper that in analysing various mineral alkalis and potashes he favoured the quantitative test based upon precipitation using alum solution. In describing his earlier method as tedious, that is, the so-called direct analysis by reaction with acid and measurement of weight loss due to evolution of fixed air, it seems surprising that he should find the 'aluminous test' less tedious. The alum earth precipitate would have to be efficiently separated and weighed as a measure of the alkali content of the original ash sample. This would be a cumbersome and lengthy process and would give no better results. Knowledge of solution chemistry was limited at this time although the process of 'precipitation' was clearly recognised as a true chemical reaction in which new substances could be formed and separated as a means of analysis. In this connection James Whatman began the manufacture of suitable filter paper in 1740 and laboratory filtration became established practice replacing earlier techniques of decantation.⁶⁵ It is surprising that Kirwan makes no reference to Home's analytical work, which may suggest he was unaware of the latter's contribution and had not seen the 1771 Dublin edition of *Experiments on Bleaching*. It seems quite inconceivable that this should be, considering that such fundamental analysis in both cases was directed towards the same industry and its raw materials. Furthermore the role played by Kirwan in the promulgation of knowledge amongst scientists of the time would not support this point.⁶⁶

VIb. Kirwan's Analyses: Summary and Conclusions

Kirwan's paper describes his methods of determining 'mere alkali' and its importance to the bleaching industry. The fixed air content, whether arising from alkali or calcareous material, was determined firstly by reaction with acid and measuring the weight loss, and secondly by the Aluminous Test. By separating soluble and insoluble portions he distinguished between true alkali (soluble) and calcareous impurities (insoluble). Surprisingly, nowhere does Kirwan mention that by subtracting the fixed air determination from the total figure given in the aluminous test (carbonate and alkali content) some indication of free caustic might be obtained. Certainly he is conscious of those instances where there is an insufficiency of

⁶² The same test is reported in Henry's *An Epitome of Chemistry*, (Manchester, 1801), p. 389, and was clearly regarded at that time as a reliable and useful test.

⁶³ The use of radishes is described in Tennant's letter to Thomson, *Annals of Philosophy*, **10** (1817) pp. 114-115.

⁶⁴ Kirwan, *op. cit.* (52), pp. 15-18 describe his understanding of the reactions and that potash and soda ash do not precipitate equal amounts of 'earth of allum'. He has no knowledge of the composition of the precipitate and by present day standards the method would be judged extremely unreliable.

⁶⁵ Eklund, *op. cit.* (45), p. 14. The author sees decantation as a methodological link with eighteenth-century chemistry practice.

⁶⁶ McLaughlin, P. J. 'Kirwan and Chemistry in the Eighteenth Century', pt. 2, *Studies, An Irish Quarterly Review*, **28** (1939), pp.593-605, on pp. 598-599.

fixed air to satisfy the calcium, potassium and sodium salts if present, as chalk and alkalis thereby indicating free caustic.

Nowhere in this paper does Kirwan state outright that it is the free caustic content which matters if the residues in unbleached linen are to be removed - by dissolution in the bucking ley, so forming soluble soaps. The process of soap making was understood as was causticisation which had been shown by Black thirty years earlier. Of course the use of alkaline substances in bleaching was based on misunderstanding and ignorance, particularly where lime additions were employed. Home (1756) had written:

They [bleachers] know that alkaline salts dissolve oils, and that a fermentation is carried on by steeping, bucking, and souring. But what the bleachers are most deficient in is a knowledge of the nature and properties of those alkaline salts, or ashes, as they call them, which they make use of.⁶⁷

The lack of understanding was not corrected apparently by Home's 1756 publication and its 1762 French translation⁶⁸ nor by Kirwan's analytical treatise. We cannot be certain of Kirwan's entire motivation in the work described in this 1789 report; clearly an objective to analyse the different substances used in bleaching and to provide 'a sure method of distinguishing the relative powers of every saline substance they [bleachers] may use' cannot be questioned.⁶⁹ However there are parts of his work on the intricacies of analysis which bear little value to practical bleaching and there is no doubt he introduced new methods of analysis, but these were later overtaken by the more rapid methods of volumetric analysis needed by industry. His masterly analysis of barilla stands as a monument of classical chemical manipulation of the time, but this did not add greatly to future development of chemical analysis or greatly aid the bleaching industry. It did however establish that Ireland could produce the salts or ashes from its own resources and be independent of foreign imports.⁷⁰ Future progress in analysis would change direction shortly, for in 1785 Berthollet had made some important observations regarding chlorine, and by 1788 the industrial chemist F. A. H. Descroizilles was developing its commercial application enhanced by analytical means which became known as titrimetric analysis.

VII. Robert Jameson (1774-1854)

Kelp production and the importation of barilla concerned both Ireland and Scotland and a publication in 1798 by Jameson, who was later to become Regius Professor of Natural History at the University of Edinburgh, is worth noting. In that year, Jameson⁷¹ published *An Outline of the Mineralogy of the Shetland Islands, and of the Island of Arran*, the appendix of which contains his observations regarding kelp.⁷² Although mainly concerned with social aspects of kelp making and the increasing prices during the period 1740-1790, it was the obtaining of good quality by the use of well-designed furnaces that concerned Jameson, as it had his father some thirty years earlier. He also clearly realised that mere taste

⁶⁷ Home (1756), *op. cit.* (7), preface.

⁶⁸ Smith, J. G. *The Origins and Early Development of the Heavy Chemical Industry in France* (Oxford, 1979) p. 116.

⁶⁹ Kirwan, *op. cit.* (52), p. 4.

⁷⁰ Philbin, Eva M. 'Chemistry', in *The Royal Irish Academy: A Bicentennial History 1785-1985*, edited by T. O'Raiheartaigh. (Dublin, 1985), pp. 275-279 on p. 276.

⁷¹ See *DNB* vol. 10 (1950 reprint), p. 671; Robson, D. A. *Pioneers of Geology* (The Hancock Museum, Newcastle upon Tyne, 1986), pp. 22-23.

⁷² Jameson, R. reprinted as, 'Observations on Kelp', *Transactions of the Highland Society of Scotland*, 1 (1799), pp.44-49.

and smell were not reliable means for assessing the quality of kelp, and in this Appendix claims to have used the analytical methods of Kirwan and Black:

I ascertained the proportion of pure or carbonated alkali in each of them [samples of kelp and barilla]; in some by using the test of sulphate of argill, [Kirwan's Aluminous Test] which is well-known to all Europe; in others, by using an acid of known strength, the method recommended by Dr Black.⁷³

Jameson then provides a table of alkali content of kelp from various sources but it is not clear if these were obtained from his own analyses or some other author. His barilla from Alicante reported as 23½% and that from Teneriffe 8½%, correspond with Kirwan's quoted amounts. The variable alkali contents found in the other kelp samples may in part account for his concern for proper sampling procedures. Jameson mentions an analysis by Bouvier regarding one particular species of seaweed (*Fucus helminthorconton*) in which no free alkali had been found and the principal soluble component was common salt.⁷⁴ From this however, Jameson appears to have drawn this conclusion:

...it is plain, that the soda found in kelp, is formed by the decomposition of the muriate of soda [common salt], by the potash, during combustion and fusion; it will also explain why kelps of a bad quality are made from rotted ware, or such as have been exposed to rain.⁷⁵

Whatever his theoretical chemical knowledge may have been, his appreciation of the intricacies of kelp manufacture and more particularly the value of its chemical analysis cannot be questioned. The same strong case for the use of chemical analysis is made in Jameson's later book, *Mineralogical Travels through the Hebrides, Orkney and Shetland Islands* (1813).⁷⁶

VIII Andrew Fyfe's Comparison of Kelp and Barilla

The purchase of kelp or other ashes by bleachers and soapers was an uncertain transaction until some method of analysis became available. Buyers realised that the value of kelp was related to the amount of caustic obtainable from it, and that more caustic could be obtained from richer kelp but at lower operating costs. The spread of prices given by Fyfe bears little relation to the amount of true alkali present:⁷⁷

	Price/ton	Alkali %
Collonsay	£12 12 0	6.19
Ditto	12 0 0	4.84
Mull	11 11 0	0.808
Barra	11 0 0	6.94
Barra (driven ware)	8 0 0	1.107
Loch Maddy	8 10 0	1.21
Ditto	9 0 0	1.42
Shetland	8 5 0	3.09
Ditto	8 5 0	2.89

⁷³ *Ibid.* p. 47.

⁷⁴ *Ibid.* p. 49, Jameson cites Bouvier, 'Analyses De La Coralline, *Corallina, Ossificinalis*, de Linneus, Lue á la Société Phylomatique', *Annales de Chimie*, 8 (1791), pp. 308-318, (not seen).

⁷⁵ *Ibid.*

⁷⁶ Jameson, Robert. *Mineralogical Travels through the Hebrides, Orkney and Shetland Islands*, vol. 2, (Edinburgh, 1813), pp. 242-251.

⁷⁷ Fyfe, A. 'Essay Upon The Comparative Value of Kelp And Barilla, Founded Upon Accurate Experiments', *Prize Essays and Transactions of the Highland Society of Scotland*, 5 (1820), pp. 10-65, on p. 29. Article dated and first printed in 1816.

Ditto	8 0 0	4.64
Mull	50 0 0	3.07

The Clows suggested that it was through the analytical developments of Black that such assessments of raw materials had beginnings;⁷⁸ certainly his was a more fundamental understanding of chemical reaction than that of Home. It should be noted however that Home published his method of analysis in the 1756 edition of *Experiments on Bleaching*, fifteen years before Black's paper appeared in the second edition.

Whilst the analytical data shown in the above table no doubt provided guidance to prospective buyers, particularly where adulteration might be suspected, we should not place too much importance on the fact that prices appear unrelated to alkali content. We cannot now be certain what chemical characteristics soapers or glass makers were seeking. Kelp being a mixture of sodium carbonate, salt, and sodium and magnesium sulphate, may well have been ideally composed for glass and soap makers, whereas for bleachers, soluble alkali salts were of greater importance. The price variations given by Fyfe may indicate misunderstandings of the active constituents in these kelps from different locations, but it may also reflect fluctuations decided by other factors now outside our understanding. It would be quite wrong to take Fyfe's prices as proving a need for industrial chemical analysis; it seems more likely that the need for analysis sprang from the realisation of buyers that assessment by taste, smell, colour, and compactness of raw material gave insufficient information. The general misunderstanding about the use of alkaline salts and the absence of analytical data are seen in a legal case of 1749 cited by Durie.⁷⁹

Fyfe's paper of 1820 shows comparisons between kelp and the more favoured barilla using analytical methods similar to those used by Richard Kirwan. The problem of sampling also troubled Andrew Fyfe. In his 'Essay' printed in 1816, he noted:

From the very heterogeneous nature of kelp, it is impossible that an analysis of any sample can give a fair view of the composition and proportion of the ingredients of any other sample; for this reason, a minute determination of the exact proportion of all the ingredients is of little consequence.⁸⁰

For Andrew Fyfe junior, M.D., of Edinburgh, analytical emphasis centred on the determination of the principal active substance, the alkali, either free or combined with carbonic acid; he was not apparently seeking a full chemical analysis. Writing in 1816, the term 'fixed air' was no longer in use and as Robison (1803) had commented, 'French chemists have named the compounds which contain this acid, carbonats'.⁸¹

Whatever Fyfe's main objective was, he reported a range of qualitative and quantitative tests, many of the latter being replicas of Kirwan's, which suggests little analytical progress during the previous twenty seven years. Fyfe suggests that it is unnecessary to prove the presence of mineral alkali for soap making,

⁷⁸ Clow & Clow, *op. cit.* (2), p. 79.

⁷⁹ Durie, A. J. *op. cit.* (6), p. 83. The case illustrated the temptation by smaller bleaching concerns to use lime instead of the more expensive ashes and a general ignorance of the processes involved; it also pointed to the need for a low priced source of alkali to which the Trustees were committed.

⁸⁰ Fyfe, *op. cit.* (77), p. 11.

⁸¹ Robison, J. editor, *Lectures on the Elements of Chemistry, delivered in the University of Edinburgh by the late Joseph Black, M.D.* vol. 2, (Edinburgh, 1803), p. 101.

for if soap is formed therein lies the proof. One may see this as extreme empiricism but in fact it remains common practice in industry to this day.

In the qualitative test number 9, page 14, Fyfe identifies iodine by reacting the dry kelp with sulphuric acid and noting the violet coloured vapours condensing as shiny dark crystals. Iodine had been first observed by Bernard Courtois in 1811, only six years earlier and from a similar source.⁸²

Fyfe's quantitative estimations are similar to those of Kirwan inasmuch as he determined soluble and insoluble portions and loss in weight due to release of carbonic acid on reaction with nitric acid (there is a decimal-point error in his result). Sulphate and muriatic acid were determined by reactions with nitrate of baryta (barium nitrate) and nitrate of silver respectively but gravimetrically, that is by weighing the precipitate. "These ingredients [radicals] are in union with the alkaline bases of soda and potassa."⁸³ He then embarks upon a complicated series of crystallizations showing the presence of potassium sulphate, potassium chloride, and common salt. Like Kirwan, Fyfe also decides the methods so far employed are tedious and makes the valid point that little is gained by determining the proportion of pure soda to that of carbonate of soda; this is because the soap maker or bleacher before using the alkali always reduces it to a caustic state. He must of course be referring to their use of lime. After a descriptive reference to Kirwan's Aluminous Test and the methods used by Robert Jameson, Fyfe proclaims his preference for the methods of Joseph Black:

This consists in determining the quantity of an acid necessary to neutralize the free alkali, as well as that in combination with carbonic acid and sulphur.⁸⁴

Fyfe used sulphuric acid 'at temperature 60 (F), of specific gravity 1133' and taking water as 1000, soon realised that the value of determining the amount of acid needed by measuring the volume used. Instead of weighing the amount of acid used and determining the amount of sodium sulphate formed, he soon developed a quicker, volumetric approach:

In ascertaining the quantity of acid employed in the various trials, I always used a water measure, divided into grains. This is much easier than weighing, and is at the same time sufficiently accurate.⁸⁵

The use of litmus in these determinations is described, and a full tabulated report of results of over thirty different sources of kelp follows. This shows the alkali content to range between 1 and 6% and because of this Fyfe describes a sorting-out test, or test of goodness which a prospective purchaser could apply, based upon the method described above. Then follows a tabulated range of kelps showing alkali content and price per ton (reproduced here on page 21).

In repeating Kirwan's scheme, Fyfe followed with an analysis of the insoluble portion despite having stated earlier that it is the soluble portion only which is of interest to the bleacher or soap maker. As with Kirwan, Fyfe's results seem to illustrate his knowledge of chemical analysis more than offering useful practical information and it is difficult to see what purpose some of the results serve.

⁸² Weeks, M. E. *The Discovery of the Elements* (Easton, Pa., 1933), pp. 257-262.

⁸³ Fyfe, *op. cit.* (77), p.15.

⁸⁴ *Ibid.* p. 21.

⁸⁵ *Ibid.* p. 22.

Sulphuretted hydrogen	(%)
and Carbonic acid	14.0
Carbon.	4.1
Sulphuric acid	0.47
Silica	12.3
Lime	32.6
Magnesia	18.5
Alumina	15.4
Iron	<u>0.77</u>
	98.14
error	<u>1.86</u>
	100.0

Fyfe's analysis of the insoluble matter of kelp (14% carbon dioxide could arise from 31.8% calcium carbonate.

There is no indication as to the form of the not inconsiderable amounts of alumina, magnesia, and lime present in the original kelp sample. Clearly in the insoluble portion analysed there was insufficient carbon dioxide to allow the presence of magnesium and calcium carbonate, and yet in what other insoluble form could these elements be present? No explanation is offered of how 32.6% of lime is calculated as equivalent to 93.4% from the amount of precipitate obtained by adding oxalate of ammonia. A modern calculation based on the formation of calcium oxalate, monohydrate, would show 35.8% CaO to be present.

The paper continues with analysis of barilla in which Fyfe reports on a range of ashes from various foreign sources, determining the amount of alkali, that is, as free caustic alkali (hydroxide) and combined with carbonic acid (as carbonate) using the method described earlier, viz. 'the saturation of the alkali, by means of the sulphuric acid'.⁸⁶ Referring to Kirwan's results the similarity of the ingredients in kelp and barilla becomes obvious, with the exception that iodine does not occur in barilla.⁸⁷

A short summary then followed, indicating general understanding in preparing the soda wash or bucking solution:

The kelp is dissolved in water, and a quantity of quicklime mixed with it; the whole is well stirred, and put on a filter; what passes through is a solution of soda, with the other saline [soluble] ingredients, the lime having seized the carbonic acid of the carbonate of soda, and thus reduced it to its caustic state. In this form it is ready to be mixed with the oily matter for making soap, or for the immersion of the cloth which is to be bleached.⁸⁸

⁸⁶ *Ibid.* pp. 36-37.

⁸⁷ Kirwan, *op. cit.* (52), p. 12.

⁸⁸ Fyfe, *op. cit.* (77), p. 43.

IX. Samuel Parkes: A Further Comparison of Kelp and Barilla

Samuel Parkes (1761-1825) was an early nineteenth-century industrial chemist and general manufacturing chemist first in the Midlands and later in London. He, like Fyfe, received an award from the Highland Society of Scotland for analytical researches on barilla and kelp. Through a series of quantitative analyses he accounted for all the components in these materials and so provided chemical knowledge of potential benefit to the Society, the kelp industry, and the bleaching industry. His findings were published by the Society in 1820⁸⁹ and are based upon tests on a wide range of samples, but it is kelp from Isle of Lewis and barilla from Teneriffe which are examined in detail. In these analyses, Parkes brings forward a greater chemical knowledge than that shown by Fyfe or Kirwan.

Appreciating the difficulties of representative sampling, the proper storage of the pulverized material, and straightforward approach to moisture determination, gives this essay a mark of professionalism. Indeed this account, whilst concise and brief, provides a good basis of chemistry in all the various analytical procedures employed. The danger of co-precipitation when testing the water soluble portion with muriate of barytes (barium chloride) to precipitate sulphates and carbonates which could be weighed is discussed, and Parkes's further intention to react this precipitate with nitric acid in order to determine the carbonate as a separate entity shows progressive thinking; in fact he abandoned the method because of the likelihood of incomplete precipitation.

Parkes makes concise judgements and methods of reporting:⁹⁰

it appears that 100 grains of this barilla consist of,	
Alkaline and neutral salts.....	51.0
Insoluble matter.....	41.6
Water dissipated in drying.....	6.2
Loss in boiling and drying.....	1.2
	100.0

The main approach, that based on soluble and insoluble portions, is retained and details are given of chloride and sulphate gravimetric determinations. Here, Parkes arrives at the total soluble salts by complete evaporation of the dissolved portion of barilla rather than the less certain process of crystallization adopted by Kirwan. Carbonic acid or carbon dioxide content was determined by loss in weight when a known amount of barilla was reacted with sulphuric acid; a lead acetate test had shown the absence of sulphide which could have caused error, and from 100 parts of original barilla, Parkes showed a loss of 12 parts as carbonic acid. Knowing from previous determinations using what was regarded as pure carbonate of soda, that 12 parts denote 29 of what he calls subcarbonate of soda, so the alkali content was ascertained. In fact 29 parts of soda ash give 12 parts of carbon dioxide using modern formulae. To check this result he determined the so-called subcarbonate (meaning ordinary soda) by a different route using oxalic acid crystals to the point of 'saturation' (neutralization), and using previously determined standards confirmed the soda content. Using the data given in this paper the terms subcarbonate and 'dry soda' correspond to Na_2CO_3 and Na_2O in modern nomenclature.

⁸⁹ Parkes, S. 'An Essay Upon the Comparative Value of Kelp and Barilla, Founded upon Actual Experiments', and Addressed to the Highland Society of Scotland, *Prize Essays and Transactions of the Highland Society of Scotland*, 5 (1820), pp. 65-122, article dated and first printed in 1816.

⁹⁰ *Ibid.* p. 72.

Two different methods of determining chloride content were recorded; for muriatic acid (hydrochloric acid) he used silver nitrate in a gravimetric way, i.e. the precipitate of silver chloride was weighed and ignited. Parkes remarked on possible errors due to the presence of sulphur, and his recommendation to avoid this by addition of lead acetate seems to indicate a greater knowledge on this point than was shown by Kirwan. For the muriate of potash (potassium chloride) determination, Parkes resorts to the use of muriate of platina which to our understanding of platinum halides might suggest a step into the unknown, but more probably at that time was simply seen as a chemical substance which gave a precipitate whenever potassa was present. It was Marggraf⁹¹ (1709-1782), who in 1757 had shown that the solution formed by dissolving platinum in aqua regia gave a distinct yellow precipitate in the presence of potash but not sodium salts. Parkes saw the method as providing a quantitatively reliable precipitate, and for the analytical purposes of that time, no necessity to understand the chemical nature of the platinum test solution (hexachloroplatinic acid), or the precipitated compound (potassium chloroplatinate). He had determined standards, using what was thought to be pure potash, and against these devised a reproducible method. This, when used with the above method for chloride determination gave a means of calculating both muriate of soda (common salt) and muriate of potash (potassium chloride). He had earlier referred to this test in his *Chemical Catechism*:⁹²

If a little of any alkaline solution be poured into a solution of the ore of platina in nitro-muriatic acid [aqua regia], a yellow precipitate will be seen, if the alkaline solution contained potass. If it contained only soda, no precipitation will occur.

Unlike Kirwan, Parkes did not favour fractional crystallization as an analytical means:

There is indeed no method that I know of, whereby a saline [soluble] mass, consisting of the sulphate and carbonate of soda, and the muriates of potash and soda, can ever be analyzed with correctness, except by means of reagents, or chemical tests.⁹³

The same point was made by William Henry in 1800⁹⁴ in stating that 'Crystallization is incompetent to separate the whole of the sulphate'. His method consisted of causticising the solution of alkali, vegetable, mineral or volatile, by addition of quicklime, and to the clear solution, addition of a warm solution of barytic earth, meaning probably, barium carbonate or hydroxide to precipitate the sulphate:

The barytes seizes the sulphuric acid; and leaves the alkali pure which may, if required be afterwards saturated with carbonic acid, in any of the common modes.⁹⁵

Another point which indicates Parkes's wider chemical knowledge than that of for example, Kirwan, is in his method based upon solubility of pure alkalis in alcohol. In this, the soluble salts are causticised and the clear filtrate evaporated to dryness, the solid residue then taken up in alcohol. Parkes sees this as 'the only method for preparing pure soda or potash' but then points out its limitations in that absorption of

⁹¹ Partington, J. R. *A History of Chemistry*, vol. 2 (London, 1961), p. 728.

⁹² Parkes, S. *A Chemical Catechism* (London, 1806), p. 188.

⁹³ Parkes, *op. cit.* (89), p. 79.

⁹⁴ Henry, W. 'Further Remarks on the Preparation of prussiate of Pot-ash -- Method of purifying Caustic and carbonated Alcalis from Sulphate of Pot-ash', *Nicholson's Journal of Natural Philosophy, Chemistry and the Arts*, 4 (1801), pp. 171-172.

⁹⁵ *Ibid.* p. 172.

carbonic acid from the atmosphere during filtration will cause inaccuracies.⁹⁶ He seems to disregard the possible errors caused by other alcohol soluble salts being present.

For a full chemical analysis, Parkes then examined the water insoluble material in the original barilla sample. After treatment with muriatic acid, any insoluble residues were regarded as alumina and silex (silica) and were simply washed, dried, weighed and reported as such. Magnesium and calcium determinations were then made on the acidified filtrate. For magnesium, Parkes made the solution just alkaline with ammonia and separated off the magnesium (as a hydroxide) retaining the filtrate for the calcium determination. The magnesium (as hydroxide) precipitate was then redissolved in muriatic acid and the hot solution treated with 'subcarbonate of soda' (sodium carbonate) to precipitate out the magnesium, which after gentle ignition was weighed as carbonate of magnesia. The calcium was determined by adding ammonium carbonate to the clear ammoniacal filtrate from above and precipitating the calcium as insoluble lime. As an explanation for this separation of calcium and magnesium carbonates, Parkes points out that 'Caustic ammonia precipitates magnesia from its acid solutions, but does not precipitate lime.'⁹⁷

This was probably an adequate explanation for the time. It shows how chemical analysis was so often built upon empirical operative observation. Furthermore, it was not necessary for Parkes to know that the calcium remained soluble in the ammoniacal solution simply because of the solubility of calcium hydroxide in ammonium chloride, both being products of a reaction in solution. Conversely, some early reasons for chemical analysis originated from a desire to give understanding to empirically developed processes. The completed analysis of barilla from Teneriffe showed:⁹⁸

Water dissipated by drying	6.20%
Carbonaceous matter	7.20
Sulphate of soda	2.70
Subcarbonate of soda	28.56
Muriate of potash	9.00
Muriate of soda	7.50
Alumina and silica	16.50
Carbonate of magnesia	13.50
Carbonate of lime	6.75
Water not dissipated by the first drying, and loss,	2.09
	100.00

The remainder of Parkes's paper consists of analyses of kelps from other locations and the methods employed are very similar to those discussed above. However there are some points of emphasis and difference worth noting. In continuing to use oxalic acid crystals to determine the point of saturation of the soluble salts from kelp, achieving accuracy to the point of one crystal difference, Parkes casts doubt upon the results of other analysts, even the eminent Kirwan. Such criticism rests upon Parkes's obvious concern over water of crystallization and how this must be considered in calculating the amount of soda present from the oxalic acid addition - a crude modern day acid titration.

⁹⁶ Parkes, *op. cit.* (89), p. 80.

⁹⁷ *Ibid.* p. 84.

⁹⁸ *Ibid.*

Like Francis Home, Parkes was a projector who saw the value of industrial chemistry and analysis; the usefulness of chemical knowledge is clearly stated regarding a bleach field known to him:

... where they formerly used 12 cwt. of Dantzic weed ash to bleach a 1½ ton of linen yarn - since they have become chemists and have learnt how to ascertain the goodness of the material [by analysis?] they are enabled to finish the same quantity of yarn with 2 cwt. of Caustic American Potash, which costs them not more than one quarter of their original expenditure.⁹⁹

X. Conclusions

We cannot be certain what motivated Black and Home in their work directly related to the bleaching industry. Earlier sections in this chapter have shown that their chemical achievements occurred at a time now described as the Scottish Enlightenment, when anticipations concerning the usefulness of chemistry were running high, reinforced by accumulating knowledge.¹⁰⁰ It seems reasonable that Black and Home, motivated by this growth of chemical knowledge, should seek to establish its practical application in the already expanding industrial processes.

The Scottish Board of Trustees saw the need for a low cost alkali without the restraints of imported material. The opportunity for chemistry and the application of scientific knowledge was therefore recognised and became a part, if only very small, of the early industrial revolution. It would however, be a false assumption to suppose that this period of early chemical manufacture, even into the mid-eighteenth century, merely reflected the application of chemical or scientific discoveries to the technology of the time, and that industries actually waited upon developments in the field of what became known later as pure chemistry.

At this time, the role of chemical analysis was not clearly defined or obvious, and those active in this practice were singularly few considering the growing interest in chemistry. Where analytical results were obtained, could these be realistically employed by early chemical plant artisans? How did Kirwan expect ordinary commercial bleachers to interpret his analyses, aspects of which bore no connection to degrees of goodness? Bleaching processes were already established when legal intervention (perhaps based on ill-judged chemistry) prohibited the use of cheap lime, although it was chemistry on which repeal of these laws was to depend. All this is not to say that applied chemistry had no serious effect on the industrial revolution, but analysis was not the most important factor. The analytical chemistry of Home and Black was unlikely to be seen as an immediate impetus to greater production in the textile industry, although providing useful practical results from the better theoretical understanding of the processes and materials in use. The relatively simple observation by Home that sulphuric acid allowed rapid bleaching probably affected the overall industry more than any advantages gained from chemical analyses of already 'empirically understood' bucking solutions or alkali samples. Certainly the discovery of acid washes released the production strangle-hold caused by inordinately lengthy bleaching processes.

⁹⁹ Parkes, Samuel. *Chemical Essays*, vol. 4 (London, 1815), p. 73. Noting the date of this publication it is not surprising that Parkes gives greater attention to chlorine bleaching (page 39 onwards). There is clear acknowledgement to the earlier work of Francis Home.

¹⁰⁰ Christie, J. R. R. 'The Origins and Development of the Scottish Scientific Community, 1680-1760', *History of Science*, 12 (1974), pp. 122-141; also Donovan, *op. cit.* (14); and Crosland, M. P. 'Rise and Fall of Scottish Science', in *Emergence of Science in Western Europe* (London, Macmillan, 1975).

The cause of great change in industrial processes undoubtedly lay in the discovery and development of the means of producing useful raw materials by synthetic methods. But could chemistry or chemical analysis have saved the disastrous decline in the kelp industry? There are many answers to this question. For example, the Highland Society in offering awards to Fyfe and Parkes for their analytical essays, suggests a belief that chemical knowledge would somehow stem the industry's decline. But, on the other hand, if greater chemical knowledge had existed, then the decline in the kelp industry would have been further exacerbated, in that synthetic production of alkali and the perfection of chlorine bleaching would have occurred that much sooner.

Established practices of bleaching were, judged by modern standards, slow to change, and whilst the economic trauma of the kelp decline as felt in Scotland took dreadful toll, matters could have been worse.¹⁰¹ Patrick Neill, Secretary to the Natural History Society of Edinburgh, could not teach the peoples of Orkney and Shetland to conserve their land and fishing interests,¹⁰² and in so doing maintain a broader economic base, but other chemical interests helped sustain a small market in kelp, for an hitherto unknown element was discovered in these sea plants, iodine.¹⁰³ Indeed the place and history of early iodine seems little researched in comparison with kelp interests and yet these two subjects overlapped each other. Iodine and its salts were still being made from kelp as late as the 1850s and as long as this market existed the production of soda from kelp would continue even alongside that produced synthetically from salt by the Leblanc process.¹⁰⁴ However, William Watson writing in 1924, comments:

The manufacture of kelp, once a considerable industry in the Northern Hebrides, has declined since the iodine, for which it is chiefly valuable nowadays, has been supplied from the nitrate fields of Chile.¹⁰⁵

Even so, the kelp industry continued though in reduced size and in the 1870s attempts were made at revival which led to the more specialised interests in alginic acid and production of alginates.¹⁰⁶

What has been shown in previous sections is that as chemical knowledge grew so incursions into industrial processes occurred, the motivation for which appears very mixed. The division in chemistry known as pure and applied did not at this time exist, and there was also no well defined difference between chemistry and analytical chemistry. All was one new science in a period before chemical laws were publicly stated, but when they were being tacitly acknowledged in practical chemistry and when theories of phlogiston (and caloric) were being superseded.

¹⁰¹ Clow, *op. cit.* (2), pp. 85-90.

¹⁰² Neill, P. *A Tour Through Some of the Islands of Orkney and Shetland* (Edinburgh, 1806), in which the author foresees the synthetic production of alkali and its economic consequences.

¹⁰³ Ure, Andrew. 'On Iodine', *Philosophical Magazine*, **50** (1817), pp. 161-164.

¹⁰⁴ Edward Bullock & Co. of Galway displayed various preparations from sea-weed including soda, potash and iodine and iodides at the Great Exhibition of 1851. There were four other exhibitors of potash and soda made from kelp which suggest this industry, though in decline, still existed.

¹⁰⁵ Watson, William J. *Ross and Cromarty* (Cambridge, 1924), pp. 61-2.

¹⁰⁶ For a recent appraisal of the industry see Hendrick, J. 'The Value of Seaweeds as Raw Materials for the Chemical Industry' *Journal of the Society of Chemical Industry*, **35** (1916), no. 10, pp. 565-574; this article includes analyses of a wide source of kelp samples and are useful comparisons against the earlier results discussed in this dissertation.

Indeed, progress in chemical understanding owed more to analytical developments than the other way round, and confirmation of chemical laws depended upon analytical practice and knowledge.¹⁰⁷ The remark made by Dr. D. W. F. Hardie in 1952:

The chemical industry made its appearance and developed for over fifty years before the growth of pure science added significantly to its fundamental techniques.¹⁰⁸

may at first sight stand in question, particularly in the light of apparent chemical interventions of Black, Home, Kirwan *et al.* In the context of this dissertation however, it may simply require finer definition and timing. If Hardie (1952) proposed that chemical truths only made their industrial appearance mid-nineteenth century, and he cited the work of Ferdinand Hurter in this role, surely this was not meant to imply the total absence of scientific intervention prior to this time?

It is true that there were parts of industry, such as alum manufacture,¹⁰⁹ into which chemical knowledge made scant entry but this was not the case generally as is shown in the chapters which lie ahead. In the period covered by this thesis there was much overlapping of chemical and technical innovation and discovery. Indeed, during the period of the analytical achievements discussed in this chapter, it should be noted that the introduction of chlorine into bleaching was also taking place. From these early analysts the foundations of what later developed into the heavy chemical industry can be identified. Parkes's analytical work justifies serious attention although it must be accepted that his greatest achievements as a manufacturing chemist were *Chemical Essays* together with *Chemical Catechism* and the part he played in the successful ending of salt duties in 1825 in which analysis had no apparent role.¹¹⁰

It was from Home's quantitative method of determining the strength of blue pearl ash by neutralization or saturation, in which he used a teaspoon measure, that a branch of analysis was to develop. This became known as titrimetry and the next chapter considers the gradual improvements in technique and understanding which allowed its development within an industrial context. The similarity of Home's original method to one often employed in some industrial situations to the present time is worth noting; described as 'volumetric analysis without weights', it was the simplest means of gauging the strength of an acid or alkali. No doubt the method varied from one practitioner to another, but the three main requirements in this acid/alkali balancing procedure were:

1. A balancing device, or a balance without the need for weights.
2. A sample quantity of pure substance against which the unknown would be compared (many early laboratory determinations were mere comparisons, even to recent times).
3. A measuring cylinder or burette of some kind to dispense the acid or other liquid the strength of which it is not necessary to know as long as it is conveniently within operating range.

¹⁰⁷ Brock, W. H. 'An Attempt to Establish the First Principles of the History of Chemistry', *History of Science* 6 (1967), pp. 156-169.

¹⁰⁸ Hardie, D. W. F. 'The Macintoshes and the Origins of the Chemical Industry', (Hurter Memorial Lecture), *Chemistry and Industry*, June 28th 1952, pp. 606-613

¹⁰⁹ Singer, C. J. *The Earliest Chemical Industry* (London, 1948).

¹¹⁰ Kurzer, F. 'Samuel Parks: Chemist, Author, Reformer - A Biography', *Annals of Science*, 54 (1997), pp. 431-462.

Any reasonable amount of pure alkali or other substance was put on one side of the balance and counterpoised by a quantity of the unknown material. If the amount of acid used in neutralizing the pure standard substance was called 100, the amount used for the unknown sample corresponded to the percentage of similar material it contained. There would be exceptions of course, particularly if other carbonates, oxides etc., were present, but the method must have been of great industrial value if only because it gave a rapid measure of the constancy of quality.

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CHAPTER TWO

TITRIMETRIC ANALYSIS

I. Historical Aspects concerning the early growth and developments of Titrimetric Analysis

All the analyses examined so far were made before the adoption of chemical formulae and atomic weights. The methods used and the calculations necessary to provide a numerical result may to modern eyes appear questionable, but this is not to deny there existed a conception that a chemical reaction of some kind was the underlying process on which analysis depended. We cannot be certain how such reactions were visualised by these early analysts for they lacked our modern theory and terminology and could only use common name descriptions. It is possible that chemical reactions, although based on limited theoretical understanding, could nevertheless be described by using language and theory very different from present day.

Decomposition, an easily observable process and a major factor in analysis, was clearly embodied in Macquer's (1749) definition of *chemistry*:

The object and principle [sic] end of chemistry is to separate the different substances that enter into the composition of bodies; to examine each separately; to discover their properties and relations; to decompose, if possible, these substances; to compare them together, and combine them with others; and to reunite them into the original substance with all of its properties.¹

This statement suggests it is a definition of analysis rather than an overall comment on chemistry; it is a reflection of the unity between chemical knowledge and analysis at that time. The understanding of acid-alkali reactions may have origins in iatrochemistry for it was through Tachenius (1620-99 approx.), following Sylvius de la Boë (1614-1672), that an enunciation of this principle arose insofar as 'all salts can be divided into two parts, into alkali and acid'.² In support Tachenius gave a clear statement on the decomposition of sal ammoniac (ammonium chloride) to produce spiritus salis (hydrochloric acid) and a volatile alkali similar to that obtained from urine (ammonia). It cannot be said that he first described what we know as a reversible reaction, but it seems reasonable to suggest that a tacit understanding of the idea developed from his work.

There was no quantitative atomic theory to explain chemical reactions in the eighteenth century but this did not hinder the development of an empirical principle of equivalence. This has been suggested in the preceding chapter and it clearly evolved without sought-after theoretical justification. Indeed, the practical value of an atomic theory was slow to develop; in both the pre-and post-Dalton period, analysts saw no immediate advantage in having a theory of matter. Whilst we may now see such theories as of immense importance it does not follow that a similar attitude existed immediately following Dalton's revelations. Even as early as 1700, 'atomistic' viewpoints, based on corpuscular theory, where all atoms

¹ Macquer, P. J. *Éléments de chimie théorique* (Paris, 1749), p. 1, as quoted by Eklund, J. 'The Incomplete Chymist Being an Essay on the Eighteenth-Century Chemist in his Laboratory, with a Dictionary of Obsolete Chemical Terms of the Period', in *Smithsonian Studies in History and Technology*, no. 33 (1975), pp. 1-49, on pp. 2-3.

² Tachenius, O. *Hippocrates Chymicus* (2nd edn, Paris, 1669), ch. 2, p. 11, as quoted by Partington, J. R. *A History of Chemistry*, vol. 2 (London, 1961), p. 293; see also Holmes, F. L. *Eighteenth-Century Chemistry as an Investigative Enterprise* (Berkeley, 1989), pp. 33-55.

consisted of the same material (*i.e.* matter), but varied in shape and size only, were commonly held by chemists, but this had no relevance to practical chemistry or analysis. There are no grounds to assume that the early chemical industries would have benefited if only the chemists of the time had known about atomic weights. Wollaston's equivalent weights (see chap. 7, sec. IV) did not depend upon knowledge of atomic weights and could be calculated by knowing the weight of an element which would combine with a given weight of oxygen.³

But this is not to diminish Dalton's place in chemical history, for it was he who discovered the law of multiple proportions and confirmed the general laws of chemical combination. The part played by analytical chemistry in formulating these laws should not be under-stated for it was from analytical results that Dalton showed how atomic weights could be determined. It was this which ultimately lifted the understanding of analysis from a comparative to an absolute discipline, and gave greater meaning to the concept of purity.

Whenever chemical content was measured, analysis existed, and priority of invention on this point though of little merit in itself, has been given to van Helmont whose interest in quantification, the use of weighings in chemical reactions, and interest in specific gravity measurements have been established.⁴ Wherever the decomposition of a substance or its combination with another element or substance is effected, the means for measuring becomes available. It was on addition or combination in the form of a chemical reaction that most early manufacturing processes depended.

The mere observation of a simple chemical process, represented by $A + B = AB$ leads to an empirical conclusion that so much of A appears to produce the optimum or maximum of AB, when reacted with so much of B. From this simple empirical observation there is created a chemical equation which then provides a basis for future analysis. Through an addition or synthesis reaction, $A + B$, so much of product AB is formed. Conversely, AB may decompose into constituent parts and by simple calculation of difference, any one constituent may be determined. Also, substance A reacted with substance B in a definite proportion, provided the material and conditions were always the same. In these simple empirical observations lay the logic for determining the amount present of one substance by using a known amount of another, the standard, which reacts with it. As Macquer had implied (see previous page), at this stage chemistry and analysis were the same. But there is a problem in this apparent simplicity, for it is only through analysis that the purity of the standard substance used for comparison can be ascertained. The purity of this standardising or comparison substance lies at the heart of early titrimetric analysis which undoubtedly had its origins in the pre-chlorine bleaching industry.

³ Wollaston, W. H. 'A Synoptic Scale of Chemical Equivalents', *Philosophical Transactions*, 1 (1814), p. 7.

⁴ Debus, A. G. *The Chemical Philosophy*, vol. 2, (New York, 1977), p. 327.

II. Crystallization

One way in which pure substances can be formed is through crystallization. This found early use in one of the oldest chemical industries, the alum industry,⁵ where the ease of crystallization resulted from the fact that alums are generally much more soluble at high temperatures than at low. Given these properties, crystallization became a very easy means of obtaining relatively pure material. Unfortunately for early pre-Dalton analysts, this gave no guarantee of absolute purity, but nevertheless it did provide a workable basis for analysis.

Seventeenth- and eighteenth-century chemists were well aware of crystallization techniques. For example, Joan-Baptista van Helmont (1577-1644) clearly describes how to isolate common salt from the crystals formed from urine.⁶ His contemporary, Edward Jorden (1569-1632) had similar interests and identified specific crystalline substances after distillation and recrystallization processes.⁷ He described these in the several editions of *A Discourse of Natural Bathes and Minerall Waters* (1632), based on a study of the natural spa waters at Bath, where he also commented on precipitation techniques and the use of an acid-base indicator, which in the opinion of Debus is probably the first clear reference to an acid-base indicator⁸. Many of the analyses discussed so far have employed these methods, sometimes as a means of chemical identification through familiarity of crystal shape or form, and sometimes as a quantitative means.

Nevertheless, in mixtures of salts, if the process of crystallization is stopped well before the solution is completely evaporated then the main constituent in the crystalline mass will probably be that salt which is least soluble. Repeated crystallization would lead to greater purity of product. Possibly of more value was the fact that through familiarity of crystal form a means of identification became available, and from the nature of a crystalline salt the reacting acid and alkali could be identified.⁹

A leading French writer of chemistry, Pierre-Joseph Macquer¹⁰ recommended that repeated crystallizations gave a means of achieving high purity. This is clearly stated in his *Dictionnaire de chymie*¹¹ in terms of present day understanding and describes fractional crystallization based on repeated evaporation of concentrated solutions, followed by cooling and separation of the crystalline product. This *Dictionnaire* was of great significance and was translated into two volumes by James Keir. Schofield¹² suggests it was this translation which won high acclaim from members of the Lunar Society and perhaps influenced Keir's engagement as manager of Roger's Amblescote (*sic*, Amblecote) Glass House near

⁵ Singer, C. J. *The Earliest Chemical Industry* (London, 1948).

⁶ Partington, J. R. *A History of Chemistry*, vol. 2, (London, 1961), p. 234.

⁷ Jorden, E. *A Discourse of Natural Bathes, and Minerall Waters* (London, 1631), p. 38, in the 1632 edition as quoted by Debus, A. G. 'Solution Analysis Prior to Robert Boyle', *Chymia* 8 (1962), pp. 41-60, on p. 55.

⁸ Debus, A. G. 'Sir Thomas Browne and the Study of Colour Indicators', *Ambix*, 10 (1962), pp. 29-36, on p. 31, quoting Jorden (1631) p. 76; also see Debus, A. G. 'Solution Analysis Prior to Robert Boyle', *Chymia*, 8 (1962) pp. 41-61.

⁹ Munro, D. 'An Account of some neutral salts made with vegetable Acids and with the salt of Amber', *Philosophical Transactions*, 57 (1767), pp. 479-516.

¹⁰ DSB., Macquer, P. J. vol. 8 (1973), p. 618; see also McKie, D. 'Macquer, the first Lexicographer of Chemistry', *Endeavour*, 16 (1957), pp. 133-136.

¹¹ Macquer, P. J. *Dictionnaire de chymie*, vol. 2 (Paris, 1766), pp. 329-330, as quoted by Eklund, J. 'The Incomplete Chymist being an Essay on the Eighteenth-century Chemist in his Laboratory, with a Dictionary of Obsolete Chemical Terms of the Period', in *Smithsonian Studies in History of Technology* no. 33 (1975), p. 15.

¹² Schofield, R. E. *The Lunar Society of Birmingham* (Oxford, 1963), p. 81; see DSB., Keir, J. vol. 7 (1973), p. 277.

Stourbridge. Keir's familiarity with this topic is seen in his analytical results of Indian Alkali (see p. 12) although he gives no hint that this was his method of ensuring the purity of his titration standard.

Crystallization developed as a means of practical chemical production and not in order to assist chemical analysis, for nineteenth-century artisans and chemists were more interested in how to make a substance than in its composition; viewpoints rarely mentioned in histories of crystallography. But of course as more and more chemical substances were made, the need to identify and test quality grew. Perusal of textbooks of the period and those appearing well into the nineteenth century testify to the practical needs of manufacture and chemical preparation; Ure's *Dictionary of Chemistry* (1821) perhaps serves well to illustrate this point.

III. Chemical Indicators: beginnings of Titrimetry

Some simple qualitative tests using colour indicators were known before the work of Robert Boyle in 1663, but it is to him that a titrimetric principle for analytical purposes is attributed.¹³ Although not clearly stated as a chemical procedure, Boyle recognised that the concentration of an acid might be determined by adding it to a suitable colour indicator solution until the colour changed; also, that alkalis are those substances which give blue or green coloration with certain vegetable extracts. It is for these observations that Boyle appears to have priority of discovery. However, it was known before Boyle's work that acids change the colour to red of certain other vegetable extracts. By using a tincture of Lignum Nephriticum Boyle describes what is almost a titrimetric method:

I drop into the infusion [extract of Lignum Nephriticum] just as much distilled vinegar, or other acid liquor as will serve to deprive it of its blueness..... And therefore allow myself to guess at the strength of the liquors examined by this experiment, by the quantity of them which is sufficient to destroy or restore the ceruleous colour of our tincture.¹⁴

This does not fully describe a titrimetric analytical procedure, but does offer a simple method of identifying an acid or an alkali and also of gauging their approximate strength or concentration. What began as a qualitative observation changed into a quantitative procedure - a not uncommon development in analytical chemistry. Whatever developments took place in titrimetry following Boyle's observations, the use of coloured substances as indicators became well established and indeed retained this role for some two hundred years, after which synthetic organic compounds became available.

Within this early use of colours as indicators, one can identify the beginnings of titrimetric analysis. In acid-base titrations the colour change is usually reversible and this can be a requisite in certain circumstances. Baker¹⁵ uses this criterion in claiming Boyle as the true originator of chemical indicators, but as with many discoveries, it is the person who publicly states their full interpretation, meaning and application, over and above their simple observation, who rightly claims priority.

It was perhaps Boyle's interest in colour changes which led him to devise a test to distinguish between what was then known as volatile animal alkali (ammonia) and fixed vegetable alkali (potassium or

¹³ Boyle, R. *The Experimental History of Colours* (London, 1663), (not seen), reprinted in *The Works of the Honourable Robert Boyle* edit. by Thomas Birch, (London, 1774), vol. 2, pp. 5-81.

¹⁴ *Ibid.* (1774), p. 47.

¹⁵ Baker, A. Albert, 'A History of Indicators', *Chymia*, 9 (1964), pp. 147-167.

sodium carbonate). He found that by mixing two completely colourless solutions of mercury sublimate (mercuric chloride) and either ammonia (as hydroxide) or alkali (as carbonate), a white or orange precipitate was formed. Could it be that Boyle realised that in any reaction involving a colour change a possible means of analysis was available? It certainly seems he realised that a colour change was more important than the colour itself, particularly when used in a succession of tests. More fundamental to future analytical developments was Boyle's tacit appreciation that the presence of a substance might be deduced from some other secondary reaction under known conditions.

There is a temptation to assume that little analytical progress occurred between the early titrimetric statements of Boyle and the more developed methods of Geoffroy and Lewis which are discussed in the following sections. One notable figure in this period was Guillaume (Wilhelm) Homberg who in 1699 quantitatively reacted different acids with fixed quantities of potassium carbonate until effervescence ceased.¹⁶ The reaction between an acid and an alkali had been observed from the period of iatrochemistry but Homberg applied a quantitative approach which later developed into one of titrimetry. It should be noted that the chemical understanding of alkali carbonates (the products of alkali acid reaction) remained somewhat confused until Black's later explanation,¹⁷ but effervescence with acids was well observed and eventually judged as an indicator in itself. The work of Holmes in interpreting Homberg's thinking and his setting within the Paris Academy of Sciences is worth noting,¹⁸ but it is in the titrimetric work of Geoffroy and more importantly, that of William Lewis that modern ideas of titrimetric analysis become more apparent.

IV. Titrimetry and Volumetric Analysis

These methods came into use during the middle of the eighteenth century, the same period in which industrial chemical manufacture commenced.¹⁹ This form of chemical analysis reflected the growing use of chemicals and their manufacture in a period of industrial activity now referred to as the Industrial Revolution. Whatever interconnections existed between this sudden growth in industry and the early large scale manufacture of chemicals to fuel that expansion, it is the concern of this chapter to examine a system of analysis which gave support to commercial chemical production.

It would be difficult to argue that titrimetry or volumetric analysis had a place any greater than one of support to manufacturing operations and use of chemicals; clearly chemical production existed before the adoption of chemical controls through analysis. But this remark is not to belittle the value of the early

¹⁶ Homberg, G. 'Observation sur la quantité exacte des sels volatiles acides contenus dans tous les différens esprits acides'. *Mémoires de l'Académie Royale des Sciences*, (Paris, 1699), pp. 44-51, (reprinted Paris 1718), as quoted by Madsen, E. Rancke. *The Development of Titrimetric Analysis till 1806* (Copenhagen, 1958), p. 20.

¹⁷ Robison, J. (editor) *Lectures on the Elements of Chemistry, delivered in the University of Edinburgh; by the late Joseph Black, M.D.*, 2 vols., (Edinburgh, 1803), on p. 384, vol. 1, '...like the alkalis, they [acids] change the colour of infusion of the purple or blue flowers of vegetables; but whereas the alkalis change them to green, or abolish the red and deepen the blue, the acids, on the contrary, change them into bright red, or into scarlet, and an extremely small quantity is sufficient'. Robison then names several tinctures in common use: archil, cudbear or litmus, scrapings of red cabbage, radish, cyanus, mallow flowers, march violet, convolvulus, and alkanet. '...they [acids] readily unite with any of the alkalis, and if these are in their ordinary state, a violent effervescence is produced. The mixture makes no change in the colour of the vegetable infusions. This gives us the first employment for our tests and test papers. By which we discover the exact saturation of the ingredients, which is another proof of the chemical combination.'

¹⁸ Holmes, F. L. *Eighteenth-Century Chemistry as an Investigative Enterprise* (Berkeley, 1989), pp. 33-38.

¹⁹ Christophe, R. 'L'Analyse volumétrique de 1790 à 1860 Caractéristiques et importance industrielle. Évolution des instruments', *Revue d'Hisdes Sciences* 24 (1971), pp. 25-44

analysts considered so far, for example Kirwan, Parkes and others. Chemical activity in whatever form often advanced as an indirect result of chemical truths made apparent by analytical developments.

The place and usefulness of analysis in the early bleaching industry have been shown in chapter one. Some of those analytical procedures used to determine the quality of alkali raw material bordered on true titrimetry, and when chlorine bleaching was adopted (chapter three) process control by analysis became an immediate necessity. Disregarding the antiquity of alum and common salt production, it is no coincidence that titrimetrical developments centred upon the most essential manufactures of the new chemical industry, viz. acids, alkalis and their combined usage in the bleaching industry. Indeed early titrimetry (this term having appeared in published papers only from the early nineteenth century)²⁰ was essentially a process of balancing acid against alkali to obtain a numerical result as an indication of the strength of one or other component. The quantity of substances needed to complete a chemical reaction were determined either by weighing or volume measurement. Strictly speaking, volumetric analysis only came into being as a branch of titrimetry and depended upon what were termed standard solutions containing known weights of substances. (see chapter seven in which the concept of 'Normality' is considered). Curiously another branch of titrimetry involving the weighing of the apparatus before and after titrations seems to have found no general application. A notable exception is seen in a published paper by George Fordyce (1736-1802) which describes, possibly for the first time, the use of alkali hydroxide instead of alkali carbonate in order to determine the amount of sulphuric acid.²¹ His paper of 1792, describes an attempt to show the source of additional weight of metals when calcined. The quantitative experiments involved reacting sulphuric acid and aqua kalipuri (potassium hydroxide solution), and is quoted by Madsen as a very early method which later became known as volumetric analysis.²² Fordyce's use of a colour change indicator to show completion of the reaction and his observation that the colour change is more easily seen if the alkali is added to the acid rather than the reverse is noteworthy. In the strict sense of volumetric analysis, whilst he uses solutions of fixed concentration, these cannot be seen as 'standard solutions' using known weights of chemical compounds, but his results were nevertheless of value as comparative measures.

The importance of sulphuric acid, in allowing the expansion of the textile industry, has been mentioned and also the value of soda obtained from seaweed has been a constant theme in this study. It is not surprising therefore that early titrimetry developed from reacting an acid with an alkali and that a concept of purity as a pre-requisite of analysis, if only in comparative testing, developed simultaneously. It was fortunate that sulphuric acid, potash and soda were relatively easy to obtain in a fairly pure form, since these chemicals found such an important place in early industry.

Sulphuric and hydrochloric acids, soda and potash, and a little later, bleaching solutions using chlorine, were important chemical products of commercial interest. Nitric acid or aqua fortis remained an artisanal interest although pre-dating the other mineral acids; sal ammoniac like alum, whilst having a

²⁰ Szabadváry, F. *History of Analytical Chemistry* (Oxford, 1966), p. 197.

²¹ Fordyce, G. 'On the Cause of the additional weight which Metals acquire by being calcined', *Philosophical Transactions*, 82 (1792), pt.1, pp. 374-382. See also *DNB* (London, 1908), vol. 7, p. 432; Howell, W. B. 'Doctor George Fordyce and His Times', *Annals of Medical History*, 2 (1927), pp. 281-296.

²² Madsen, E. Rancke. *The Development of Titrimetric Analysis till 1806*, (Copenhagen, 1958), p. 163; Szabadváry, op. cit. (20), p. 212.

wide range of applications, never experienced the explosive growth in production as was demanded of soda and vitriol. It seems natural therefore that technical methods of checking chemical quality by the manufacturer and by the purchaser should have developed around these commercially prepared substances. At this early stage of chemical production it is interesting to note that producers rarely needed to use their own products; their chemicals were to be sold to other users thus creating a demand for quality assessment through the practice of chemical analysis. Chemical substances could be more reliably tested by chemical means although colour, taste, smell, texture and appearance remained of value.

It is reasonable to assume that titrimetry developed from a need for rapid analytical results, even if lacking in accuracy, but there is little archival evidence to confirm this. Certainly the method offered a speedy result which motivated its early development.

V. The Titrimetric Contribution of Claude Joseph Geoffroy (1680's - 1752): Geoffroy le Cadet

Taking Boyle's work as an initial step leading to what became titrimetric analysis, there was little further progress until the work of C. J. Geoffroy in 1729, published in an essay submitted to the French Academy.²³ It described the analysis of vinegar and its possible concentration by removal of water by freezing:

For chemical operations, from the vinegars which have these properties it is still necessary to choose the one which is most charged with acids. There are several ways of accomplishing this: one of the main ways was indicated by late M. Homberg in *Mémoires de l'Académie*, 1699, page 49, and by M. Stahl in his *Opusculs chymiques* [Chemical treatises], page 418; and in following their idea I took for my tests two portions of each type of vinegar which I weighed very accurately and placed in round-bottomed glasses; I gradually added very dry, finely powdered, pure salt of tartar [potassium carbonate].

I continued to do this until fermentation ceased. The acid of the vinegar grew less; the liquor became slightly salt, and fermentation ceased. I knew the strength of vinegar from the greater or lesser amount of salt of tartar which was required to absorb the acid of this liquor and with which it had become saturated in fermenting; this usually goes as far as four grains for the weakest Paris vinegars, and up to eight for the strongest. Orleans vinegars absorb eleven, and one vinegar made from good wine which I tested can go as far as twelve.²⁴

Clearly this is another instance of an acid alkali reaction being used in an analytical way and contains aspects of what we now term titrimetry. Geoffroy determined the added amount of potassium carbonate by weighing, that is, gravimetrically, and no doubt obtained improved accuracy. But his end point, or the point of full 'saturation' or completion of reaction, can only have been within the observable accuracy given by cessation of effervescence; this method again only gave comparative results for the acid content and not absolute values inasmuch as the strength of acetic acid measured, was only related to the amount of potassium carbonate used in the complete saturation.

This report of 1729 seems to be the first description of an analytical process involving neutralization between an acid and an alkali, although no attempt has been made in this study to prove priority of

²³ Geoffroy, C. J. 'Examen du Vinaigre Concentré par la Gelée' *Concentré Mémoires de l'Académie Royale des Sciences* (Paris, 1729), printed 1731, pp. 68-78.

²⁴ *Ibid.* pp. 68-9, (my translation).

discovery.²⁵ More than twenty years were to elapse before the appearance of Home's *Experiments on Bleaching* (1756) in which methods are adopted that clearly resemble the earlier work of Geoffroy. But this does not mean that Geoffroy's crude titrimetric method was forgotten entirely, for during this period certain chemically-minded physicians were taking great interest in the nature and testing of so called mineral waters. It seems natural that titrimetry should be seen as a possible means of examining these if only because Geoffroy's work appeared to take place in aqueous medium.

It would be difficult to show any practical bearing on the early origins of titrimetry by the work of Geoffroy's more famous elder brother, E. F. Geoffroy (1672-1731) in his construction of what became known later as an affinity table. However, the topic is important and deserves mention.²⁶ E. F. Geoffroy published his 'Table des différents Rapports' in 1718²⁷ and this was the first of several tables prepared by others which followed soon after. By this method the order of affinity of a base (earths, metals, and alkalis) for a series of acids and vice versa could be illustrated. The assumption was that an acid with a higher affinity for a base would displace one with a lower. This was not always found to be the case although the practice of presenting chemical data in this way encouraged chemists to see all reactions in terms of affinities. Such systematization of empirical knowledge without theoretical basis or concept can however be regarded as only a partial explanation of Geoffroy's affinity table.²⁸

From Geoffroy onwards it seems probable that these tables came into common use resulting in a growing use of chemical symbols as a means of representing chemical reactions. Whilst symbolism perhaps contributed to a better understanding of simple analytical procedures, more rewarding was the idea that affinity tables pointed to concepts of compound formation in regular proportions. Indeed this is part of the recent interpretations by Klein²⁹ and by Duncan.³⁰

VI. William Lewis (1708-1781): Experimental Chemist

It has been shown how the titrimetric method of analysis had origins in the work of Boyle in establishing the use of coloured indicators and aspects of reactions between acids and alkalis. Part of this thesis considers the use of simple acid-alkali balancing as a useful analytical procedure, and its use in early kelp assessment has been shown through the work of Home. Analytical results, while of great value, remained only relative or comparable to other standard substances, of whose purity there could be no absolute certainty. Through modern eyes it would be easy to assume that such analytical limitations might remain until such time as purity could be better expressed. For example, given a sample of pure sodium carbonate, we would express this as 100% Na₂CO₃, but this only became possible when knowledge of

²⁵ The publication in 1718 of a table of affinities by Geoffroy's brother Étienne-François, suggests an implicit concept of neutralisation (see following footnote).

²⁶ Crosland, M. P. *Historical Studies in the Language of Chemistry* (London, 1962), pt. 4, chap. 1, pp. 240-243. This author maintains that the primary importance of the affinity tables was simply as a classification of experimental evidence, summarizing chemical reactions and predicting others.

²⁷ Geoffroy, E. F. 'Table des différents Rapports observés entre différentes substances', *Mémoires de l'Académie Royale des Sciences*, (Paris, 1718), p. 212, (not seen).

²⁸ Klein, Ursula, 'Experimental Practice and Layers of Knowledge in Early Modern Chemistry 1.' *Preprint 25* (Max Plank Institute for the History of Science, Berlin, 1995), pp. 73-127.

²⁹ *Ibid.* p. 107.

³⁰ Duncan, A. *Laws and Order in Eighteenth-Century Chemistry*, (Oxford, 1996), chap. 4.

chemical formulae and atomic weights had been established.³¹ The value of crystallization has been mentioned earlier but this gave no proof of absolute purity.

It is against this background and the results of earlier chemists already discussed, that the analytical work of William Lewis shows a significant change of perspective. Lewis and Samuel More analysed Virginian Saltpetre; the details and results of this work are in the archives of the Royal Society for the Encouragement of Arts, Manufactures & Commerce, London (hereafter sometimes referred to as the Society of Arts).³² It is from this collection of primary source material that it is possible to trace a direct influence on commercial matters, in particular the place and value of analytical chemistry. Their work not only reflects the knowledge and practice of the period but contains aspects of procedure which only became standard practice long afterwards, namely the use of a reference or standard: 'This Experiment was also tryed with the refined Salt Petre of the Shops'.³³ Also their frequent duplication of tests in order to obtain concordant results is noteworthy: 'It was some [sometimes] difficult to get the exact point of Saturation, and the Trial was 3 or 4 times repeated'.³⁴ It must be noted that Lewis was aware of the limitations of his procedures and from this viewpoint the assessment provides useful insight.

A study of Lewis would be incomplete without reference to the activities and worthy functions of the Society of Arts; Mercer's studies of the Society's early history reveal its valuable influence often through such chemically minded enthusiasts as Lewis and his contemporary, Samuel More.³⁵ Whether in the form of premiums or more esteemed gold medals, their efforts and those of others were recognised and fully documented in the Society's records. In More's appearance before a Select Committee of the House of Commons in June of 1780 his self-description must surely have been uncommon for that time:

I was bred a chymist and am acquainted with the Science of Chymistry. I have always made the Arts that depend on Chymistry my particular study.³⁶

Of course More was not without notable 'chemical artist' contemporaries, for example, Dossie, Shaw, Morris and Fordyce who were also conscious of the application of chemistry to industrial processes.³⁷

Premiums were being offered for the manufacture of potash in North America; for the purification of train oil; for a native varnish to replace the imported French product; for the manufacture of sal ammoniac in England. With some of these Lewis and More were already concerned. From 1763 he [More] and Lewis were working together on Virginian nitre: an account of More's work is in the Chemistry Committee Minutes for 16th July

³¹ See Brock, W. H. 'An Attempt to Establish the First Principles of the History of Chemistry', *History of Science* 6 (1967), pp. 156-69, on p. 158, '...chemists possessed no perfect concept of purity until Lavoisier formally defined pragmatic elements to which Dalton could apply a theory of homogeneous atoms.'

³² The Society for the Encouragement of Arts, Manufactures and Commerce, founded in 1754 and granted title Royal in 1908. 'Minutes of the Committee of Chemistry', 23rd July 1763, show that More and Lewis were asked to analyse samples of Virginian Saltpetre. Their results and analytical details are in (i) Lewis, W. 'On the Virginian Salt Petre', (ii) More, Samuel. 'Experiments on the Virginian Salt Petre sent in Chrystalls', in 'Minutes of the Committee of Chemistry' 31 August 1763. Location Royal Society of Arts, London.

³³ *Ibid.* (31st August 1773), Experiment 4.

³⁴ *Ibid.* (31st August 1773), Examination of Chrystallized Virginian Nitre. W. Lewis.

³⁵ Mercer, G. E. (Secretary, 1961-73), 'Studies in the Society's History and Archives, CXLVIII "Mr. More of the Adelphi", Notes on the Life and Work of Samuel More, Secretary of the Society 1770-99', *Journal of the Royal Society of Arts*, 127 (1979, Jan. Feb. March), pp. 96-103, 173-9, 237-244.

³⁶ *Journals of the House of Commons*, 37 (1780), pp. 913-15.

³⁷ Mercer, *op. cit.* (35), p. 101

1764. On the 23rd July both he and Lewis were thanked by the Society for their "obliging care and accuracy in making the experiments".³⁸

Lewis and More then continued their researches into North American potash for which Lewis received a Gold Medal in 1767 while More received the Society's thanks. Papers on this research were published individually and their work was considered to have made a valuable contribution to the development of the process of making potash in North America.

Mercer's notes on Lewis and More are based on primary source material; More practised as an apothecary and chemist and Mercer assumes that his interest in certain chemical processes was motivated by his concern for health hazards arising from industries such as water gilding and white lead manufacture. The Society's interest in these two industries is confirmed in a collection of manuscripts entitled 'Discourses', written by Samuel More in the period 1794-1799.³⁹ More's connections with John Wilkinson the iron master, and Wedgwood are described by Mercer,⁴⁰ and his reputation as a chemist of high standing shows in his appearance as an expert witness to a Government Select Committee in 1780.⁴¹ In this, the duties levied on fossil alkali against the quality are considered and the suppliers named as Keir, Black, Watt, and Collison. Clearly, More was acquainted with members of the Lunar Society and Mercer suggests friendship with Erasmus Darwin and Withering.

The following advertisement appeared in the *Daily Post* on 11 January 1737:⁴²

On Wednesday the 12th Instant, at Four o'Clock in the
Afternoon, at the Elaboratory in New-street, Fetter-lane
WILL begin a COURSE of CHEMISTRY,
with a View to the Improvement of PHARMACY, TRADES,
and the ART itself.
By WILLIAM LEWIS.
Schemes of the Course are to be had at Mr. Willock's
Bookseller, in Cornhill; and at the Elaboratory.

Mercer has suggested⁴³ that More must have attended these lectures - but offers no supporting evidence - and that his friendship with Lewis originated here. That this friendship existed cannot be doubted, and also their shared beliefs, together with other Society members, in the benefits of chemical research to industry. In 1747, Lewis retired to Kingston and it was here that he wrote *An Experimental History of Materia Medica*.⁴⁴ In developing further his ideas on the usefulness of chemical knowledge to industry, he wrote his other major work, *Commercium Philosophico-Technicum; or, The Philosophical Commerce of Arts*.⁴⁵ To what extent Lewis's contemporaries influenced this work is uncertain, for he was

³⁸ *Ibid.* p. 173.

³⁹ In 1795, More commented on the award of the Society's Gold Medal for work on dust prevention in white lead manufacture. It is known that Mercer made extensive use of More's 'Discourses' and the Minutes of the Society when writing his *Notes on the Life and Work of Samuel More*: private communication dated 28th November 1994 from the Library Administrator, Royal Society of Arts, London.

⁴⁰ Mercer, *op. cit.* (35), pp. 173-4.

⁴¹ *Journals of House of Commons*, vol. 37 (1780), pp. 913-15, and 929.

⁴² Cited by Gibbs, F. W. 'William Lewis, M.B., F.R.S. (1708- 1781)' *Annals of Science* 8 (1952), pp. 122-151, on p. 124.

⁴³ Mercer, *op. cit.* (35), p. 101.

⁴⁴ Lewis, William. *An Experimental History of the Materia Medica* (London, 1761). See account by Gibbs, *op. cit.* (42), p. 131.

⁴⁵ Lewis W. *Commercium Philosophico-Technicum; or, The Philosophical Commerce of Arts: Designed as an Attempt to Improve Arts, Trades, and Manufactures* (London, 1763-1765). The title page of volume 1. continues: 'by W. Lewis. MB. and FRS. London, 1765. William Lewis Kingston on Thames. 7th April 1763.' A second volume is dated 1764 and contains the extensive treatise on platinum (chap. VII, History of Platina, pp. 443-612).

not without the friendship of chemists of high repute such as Stephen Hales, Robert Dossie, Peter Shaw, Peter Woulfe, Dr Morris and Dr Fordyce, all of whom were equally associated with the Society and keen to bring about the use of applied chemical knowledge to present and future industries. Documented proof of the association between Lewis and Stephen Hales is shown in several letters from the latter and held in the 'R.S.A. Guard Book' volume 4. In number 108, dated 15th February 1760, Hales of Teddington, refers to his 'ingenuous neighbour Dr Lewis of Kingston' in discussing the marking of sheep by the methods suggested by Lewis. Certainly Lewis's analysis of American potash must stand as a very early example of a working chemical consultancy.

Later in this chapter the question arises as to why the analytical methods devised by Lewis were not apparently better known. That question will remain unanswered and the same enigma is described by Gibbs:⁴⁶

He [Lewis] was celebrated as a physician and occupied a secure place as the foremost British pharmaceutical writer of his day; his books were widely used, in particular by Cullen and Black at Edinburgh. Yet apart from a few scattered references to him in the literature of pharmacy, one can search the histories of the special sciences in vain for an indication of the extent of his work....Lewis was one of the best known and least known scientists of his period.

In 1931, Edward Kremers compiled a bibliography of Lewis's publications clearly showing a prolific output in his time.⁴⁷ Surprisingly he states:

Since Lewis made no experimental contributions to chemistry, we are not surprised that his name is not mentioned in the histories of chemistry,⁴⁸

Gibbs points correctly to the inaccuracy of the present *DNB* entry about Lewis which was reproduced in Kremer's bibliography. The true identity of William Lewis has perhaps posed difficulties in past researches which hopefully will be resolved in the forthcoming *New DNB*.

VII. Philosophical Commerce

If Lewis greatly influenced the application of chemical knowledge to the germinating chemical manufacturing industries, then it must have been through his London lectures and published writings.⁴⁹ There seems little record of his lectures; no extant copies compiled by some enthusiastic student as in the case of Black's or Neumann's lectures for example, but his text books can be examined. Perhaps his most important work was *Commercium Philosophico Technicum; or, The Philosophical Commerce of Arts*.

In the preface of the first volume Lewis describes his chemical observations regarding the affinity and reaction between quicklime and vitriolic acid:

Thus, when quicklime is dissolved in water, if we add to the transparent fluid a little vitriolic acid, the acid particles unite with the dissolved particles of the lime into a new compound; which notwithstanding the pungent taste of the one ingredient, the corrosive acidity of the other, and the solubility of both, proves insipid and indissoluble, and which therefore, separating from the water, renders it at first milky, and on standing settles to

⁴⁶ Gibbs, *op. cit.* (42), p. 122.

⁴⁷ Kremers, Edward. 'William Lewis', *Journal of American Pharmaceutical Assoc.*, 20 (1931), pp.1204-1209.

⁴⁸ *Ibid.* p.1205.

⁴⁹ Gibbs, *op. cit.* (42), see bibliography pp. 149-151.

the bottom, in the form of powder or small crystals, of the same general properties with the native gypsums or plaster-of-Paris stones.⁵⁰

Page XI of the same preface refers to the *Proposals*,⁵¹ dated 15th January 1748 which contain almost two hundred and fifty items on technical, commercial, and theoretical matters related to the developing industries of that time. Analytical topics were included. For example Lewis proposed 'A practical method of examining the degree of purity and strength of aqua fortis [nitric acid]', while water of crystallization, affinities, and specific gravity measurements were clearly also of concern. The *Proposals* came to fruition as the two volumes of *Philosophical Commerce of Arts* published fifteen years later.⁵² In that time Lewis had been advised to publish in a more methodical vein since:

Many of the arts have natural and strong connections with one another; working upon the same materials.....The discoveries and improvements made in one art....are generally little known to those who are employed in another, so that the workman can seldom avail himself of the advantages which he might receive from the correlative arts.⁵³

Such were the guidelines used by Lewis while Gibbs suggests possible support for the work from other Royal Society members such as Stephen Hales, Henry Pemberton, William Brownrigg, Heberden and others.⁵⁴

Another major work from Lewis was *The Chemical Works of Caspar Neumann M.D.*⁵⁵ The title page carries this heading and continues:

With large Addition, Containing the late Discoveries and Improvements made in Chemistry and the Arts depending thereon, by William Lewis. M.D. and Fellow of the Royal Society. London. MDCCLIX.

In the preface we read:

Neumann's lectures are a valuable magazine of chemical knowledge. The Author [Neumann], biased by no theory, and attached to no opinion, has enquired by experiment into the properties and uses of the most considerable natural and artificial production, and the preparation of the principal commodities which depend on chemistry.

According to Thomson⁵⁶ much of the translation for Lewis's publication was carried out by Alexander Chisholm. The story of Lewis's meeting with Chisholm in a London bookshop in about 1750, and his engagement as assistant to Lewis is told by Thomson and by Gibbs.⁵⁷ Lewis's researches into platina (platinum) are discussed by Gibbs who points out that early specimens of the metal examined by Lewis were procured from Jamaica by Brownrigg who passed the material to the Royal Society.⁵⁸ Clearly Lewis was highly esteemed as a research and analytical consulting chemist. Possibly arising from his knowledge of platinum, Lewis commented on the calcination of metals:

⁵⁰ Lewis, *op. cit.* (45), v, (preface).

⁵¹ Lewis W. *Proposals For Printing by Subscription, commercium Philosophico-Technicum; or, The Philosophical Commerce of Arts: Designed as an Attempt to Advance Useful Knowledge* (London, 1748).

⁵² See *Monthly Review* 34 (1766), p. 169.

⁵³ Lewis, *op. cit.* (45), xi (preface).

⁵⁴ Gibbs, *op. cit.* (42), p. 127.

⁵⁵ Lewis, W. *The Chemical Works of Caspar Neumann M.D.* (London, 1759).

⁵⁶ Thomson, Thomas. *The History of Chemistry*, vol. 1, (1830), p. 266.

⁵⁷ Gibbs, *op. cit.* (42), p. 128.

⁵⁸ *Ibid.* p. 129; McDonald, D. and Hunt, L.B. *A History of Platinum and its Allied Metals* (Johnson Matthey, 1982), p. 38.

It is well known to the chemists that the metals called imperfect, or those which calcine in the fire, gain weight in their calcination; a phenomenon not a little astonishing, and of which they have not been able to assign any probable cause, unless it be the absorption of air... ..As platina appears plainly, from many of its properties, not to be one of the imperfect metals. Mr Macquer very justly suspects that the increase in weight in the above experiments was owing to the calcination of some heterogeneous substance mixed with the platina.⁵⁹

It is by these publications and the analytical work on American potashes that Lewis influenced industrial development by showing that industrial processes could benefit from the application of chemical knowledge. However, if this new perspective was only slowly adopted, it does not diminish Lewis's important contribution. *The Philosophical Commerce of Arts* and the 'Experiments and Observations on American Potashes'⁶⁰ were influential sources of chemical and analytical knowledge applicable to existing manufacturing processes and those in early stages of development. Lewis's method of writing differed from other writers of the period. For example, Dossie and Peter Shaw⁶¹ published in the same period, but lacked the practical presentation offered by Lewis. The latter saw himself, as evidenced in the works described above, as a practical research chemist. His methodical presentation of the properties of many chemical substances clearly assisted their industrial application. This was often achieved through association with entrepreneurs such as Wilkinson and Wedgwood and visits to several industrial sites. However, Lewis's emphasis on practical application was not without firm theoretical belief.⁶²

Gibbs placed some emphasis on the sale of Lewis's library following his death in 1781 and provided details of two main sales of what would have become valuable archival material.⁶³ This would have confirmed the important role of Chisholm to whom Lewis apparently entrusted the writing-up of many experimental results in the form of chemical diaries. Thomson⁶⁴ points out that:

At Dr. Lewis's death, all his books were sold by auction,... ..They were purchased by Mr. Wedgewood [sic, Wedgwood], senior, who at the same time took Mr. Chicholm [sic, Chisholm] into his service, and gave him the charge of his own laboratory.

VIII. Titration of American Potashes

It is in Lewis's work on American Potashes that one can see advancement in analytical methods and in particular the use of a titrimetric means of determining alkali content using a colour indicator. His original report is held by the Royal Society of Arts; the title page of the printed transcription reads:

*Experiments and Observations on American Potashes with An Easy Method of determining their respective Qualities. By W. Lewis, M. B. F. R. S. Made at the request of the Society for the Encouragement of Arts, Manufactures, and Commerce, in consequence of an Application from the House of Representatives of Massachusetts Bay. Printed by order of the Society. 1767.*⁶⁵

⁵⁹ Lewis, *op. cit.* (45), vol. 2, p. 461.

⁶⁰ Lewis, W. 'Experiments and Observations on American Potashes. With an Easy Method of determining their respective Qualities', (London, Printed by order of the Society of Arts, 1767), 34 pp.

⁶¹ Gibbs, F. W. 'Robert Dossie 1717-1777 and the Society of Arts', *Annals of Science*, 7 (1951), pp. 149-72; 'Peter Shaw and the Revival of Chemistry', *Annals of Science*, 7 (1951), pp. 211-237.

⁶² Lewis, W. *op. cit.* (45), pp. viii and ix, (preface), regarding chemical combination.

⁶³ Gibbs, *op. cit.* (42), pp. 143-144.

⁶⁴ Thomson, *op. cit.* (56), p. 266.

⁶⁵ Location, Royal Society of Arts London. Collection of Tracts and Pamphlets, vol. E, no. X. I.

Eight potash samples were sent to Lewis by the Society and his report begins with a detailed comment on their physical appearance, taste etc. and the wide variation of solubility in water. This was not Lewis's first encounter with potash, for he mentions a comparison with earlier specimens (also from America) of visually better quality than the American grades now under examination. On addition of acid to the solutions (lyes) Lewis reports 'an impregnation of sulphureous matter' but not from all the samples.

Using four ounce samples he determined the total dissolved solids in the clear filtrates by complete evaporation. After drying the crystals at 'a moderate heat, below red hot' he showed by weighing, that all eight samples contained over three ounces of soluble salt in four ounces of original material. At this early stage in the analyses, Lewis already has a feel for the most caustic samples which he noted melted more easily.

Quantitative recrystallizations were carried out in an attempt to separate any salts present other than the alkali (potash). Lewis easily identified the initial non-alkali crystals, since in his experience true alkali would not crystallize out at the chosen dilution. Thus vitriolated tartar (potassium sulphate) and sea salt were isolated and a dried mixture of these, when tasted, indicated their presence together with some alkali; such was the application and apparent sensitivity of tasting in this period. Later in the report Lewis showed little enthusiasm for the method of crystallization:

[this] was found so difficult and tedious, that the enquiry was dropt, and another way of examination tried.⁶⁶

That other way was to be:

...the quantity of true alcali in the salts might be discovered by their power of saturating acids, compared with that of an alcali of known purity; and this method succeeded so well, that it is hereafter proposed for the assaying of Potashes, and the manner of procedure described at large.⁶⁷

At this early stage of the report, Lewis tabulated his results of the eight samples which showed marked variation in alkali content. In this thirty four page publication he describes his analytical procedures in the last four pages and it is these which are now considered.

In the opening paragraph he refers to other chemists, who, using the methods now being considered, only achieved comparative results and not absolute values. In order to achieve accuracy he emphasises certain technical details; for example, he realises that the presence of 'earthy matter' in the potash samples will affect the amount of acid needed for complete saturation and this and any other impurities must be removed before the determination. As is already known, Lewis suggests dissolving the soluble, or true alkali in water and filtering off any insoluble earthy material. He makes no claim for the originality of this procedure which certainly became a standard technique and is described in all the analytical examples so far examined. Lewis describes his method thus:

⁶⁶ Lewis, *op. cit.* (60), p. 4.

⁶⁷ *Ibid.*

The quantity of acid, necessary for the saturation of the lye, should be determined, not by drops or tea-spoonfuls, but by weight [a clear reference to Home's work]; and the point of saturation, not by the ceasing of the effervescence, which it is extremely difficult, if not impracticable, to hit with tolerable exactness, but by some effect less ambiguous and more strongly marked, such as the change of colour produced in certain vegetable juices, or on paper stained with them.

The finer sort of purplish blue paper used for wrapping sugar in, answers sufficiently well for this purpose; its colour being changed red by slight acids, and afterwards blue or purple again by slight alcalies.⁶⁸

In crediting Lewis with this early use of a chemical indicator, it seems appropriate to quote his instructions on this topic:

What I have chiefly made use of, and found very convenient, is a thick writing paper stained blue on one side with an infusion of lacmus or blue archil, and red on the other by a mixture of the same infusion with so much dilute spirit of salt as is sufficient just to redden it. The paper is washed over with a brush dipt in the respective liquors, two or three times, being dried each time, till it has received a pretty full colour, and afterwards cut in slips a quarter of an inch or less in breadth; a bit of the end of one of the slips being dipt in the liquor to be tried, the red side turns blue while any of the alcali remains unsaturated, and the blue side turns red when the acid begins to prevail. If either the acid or alcali considerably prevails, the paper changes its colour immediately on touching the liquor: if they prevail but in a low degree, the change is less sudden. The part dipt is always to be cut off before a fresh trial.⁶⁹

Lewis showed preference for spirit of salt (hydrochloric acid) rather than sulphuric acid in his belief that hydrochloric acid would not react with any sodium chloride which might be present in the soluble portion of the potashes under test. He then gave very precise instructions on the method of preparing a conveniently diluted acid solution and the method of standardising this against a carefully weighed amount of perfectly dry potassium carbonate (Lewis is assuming 100% purity). At no point does he know the true amount of hydrochloric acid in the dilute solution but this is not important for he is not calculating, as we would today, the results of a chemical reaction based on a chemical equation using molecular weights as units in the calculation. What is significant in these details is that he has standardised the acid by giving it a numerical value of strength in terms of equivalence to a known weight of what he believes is pure potash. Once this has been established, aliquots of the same acid can be used in an indefinite number of determinations.

It would be difficult to achieve greater accuracy in measuring the amount of acid used in the titration by any method other than that advocated by Lewis. In this simple gravimetric technique, a phial of dilute acid is merely counterpoised using a balance (there is no mention of its sensitivity) and after pouring off the amount needed for complete saturation of the potash, the phial is returned to the balance and again counterpoised; the weight difference indicates the amount of acid used. Lewis takes this further by using a fixed amount of sample whereby he can directly read off the amount of potash present against marked balance weights.

It would be an exaggeration to claim that Lewis introduced the idea of what became known as 'back titration' but he hints that if the end point, the change in colour of the indicator, is exceeded in error, it is

⁶⁸ *Ibid.* p. 28, see also Appendix I.

⁶⁹ *Ibid.* p. 29.

not necessary to repeat the entire experiment. This can only be taken to mean that more alkali might be added and the true end point repeated more carefully than before, and then recalculating accordingly.

Regarding the possible presence of causticity (hydroxide), Lewis offered the following observation:

A person accustomed a little to this operation [the titration], will be able to determine by it, not only the quantity of pure alcali, but whether the alcali has any injurious causticity. Plain alcalies effervesce with the acid, from almost the first drop, till the saturation is completed: those which are fully caustic, make no effervescence at all; and those which are caustic in part, do not begin to effervesce, till a considerable quantity of the acid has been added, more or less according to the degree of causticity.⁷⁰

Within this original report Lewis included a section entitled 'Hydrostatic assay of the strength of lyes, and of the quality of saline matter contained in Potashes'.⁷¹ In order to accurately determine the density of lyes he devised an improved hydrometer which gave a direct reading of the weight of potash in a pound of lye. He also recognised the importance of temperature in 'hydrostatic assays' but, more importantly, the limitations of the method:

To determine whether this salt be the pure alcali which it ought to be, recourse must be had to operations of a different kind, such as that described in the following article.

Here follows Lewis's titrimetric method.⁷²

Hydrometry, whether by the flotation of an egg or by Lewis's modified hydrometer, has proved a useful industrial analytical control but it does not differentiate chemical species (as Lewis correctly observed) and is therefore not directly indicative of chemical composition. Although not a truly *chemical* method of analysis it provided a reliable way of standardising sulphuric and other acids that were crucial to the emergence of titrimetry. The subject is vast and appears in many of the published papers so far examined. It clearly demands a separate and fuller treatment than can be given here.

IX. William Lewis: Conclusions

In his detailed paper regarding this acid-alkali titration there are features and principles of which I have been unable to find earlier record. This record of what to us may seem a simple titration must stand as one of original invention marking a very important and authenticated advance in analytical chemistry. Consider for example the contrast between Lewis's accuracy in weighing and measuring with Home's use of a teaspoon measure. At no time does Lewis allow anything less than perfectly measured volume, and he often resorts to measures of weight to reinforce what otherwise could have been taken as acceptable volumetric measurement. However this aspect alone hardly stands as invention, and neither does his use of coloured indicators; but taken together and with his rejection of liberated carbon dioxide as a reliable end point, we see Lewis's work as approaching an achievement of significance. The suggestion to use hydrochloric acid and not sulphuric is interesting inasmuch as Lewis possibly foresaw a reaction between the latter and soluble marine salt (NaCl) in the potash solution. The validity of this point is unimportant when compared with the meticulous procedure in preparing the acid solution and potassium carbonate used in the standardisation process:

⁷⁰ *Ibid.* pp. 32-33.

⁷¹ *Ibid.* pp. 18-27, on p. 18.

⁷² *Ibid.* p. 27.

Take a quantity of spirit of salt [hydrochloric acid], and dilute it with ten or twelve times its measure of water; fill with this mixture a vial that will hold somewhat more than four ounces of water: the vial which I find most commodious is nearly of the shape of an egg, with a broad foot that it may stand sure, a funnel-shaped mouth for the convenience of pouring the liquor into it, and a kind of lip or channel at one side of the mouth, that the liquor may be poured or dropt out without danger of any drops running down on the outside. Hook the vial, by means of a piece of brass wire tied round its neck, to one of the scales of a balance; and counterpoise it, while filled with the acid liquor, by a weight in the opposite scale.⁷³

This does not describe a modern burette, but the results gained from this procedure are the same but with enhanced accuracy, depending of course on the sensitivity of the balance. It is this dilute acid solution which Lewis will titrate against one eighth of an ounce of prepared pure potash. This has been made from thoroughly dried salt of tartar (potash, presumably from recrystallized material) followed by fusion, and taken up in an ounce or two of water. His description of this standardising titration follows:

Pour gradually some of the acid from the vial into the solution of salt of tartar, so long as it continues to raise a strong effervescence; then pour or drop in the acid very cautiously, and after every small addition, stir the mixture well with a glass cane, and examine it with the stained papers. So long as it turns the red side of the paper blue, more acid is wanted: if it turns the blue side red, the acid has been overdosed. That there may be means of remedying any accident of this kind, without being obliged to repeat the whole preceding part of the experiment, it will be proper to reserve a little of the alkaline solution in another vial: this is always to be added towards the end, and washed out of the vial with a little water.

When the liquor appears completely saturated, making no change in the colour of the paper, hook the vial on the scale again, to see how much it wants of its first weight: this deficiency will be the quantity of the acid liquor consumed in saturating the two drams of alkaline salt. So much as this quantity wants of four ounces, so much, in proportion, of common water must be added to all the rest of the acid mixture. If for instance the quantity consumed in the saturation is three ounces, then, for every three ounces, or three pounds, or thirty pounds, of the acid liquor, must be added one ounce, or one pound, or ten pounds of water; the acid will thus be so adjusted, that four ounces of it will saturate two drams [one eighth of an ounce] of alkali: it will be expedient to make another trial, to see whether it is exactly of this strength.⁷⁴

Put more simply, Lewis has shown that four ounces of his standard hydrochloric acid of unknown strength, will always saturate one eighth of an ounce of pure potassium carbonate; in other words he has standardised the acid against pure potassium carbonate. This was a unique feature and practical achievement of that time, for in so doing, he had demonstrated the way in which an absolute quantity could be determined. Rancke Madsen⁷⁵ has calculated the acid concentration expressed as HCl at 1.6-1.7% or 0.4-0.5 molar, but little useful historical value can be drawn from such recalculation.

Speed and simplicity are characteristics of titrimetry and are illustrated in Lewis's developments. They may not have been essential requirements in his time, but no doubt grew as the application of the procedure widened particularly into industrial processes. In standardising the acid within the range quoted above Lewis arrived at a final calculation of marked simplicity; the weight of acid consumed, multiplied by four, indicated the quantity of pure alkaline salt contained in every pound of original sample. Within

⁷³ *Ibid.* p. 30.

⁷⁴ *Ibid.* pp. 30-31.

⁷⁵ Madsen, *op. cit.* (22), p. 54.

these six pages of reporting, Lewis has described all the essential features of what we know as acidimetric titration and it represents an exceptional piece of analytical development. His rejection of approximate volume measurement in favour of weighing, the use of colour to provide clear evidence of the completion of reaction, the creation of a standardised solution, all led to a method of determining absolute content, provided of course that pure potassium carbonate was actually pure.

Lewis's titrimetric work was published in 1767 and as we have seen, contained a definite, if indirect reference to Francis Home, perhaps in response to *Experiments on Bleaching* of 1756. It must be accepted that the work on potash analysis clearly shows advanced method in principle, that is, in the use of coloured indicator, and also the care and possibly better accuracy in weighing and other measurement when compared with his earlier analysis of Virginian Saltpetre.⁷⁶ In the latter, he was obviously aware of the inadequacy of the method and maybe this in itself resulted in the improvements used in analysing the potash samples four years later. Duplication of tests and the use of a standard for comparison must stand as noteworthy; such attention to detail set standards of working for future analysts.

Oddly in both pieces of work, Lewis makes no mention of moisture content in the original sample material, and there is some uncertainty over water of crystallization. The latter was certainly not entirely understood at this time although some account had been given in *Philosophical Commerce of Arts*, four years earlier. It is nevertheless surprising that occluded moisture in such commercial products as saltpetre and potash had no consideration. Lewis's awareness of what he believed to be absolute values of content must be noted as a major advance; in the experiments to measure the strength of nitric acid obtained from the saltpetre, Lewis saw this as a mere balancing of one chemical against another in terms of saturation. The later experiments on potash show a belief in true chemical content in absolute values; we may now judge this differently inasmuch as he was without the modern foundations of chemical formulae, equations and molecular weights which we now see so essential in analysis.

In chapter one it was shown how serious interest in the quality and composition of kelp was reflected in analytical endeavours by various and often well-known chemists of the period. Their achievements followed the important work by Lewis discussed above, yet none made any reference to him, or replicated his methods. This requires some explanation the answer to which is not immediately obvious. Madsen's remark is pertinent:

It is strange that the analytical part of this treatise was not at all understood by Lewis's contemporaries, and that the treatise does not seem to have left any mark in the development of analysis.⁷⁷

Fyfe, Jameson, even Kirwan *et al* were seemingly trying to re-invent the work already done by Lewis whose innovative progress in titrimetry had been published.

It would now be difficult to determine with any accuracy the audience for this particular analytical work by Lewis; his 1767 paper was published in London and copies were sent to the colonies.⁷⁸ It is

⁷⁶ Society of Arts (i), Lewis, *op. cit.* (32).

⁷⁷ Madsen, *op. cit.* (22), p. 55. Madsen is referring to the titrimetric section in Lewis's 1767 paper.

⁷⁸ Personal enquiry to the library of the Royal Society of Arts (27th October, 1994) where the original MS is held. According to Gibbs, *op. cit.* (42), p. 132, it is written in Chisholm's hand.

surprising therefore that his analytical achievements were not better appreciated outside the interests of the Royal Society of Arts.

This short account of Lewis's writings and analytical developments clearly shows his concern for the improvement of 'the arts'. His work on the analysis of potashes was in the context of the encouragement given by the Society of Arts to import these materials from British Colonies rather than from uncertain European sources. In this he did not aim solely at a theoretical understanding of chemical processes to the same extent as Joseph Black. The latter saw chemical understanding of early bleaching methods as a means of immediate help to bleachers, but in fact this was not borne out in practice for the rule-of-thumb empirical methods continued. Lewis attempted to show that chemical analysis could be used to improve 'the arts' by providing accurate means of determining quality and hence value and suitability for the purchaser.

In order to place Lewis's work in the context of the early beginnings of the industrial revolution, Sivin⁷⁹ has used a chronological argument; he cites Ashton's⁸⁰ suggestion that 1782 was the beginning of the industrial revolution because in that year most statistics indicated a sharp increase in industrial production. But, as Sivin argues it seems reasonable to assume that by the time such early statistics became available those industries which had created saleable products had already become established and were no longer in their early year or years of founding. On this basis the industrial revolution must have begun much earlier.

By the middle of the eighteenth century the social and economic demands of a greatly increased population more probably heralded this dramatic change, visible in the growing demands on the textile, metallurgical, and ceramic industries, all of which required chemicals. Clow relates this birthdate, 1760 to 1780, with the increased number of registered patents as a barometer of the new industrial activity, but this gives no better picture than that based on the number of prizes and awards given by the Society of Arts with which Lewis was directly involved.⁸¹

Lewis undoubtedly led the field in showing that practical chemistry through analysis could provide answers to industrial questions. His analytical work and hydrometry researches, these alone, place him supreme for the period - his main texts, *Commercium Philosophico-Technicum* and *The Chemical Works of Caspar Neumann* are full of answers to manufacturing problems and possibly set a pattern for future authors in this field. Lewis's researches on platinum were extensive and represented a programme of work involving a logical analytical approach, proving the metallic status of platinum and its chemical detection as an adulterant of gold.⁸² He applied chemistry as no other person before him, proving beyond doubt that it could provide advantageous answers. This arose through his logical and systematic method of researches - he was a quantitative chemical experimentalist.

⁷⁹ Sivin, N. 'William Lewis 1708-1781 as a Chemist', *Chymia*, **8** (1962), pp. 63-88.

⁸⁰ Ashton, T. S. *Economic History of England, the 18th century* (London, 1955), p. 125.

⁸¹ Clow, A. and Clow N. L. *The Chemical Revolution* (London, 1952), pp. 1-3.

⁸² Sivin, *op. cit.* (79), p. 78. Also McDonald and Hunt, *op. cit.* (58), p. 38.

There has been little said about his theoretical thinking; but this should not be seen as wanting in his scientific position. He seems to have had a distant regard for solitary theorising. Where he found theory, for example in his consideration of the contemporary vogue for affinity tables, he immediately sought to find their practical application. For Lewis science was the application of knowledge.

Analysis has two important roles: that of proving and to some extent pushing forward theoretical research, but more often, it gives a practical service to practical problems through compositional data. It was in the latter that Lewis was so firmly engaged.

CHAPTER THREE

CHEMICAL ASPECTS OF THE EARLY CHLORINE BLEACHING INDUSTRY

I. Introduction and Development of Chlorine Bleaching

This study of chemical and analytical developments at the time of the Industrial Revolution would be incomplete without a serious consideration of the introduction of chlorine into the bleaching industry. Indeed, in this context, it is possible to show that chemical development and its industrial application were dependent upon chemical analysis.

The bleaching part of the early textile industry was a laborious and lengthy process dependent upon the cleansing properties of alkaline solutions and often misunderstood chemical ideas on the processes of acid treatment and the effect of sunlight or 'grassing'. The work of Black and Home gave a benefit to these processes through a better chemical understanding of the materials in use; but it was the availability and use of sulphuric acid which speeded up bleaching and which became so necessary to the ever increasing demand for faster methods. The bleaching process was further accelerated by the use of chlorine which eventually led to even faster rates of textile finishing. On this point alone, the chemical knowledge of chlorine, its properties to bleach linen and cotton, and the methods used to produce this gas, can be seen as major chemical contributions. Without these developments the textile industry would have been seriously retarded.

Chlorine could be prepared by reacting sulphuric acid with salt and manganese dioxide; an additional new demand for sulphuric acid arose giving credence to the now legendary association of this commercial product as a barometer of industrial growth.¹ Compared with the earlier alkali 'bucking' and sour milk processes, bleaching with chlorine was seen to be a very rapid means of achieving a better result. Its introduction into the textile industry was not rapid and this no doubt reflected natural distaste in using such an offensive material and the practical difficulties in its handling.² The term bleaching is often used to describe several stages in a complex and time consuming process; whilst the use of chlorine accelerated the overall bleaching process it did not remove the necessity for alkaline wash solutions. Soda made from Scottish kelp remained an essential ingredient of 'bucking' solutions although Madsen has suggested that the value of Home's *Experiments on Bleaching* faded after Berthollet's announcement in 1785 regarding the bleaching properties of chlorine³.

Some aspects of the introduction of chlorine into bleaching illustrate a much closer relationship between technology and chemistry than that which existed at the time of Home's and Black's work; at that time, bleaching methods had developed empirically, that is, by practical observation and adjustment without theoretical understanding of the processes involved. This was not the case with chlorine bleaching. In this, a new gas having distinct bleaching properties had been identified by eminent chemists. There was no significant period of empirical development and the need for analytical control was immediate. The bleaching potential of chlorine or oxygenated muriatic acid as it was then known,

¹ Usually attributed to Liebig, J. *Familiar Letters on Chemistry* (London, 1843), p. 30.

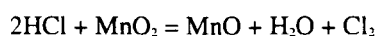
² Higgins, S. H. *A History of Bleaching* (London, 1924), pp. 96-107. See also *Encyclopaedia Britannica* (London, 1824), supplement to 4th, 5th & 6th edit., attributed to Thomas Thomson.

³ Madsen, E. Rancke *The Development of Titrimetric Analysis till 1806* (Copenhagen, 1958), p. 32.

was first recognised by the French chemist Berthollet in 1785.⁴ He clearly demonstrated its action on linen (wool and silk, being animal fibres present a different case). In 1774 the Swedish chemist Scheele⁵ had discovered chlorine which he termed 'dephlogisticated marine acid air'. Its decolourising properties were observed but apparently he did not test the effect on linen or cotton textiles.

It is not the purpose of this study to establish the priority of application of chlorine in bleaching, for this the reader should see the Clow's *Chemical Revolution*,⁶ but rather to seek out authenticated instances of the application of chemical knowledge, and in particular the benefits given by chemical analysis. The place and influence of those chemists involved in this part of what we now call the industrial revolution will occupy a central position.

Chlorine is an offensive gas; hardly an attractive feature compared with the gentler nature of alkali washing solutions or even dilute sulphuric acid as adopted after Francis Home's recommendations. The practical difficulties of chlorine production and its handling must have been considerable and off-putting for the average bleaching works. Its early production was by reacting hydrochloric acid with manganese dioxide, generally referred to as black calx of manganese. At some stage, this reaction was replaced by one using vitriol (sulphuric acid), common salt and manganese dioxide.⁷ Modern chemical equations representing these reactions are shown thus:



In the second reaction the hydrochloric acid so produced merely reacts with the manganese dioxide in the first reaction.

When Berthollet and Scheele first produced chlorine both were without the modern nomenclature shown above, also the chemical nature of the gas was not fully understood, indeed confusion was caused by the then accepted phlogiston theory. Scheele's term 'dephlogisticated marine acid air' attempted to take into account the idea that phlogiston was involved although Berthollet's terms 'oxygenated muriatic acid' or 'oxymuriatic acid' were much nearer the truth. Berthollet believed that vital air (oxygen) was evolved from solutions of dephlogisticated marine acid and that this brought about the bleaching action by converting the troublesome non-white residues into easily soluble compounds.⁸ These were readily released from the textile fibres by solution in alkaline leys; clearly, Berthollet's contribution to chemical enlightenment was considerable. A similar understanding appeared in successive editions of Thomas Thomson's *A System of Chemistry*:

⁴ Partington, J. R. *A History of Chemistry*, vol. 3, (London, 1962), p. 503, cites Berthollet, C. L. 'Sur l'Acide Marin Déphlogistique', *Observations sur la Physique* 26 (1785), pp. 321-5.

⁵ *Ibid.* p. 213. Scheele's discovery was announced in a letter to Gahn dated 28 March 1773.

⁶ Clow, A. C. and Clow, N. L. *The Chemical Revolution A Contribution to Social Technology*, (London, 1952); Higgins, S. H. *A History of Bleaching*, (London, 1924); Musson, A. E. and Robinson, E. *Science and Technology in the Industrial Revolution* (Manchester, 1969), chap. 8.

⁷ Rees, A. *The Cyclopaedia* (London, 1802-20). Reprinted in 1972 by David & Charles, Newton Abbot, as Rees's *Manufacturing Industry*. Vol. 1, p. 18, attributes this modification to 'the ingenious Mr. Watt' but offers no supporting evidence.

⁸ Partington, *op. cit.* (4), p. 503. See also Smith, J. G. *The Origins and Early Development of The Heavy Chemical Industry in France* (Oxford, 1979), pp. 139-143.

When oxy-muriatic acid dissolved in water is presented to the light in a vessel half empty, oxygen gas is disengaged and floats above, and the acid is converted into common muriatic acid; consequently oxy-muriatic acid is composed of muriatic acid and oxygen.⁹

This author makes no mention of the practical application of oxymuriatic acid in bleaching; but almost thirty years later, in the seventh edition (1831), there are significant changes both in chemical understanding and recognition of applied chemistry:

At present all the great bleaching works, in this country employ chlorine as the grand whitening agent. For the first introduction of it we are indebted to Mr Watt (see *Annals of Philosophy* VIII. 1). The process followed is to combine unslacked quicklime and chlorine by leaving them for a sufficient time in contact. The compound thus formed is usually called bleaching powder. It is chloride of lime. At first it consisted of two atoms of lime united to one atom of chlorine. But now it is manufactured in Glasgow [presumably Thomson is referring to the works of Charles Tennant] so strong, as to be a compound of one atom of chlorine and one of lime. This powder is dissolved in water.¹⁰

Advancement in chemical knowledge can also be seen in Turner's third edition of *Elements of Chemistry*:

It is well-known that muriatic acid is always generated when chlorine bleaches. From these facts it is inferred that water is decomposed during the process; that its hydrogen unites with chlorine; and that decomposition of the colouring matter is occasioned by the oxygen which is liberated.¹¹

What we now see as a great discovery of immense industrial potential may not have been so apparent at the time. Much of the understanding of chlorine bleaching arose from the laboratory work of Berthollet, and the two authors mentioned above clearly illustrate its progression.¹² Thomas Thomson's contribution on bleaching in *Encyclopaedia Britannica* states the options open to bleachers in using chlorine; of the three methods available:

...namely, dissolved in water, combined with lime in the state of liquid oxymuriate of lime, or in the state of solid oxymuriate of lime. The first of these states is the most economical; but its very noxious odour renders its application scarcely practicable on a great scale. The second state consists of two atoms of oxymuriatic acid, combined with one atom of lime, or it is a bichloride of lime; and the third state, or the dry powder, is a compound of one atom of oxymuriatic acid and one atom of lime, or it is a chloride of lime. Of these two last substances there can be little doubt that the first, or the one made in the liquid way, is the most efficacious.¹³

⁹ Thomson, T. *A System of Chemistry* (London, 1802), vol. 2, p. 68, section IX, 'of oxymuriatic acid.'

¹⁰ Thomson, T. *A System of Chemistry* (London, 1831), vol. 1, p. 61.

¹¹ Turner, E. *Elements of Chemistry* (London, 1831), 3rd edit., pp. 293-294.

¹² See Smith, J. G. *The Origins and Early Development of The Heavy Chemical Industry in France* (Oxford, 1979), pp. 136-139.

¹³ *Encyclopaedia Britannica*, (1824), supplement to the 4th, 5th, and 6th editions, vol. 2, p. 330.

II. The Development and Chemistry of Alkaline Chlorine Solutions

Much of the analysis considered so far in this dissertation has developed from the idea of there being a chemical reaction, usually between two components such as an acid and a base. Because oxymuriatic acid was regarded as an acid, it can be no surprise that alkaline solutions of dissolved chlorine received attention by chemists. They would have noticed that chlorine is more soluble in alkaline solutions than in plain water, and because of the alkalinity its noxious nature was vastly reduced. To what extent the easier transportation of alkaline solutions of chlorine over those in plain water played any part, is now difficult to assess. The association between alkalinity and detergency must also have been obvious, so too the greater stability on long standing when compared with plain chlorine water; for these reasons the much less noxious alkaline chlorine solutions became of great interest.

It will be shown later that the technical demands of the new chlorine bleaching methods motivated analytical progress but to what extent analysis helped to push forward the technology of chlorine bleaching is not always obvious. It seems doubtful whether chlorine bleaching would have developed empirically without analytical support from industrial chemists. Authentic primary material showing a direct influence of analytical chemistry on the growth of the bleaching industry has been identified. Furthermore, Musson and Robinson confirm this role of industrial analysis within their general argument based on the influence of science and technology.¹⁴

It is reasonable to assume that water-based saturated solutions of chlorine - cold 'chlorine water' - were first employed in bleaching linen or cotton goods by simple immersion. The effects of chlorine on the workmen can be imagined and these prompted attempts to find a better medium in which the chlorine might be more conveniently handled. It was Berthollet who found that the addition of alkali to chlorine water removed the offensive free chlorine without apparently affecting its decolourising function.¹⁵

Potash became the chosen alkali and in addition to the advantages mentioned above, it was noticed that much larger volumes of gas could be dissolved directly into the potash solution and the resulting liquor remained stable during transportation. Of course there was an economic disadvantage because potash remained an expensive raw material. It seems natural that a much cheaper alternative in the form of lime should be tried and this is discussed later.

Berthollet's investigations led into new areas of chemical understanding but there has been little effort to describe his methods of analysis. Granted, if an alkaline solution of dissolved chlorine was found to hold more chlorine than a similar volume of pure water then clearly this would have been proved by the 'indigo test'. It will be shown later how T. L. Rupp obtained this evidence although not without serious flaws (see below, p. 66), and the analytical comments of Watt will also be considered.

The dissolution of chlorine into potash solution is a complex reaction and because of Berthollet's limited chemical understanding he drew a wrong conclusion from his observations which were

¹⁴ Musson, A. E. & Robinson, E. *Science and Technology in the Industrial Revolution* (Manchester, 1969), p. 328.

¹⁵ Berthollet C. L. 'Mémoire sur l'acide marin déphlogistique', *Observations sur la Physique* 26 (1785), pp. 321-5 and 'Mémoire sur l'acide marin déphlogistique', *Mémoires de l'Académie Royale des Sciences*, (Paris, 1788), pp. 276-95, as quoted by Madsen, *op. cit.* (3), p. 128.

surprisingly near the truth. In passing chlorine gas into caustic potash (KOH), Berthollet observed the formation of a new salt (potassium chlorate) and ordinary muriate (potassium chloride).¹⁶ In this he saw a transfer of 'oxygen' from the oxymuriatic acid (i.e. chlorine), to form a super-oxymuriate of potash together with some ordinary muriate. But in these compounds there was no bleaching capability. In modern terms, potassium chlorate and chloride were being formed under the chance conditions of Berthollet's researches, and this discovery apparently discouraged his further interest in alkaline solutions of chlorine, at least so far as bleaching operations were concerned. There is a temptation to ask why Berthollet failed to widen his range of tests to include varying concentrations. By so doing he would have noticed that very little potassium chlorate was produced provided an excess of alkali was present. It appears that Berthollet simply applied common sense and judged that the amount of chlorate produced would in fact increase, not decrease, with higher concentrations of alkali. This must surely have been a situation in which incomplete understanding arose from inadequate analysis and possibly affected commercial progress.

The full understanding of alkaline chlorine solutions remained somewhat confused. Turner's *Elements of Chemistry* (1831), about forty years after Berthollet's work, reported on 'Chloride of Soda' as being 'Labarraque's disinfecting soda liquid'¹⁷ which was thought to be a compound of chlorine and soda 'analogous to the well-known bleaching powder, chloride of lime'. The entry continues, 'Chloride of soda may be employed in bleaching, and for all purposes to which chlorine gas or its solution was formerly applied'. Then follows a detailed recipe and method of dissolving chlorine in a carbonate of soda solution:

In some respects the nature of this liquid is obscure; but from the preceding facts, drawn from the essay of Mr. Faraday, two points seem to be established. First, that the liquid contains chlorine, carbonic acid, and soda. Secondly, that the chlorine is not simply combined with water or soda.¹⁸

Clearly the chemistry of Labarraque's liquid still posed serious uncertainties.

The use of analytical chemistry to determine alkali and chlorine concentrations should not be undervalued. Consider all the practical values of alkaline chlorine solutions:

1. the presence of alkali removed the dangerous and offensive nature of chlorine water.
2. alkali removed the odour of chlorine water but did not affect the decolourising properties.
3. stronger chlorine content became possible in an alkaline medium.
4. the alkaline solution remained stable giving easier handling in bleaching works and made possible transportation of the liquor.

Analysis could provide the means of control and so directly influence the development of chlorine bleaching. The serious error of interpretation and range of testing by Berthollet, in recognizing the formation of chlorate of potash and potassium chloride, could have been avoided merely by widening the scale of testing using known methods of titration and his own 'indigo test'.

¹⁶ Berthollet, C. L. 'Observations Sur quelques combinaisons de l'Acide marin déphlogistiqué, ou de l'Acide muriatique oxigène', *Observations sur la Physique*, 33 (1788), pp. 217-24.

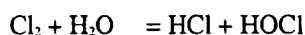
¹⁷ Turner, *op. cit.* (11), p. 433. A. G. Labarraque (1777-1850), an apothecary in Paris who introduced the use of alkali hypochlorite as a disinfectant which became known as 'Labarraque's liquid' in 1822.

¹⁸ *Ibid.*

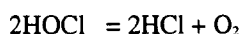
According to Smith,¹⁹ even without sound theoretical understanding of pH and the law of mass action, the French manufacturers at Javel (known for their 'eau de Javel'), used fairly concentrated alkali and so obtained a good yield of bleach without chlorate formation. The misunderstanding on this technical issue remained unresolved, indeed the matter was compounded by Rupp's report which stated that the addition of alkali increasingly reduced the decolourising property.²⁰ This was a misleading statement but it appeared to support Berthollet's ideas. The matter did not retard the industrial development of alkaline chlorine solutions and it was eventually fully explained by the work of Welter and Balard who showed that excess alkali retarded chlorate formation.²¹

III Dissemination of Chlorine Bleaching

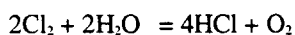
Chlorine is a powerful oxidising agent which reacts with water. A solution of chlorine water contains hypochlorous acid:



When exposed to light the hypochlorous acid decomposes:



Chlorine water on standing in the light is gradually converted into hydrochloric acid and oxygen:



Hypochlorous acid is also a powerful oxidising agent and is responsible for the bleaching action; it is in this compound that one sees a similarity with Berthollet's ideas in naming chlorine as oxymuriatic acid. It was of course Davy's researches in 1810 which identified the elemental nature of chlorine,²² but this in no way denies the scientific genius of Scheele and Berthollet from whom the discovery and the practical demonstration of its bleaching powers arose. Brande's much later understanding of the bleaching action of chlorine is of interest:²³

Hence it is probable that the bleaching agency is due to the evolution of nascent oxygen resulting from the decomposition of water; and there are other compounds containing oxygen, but no chlorine, which are also bleaching agents, such as the peroxide of hydrogen, and manganic and chromic acids. The bleaching power of dew, and sometimes of rain-water, renders it probable that they also contain some excess of oxygen, perhaps in the form of the peroxide of hydrogen.

The last sentence appears to have evolved from earlier explanations for 'grassing' in order to capture the power of sunlight, often not readily available in the Scottish climate.

¹⁹ Smith, *op. cit.* (12), p. 144.

²⁰ Rupp, T. L. 'On the Process of Bleaching with the oxygenated muriatic Acid; and a Description of a new Apparatus for Bleaching Cloths with that Acid dissolved in Water, without the Addition of Alkali', *Memoirs of the Literary & Philosophical Society of Manchester* 5 (1798), pp. 298-313, on p. 302.

²¹ Smith, *op. cit.* (12), pp. 147, 159.

²² Davy, H. 'Researches on the Oxymuriatic Acid, its nature and combinations', *Philosophical Transactions*, 100 (1810), pp. 231-57.

²³ Brande, W. T. *A Manual of Chemistry* (London, 1841), p. 364.

Musson and Robinson have made a comparative study of how and where chlorine was introduced into the United Kingdom bleaching industry.²⁴ They point out that the two works mentioned above, Higgins (1924) and Clow & Clow (1952), appear to draw on information, probably gleaned from Rees's *Cyclopaedia* (1819), Parkes's *Chemical Essays* (1815) vol. IV and various papers within *Annals of Philosophy* of 1815 and 1816. All of these sources give accounts of how such knowledge came to Britain from France, the country of its original invention. By drawing on a wide field of primary source material, for example the Boulton and Watt papers including the manuscripts of James Rennie and letters from other industrialists and scientists, Musson & Robinson have provided a wider and more reliable contextual background than earlier authors. Sykes confirmed that interest in bleaching with oxymuriatic acid spread rapidly; in a valuation of stock at the company of Holme & Slater Ltd in 1792 there are listed hydrochloric acid and manganese which suggests chlorine bleaching had been tried, even if not already in use.²⁵ Clow and Clow suggest however, that commercial chlorine bleaching was in use before 1790.²⁶

It is commonly accepted that chlorine bleaching entered Scotland by two distinct routes; firstly by the efforts of James Watt and his father-in-law James McGrigor; secondly, by Patrick Copland of Marischal College, Aberdeen and the industrial works of Gordon, Barron & Co. Understandably the chemical knowledge of the bleaching property of chlorine was not confined to these two instances. Indeed, Rees suggests a train of communication regarding the action on vegetable substances, direct from Scheele to Richard Kirwan, who then passed the information to Mr Charles Taylor, Secretary of the Society of Arts; unfortunately no supporting evidence is offered.²⁷ However, interesting references to Taylor's role in chlorine bleaching are made by Sir Henry Trueman Wood in his *History of the Royal Society of Arts*:

Taylor was a competent chemist, and, according to his statement to the committee, he was known to almost all the chemists in Europe. He informed the committee that he was the inventor of a method of calico printing "by wooden cylinders and sliding metallic cylinders". He also claimed to have furnished the Government with valuable information on indigo,^[28] which had led in the eight years from 1789 to 1797 to an increase in the value of the export of indigo from the East Indies from £110,000 to £558,000. Taylor was for some time engaged in the cotton manufacture in Manchester, but, as the short notice which appeared in the *Transactions* after his death states, "the opulence which flowed so exuberantly to many of his fellow-townsmen did not find its way to him". He was also the first to utilise Berthollet's discovery of the applicability of chlorine for bleaching, and was said to be "the first to produce for sale in the Manchester market an entire piece of calico bleached by oxy-muriatic acid". His death took place in 1816, after sixteen years' service.²⁹

From the late 1780s onwards Berthollet's method of bleaching by chlorine began to spread in France. One of the first to use this process was F. A. H. Descroizilles³⁰ (1751-1825) and according to Duval,

²⁴ Musson and Robinson, *op. cit.* (14), pp. 255-261.

²⁵ Sykes, A. J. *Concerning the Bleaching Industry* (Bleacher's Assoc., 1925), p. 114.

²⁶ Clow, *op. cit.* (6), p. 188.

²⁷ Rees, *op. cit.* (7), p. 181. There is no reference to marine acid or Kirwan and Scheele in the index of either the Society of Arts' Minutes or the 'Minutes of the Committee of Chemistry' for the period of Charles Taylor's Secretaryship of 1800-1816. Where Rees obtained this information remains a mystery, unless some private communication existed between Kirwan and Taylor regarding marine acid, which is now lost.

²⁸ For a brief history of indigo see Travis, A. S. *From Turkey Red to Tyrian Purple* (Jerusalem, 1993-1994), pp. 28-9; reviewed by Page, F. G. *Ambix*, 41 (1994), p. 168.

²⁹ Wood, H. T. *The History of the Royal Society of Arts*. (London, 1913), p. 335.

³⁰ Duval, C. 'François Descroizilles, The Inventor of Volumetric Analysis', *Journal of Chemical Education*, 28 (1951), pp. 508-19, on p. 513.

Descroizilles's bleaching and analytical interests arose after seeing a failed demonstration of chlorine bleaching in which part of the bleached cloth disintegrated.³¹ He realised the importance of being able, by some method as yet not discovered, to measure the bleaching strength of the solution in use. He quickly developed such an analytical method for which he is now well-remembered.

IV. Descroizilles's Method of Analysis

Descroizilles's own description appeared in 1795,³² but Berthollet had described the method earlier in 1789.³³

To avoid all accidents, owing to the too great strength of the liquor, we need an adequate method by the use of which it can be measured. M. Descroizille used for this purpose indigo solution in sulphuric acid. He dissolved one part of finely powdered indigo in eight parts of concentrated sulphuric acid, heating it on a water bath for several hours until dissolution was complete, and then diluted it with a thousand parts of water. To examine the strength of the chlorine water he placed a given amount of the indigo solution into a tube mounted with marks, and added chlorine water until it decolourized.^[34] Now it must be determined that in the case of a chlorine water, which proved to be suitable for textile whitening, how much is needed for the decolourization of the given amount of indigo solution. This quantity will serve for the comparison of various chlorine water samples, and these can then be used for the comparison of others.

Szabadváry points out that Berthollet's description is the reverse of that given by Descroizilles.³⁵ Berthollet states that to a measured volume of standard indigo solution, the bleaching solution of unknown strength is added,³⁶ while the reverse i.e. the indigo solution is added the bleach solution, is given by Descroizilles³⁷ who claimed to have tried both. The best choice would no doubt depend on the sharpness of the colour change and its disappearance. Certainly Berthollet gave serious attention to the theory and practical application of chlorine in bleaching, and made considerable contribution to analytical methods used in testing commercial alkalis, often as developments of the methods devised by Francis Home and Richard Kirwan.

Partington states that Berthollet had suggested the above method somewhat earlier, as a means of indicating the strength of bleaching solutions, and that Descroizilles had developed it further into a practical volumetric means.³⁸ This is somewhat contradicted by Szabadváry who states that Berthollet (and Lavoisier) merely used the method to determine the comparative colour strength of samples of indigo by adding measured amounts of chlorine water to effect decolourization.³⁹ Whatever true priority may exist on these points, the method became widely known and the two examples which follow support this view.

³¹ *Ibid.* p. 514.

³² Descroizilles, F. A. H. 'Description et usages du Berthollimètre', *Journal des Arts et Manufactures*, 1 (1795), pp. 256-276.

³³ Berthollet, C. L. 'Description Du Blanchiment des Toiles & des Fils par l'acide muriatique oxigéné, & de quelques autres Propriétés de cette Liqueur relatives aux Arts', *Annales de Chimie*, 2 (1789), pp. 151-190, on p. 177, as quoted and translated in Szabadváry, F. *History of Analytical Chemistry* (Oxford, 1966), p. 210.

³⁴ The same method was described by Thomas Thomson in *Encyclopaedia Britannica* (1824), supplement, p. 331, see below sec. VII.

³⁵ Szabadváry, F. *History of Analytical Chemistry* (Oxford, 1966), p. 210.

³⁶ Berthollet, *op. cit.* (33).

³⁷ Descroizilles, *op. cit.* (32), p. 262, 'laissez couler, avec précaution, la liqueur bleue dans le berthollet, qui en détruira sur-le-champ la couleur, en la faisant passer au fauve'. [cautiously pour the blue solution into the berthollet solution].

³⁸ Partington *op. cit.* (4), p. 507.

³⁹ Szabadváry, *op. cit.* (35), p. 210.

V. Robert Roe

The library of Trinity College, Dublin holds an original pamphlet by one Robert Roe, entitled *Experiments on the Oxygenated Muriatic Acid used in Bleaching with Remarks on the Blue Test Liquor &c.*, dated 1st August 1791 and addressed Ring's End (an area just south of Dublin). The same Robert Roe was elected to the Royal Irish Academy on 9 May 1789 and is entered as number 71 in the Academy Roll. Roe's pamphlet emphasises the value of analytical methods when applied to chlorine bleaching solutions. The strength of these could not be judged by appearance and therefore the role of analysis would be crucial to their safe use. A saturated solution could be deleterious to the textile fibres while one of only weak strength would be ineffective.

From wherever he found details of the so-called indigo test (see below, p. 74) Roe appears to have been the first to state five necessary purposes of analysis:

.....for it was necessary he [the practical bleacher] should know at what strength he bought it [the chlorine solution] at what Strength it was necessary to use it for different Purposes, how much it was reduced in the Process of Bleaching, in order to recruit it [maintain its strength] and, finally, when it might be thrown away without loss.⁴⁰

Such reasoning has remained relevant to the present day and reflects highly on Roe's 'philosophy of arts'. Recognition is given to Berthollet and the origin of the indigo test from M. Descroizilles but Roe remarks that neither had considered the impracticability of the test and its recommended apparatus when attempting to determine the strengths of highly saturated bleaching solutions:

I don't conceive this Method could ever be used to try a strongly impregnated Liquor; for Instance, let us suppose a Liquor 700 strong, which we shall meet in the following pages, and that we introduce half an Inch of this strong Liquor into a Glass Tube, then we must necessarily have 700 Half Inches of Tube (nearly 30 feet) in order to determine its Strength, which we see is totally impracticable⁴¹

Clearly Roe must be taking an extreme stance and appears to be ignoring the possibility of accurately measured dilution; a point he then retracts and expands upon in a later paragraph. To this day, dilution to convenient concentrations remains an important characteristic of all areas of analytical chemistry.

The same pamphlet contains Roe's detailed description of the apparatus he used for preparing the gas and its dissolution into alkaline solutions and water.⁴² He rejected Berthollet's recommended arrangement and chose a simple system of tubulated retorts leading into vitriol bottles as receivers:

...many of which can be attended by a single Man, and with the small Address of agitating the Receivers when filled with Gas, will succeed as well as the most complicated Apparatus that has yet been contrived.⁴³

Commenting on two known chemical reactions to generate the gas, i.e. muriatic acid with manganese [the dioxide], and common salt with vitriolic acid and manganese, his reaction vessel was:

⁴⁰ Roe, R. *Experiments on the Oxygenated Muriatic Acid, Used in Bleaching, with Remarks on the Blue Test Liquor, &c.* (1791), p. 1.

⁴¹ *Ibid.* p. 2.

⁴² *Ibid.* p. 3

⁴³ *Ibid.* p. 4

a Kind of Alembicks with Stone-ware Bodies and Glass Heads fitted thereto, because the Cake of Glauber Salt [sodium sulphate] and Manganese remaining after Distillation, can rarely be got out of a Retort without breaking it.⁴⁴

Five sets of experimental results follow, and the various liquor strengths, determined by the 'Blue Test' show that a caustic lye made by adding 38 lb. of quick lime to 114 lb. of Pearl Ash mixed with water to give a density of 9 lb. per gallon, was the most effective. Measurements were taken after overnight standing and in Roe's own words:

Here we see another important Fact, viz. that Caustic Lye is more susceptible of imbibing the Gas, and retaining it than mild Lye of equal Strength.⁴⁵

Experiment No. V., was made using water to dissolve the gas but this gave a 'Blue Test' result of less than a tenth of that using caustic lye:

The Operation was insupportably offensive, though conducted with the same care as the others, and the Liquor also very offensive, and so incapable of retaining the Gas.⁴⁶

Such a liquor (chlorinated water) whilst having bleaching properties, 'must always be made on the spot where it is to be used, as it will not pay for carrying it far, and it must be used immediately, as it will not retain the Gas for any considerable Time'.

Roe's final paragraph states his presumption that:

The Reader has already received general Instruction from Mr Berthollet's *Treatise* on this Subject, which is in the Hands of almost every one; and as a repetition of any Part of his Work would be superfluous, the Intention of these few pages is to add Precision for the Use of People in Practice, where he has been general; and under this Head there still remains much to be added, which I hope a little Time and Observation will supply.

Ring's-End, 1st Aug. 1791.⁴⁷

Roe clearly showed the value of the 'Blue Test' to determine the strength of bleaching solutions based on dissolved 'oxygenated muriatic acid'.

VI. Theophilus Lewis Rupp

On 9 February 1798, a paper was read at a meeting of the Manchester Literary and Philosophical Society and was later published in that society's *Memoirs*.⁴⁸ It bore the title, 'On the Process of BLEACHING with the oxygenated muriatic Acid; and a Description of a new Apparatus for Bleaching Cloths with that Acid dissolved in Water, without the Addition of Alkali, By Theophilus Lewis Rupp.'

According to Musson and Robinson,⁴⁹ Rupp was a German who had settled in Manchester as a cotton manufacturer sometime in the late eighteenth century. He was a member of the Manchester Society and

⁴⁴ *Ibid.* p. 4.

⁴⁵ *Ibid.* p. 5.

⁴⁶ *Ibid.* p. 6.

⁴⁷ *Ibid.* p. 8

⁴⁸ Rupp, *op. cit.* (20), pp. 298-313.

⁴⁹ Musson and Robinson, *op. cit.* (14), pp. 82-3 and 317-19.

showed little hesitation in expressing dissatisfaction with inadequate application of chemical truths to industry. For example, from the above paper:

The chemist, in particular, if we except the pharmaceutical laboratory, has but little claim on the arts: on the contrary, he is indebted to them for the greatest discoveries and a prodigious number of facts, which form the basis of his science.

In the discovery of the art of making bread, of the vinous and acetous fermentations, of tanning, of working ores and metals, of making glass and soap, of the action and application of manures, and in numberless other discoveries of the highest importance, though they are all chemical processes, the chemist has no share. ...The art of dyeing has attained a high degree of perfection without the aid of the chemist, who is totally ignorant of the rationale of many of its processes.⁵⁰

Rupp deplored the general lack of applied science and questioned the role of chemists. These may seem to us as exaggerated and misplaced comments, but Rupp was a chemist of some standing, and well-known to the greater figures of Dalton and Henry and other members of the Manchester Literary and Philosophical Society. He claimed that the theory underlying bleaching was not understood and whatever imperfect ideas had been expressed, 'none could be antecedent to the era of pneumatic chemistry'.⁵¹

Scheele's discovery of chlorine was seen by Rupp as an important step in chemistry but he paid greater tribute to Berthollet's immediate application of it to a commercial role. Whatever practical problems arose from the use of this new gas - Rupp speaks of 'prejudice and ignorance of bleachers in chemical processes', although manufacture and handling of the gas must surely have been the greatest difficulties - he claims that 'these problems were soon removed by Mr. Watt at Glasgow, and Mr. Henry and Mr. Cooper at Manchester'.⁵²

The method of preparing the gas had received Rupp's attention and whilst he acknowledged those of Watt and Berthollet, some modification seemed appropriate:

M. Berthollet's apparatus however is too complex for the use of a manufactory; Mr Watt's is better; but a range of four, five, or six hogsheads, or rum-puncheons, connected with one another, in the manner of Woulfe's distilling apparatus, is preferable to either of them.

...I always found the liquor to be strongest when the distillation was carried on very slowly. I have also found, that the strength of the liquor is much increased by diluting the vitriolic acid more than is usually done. The following proportions afforded the strongest liquor,

Three parts manganese
Eight parts common salt
Six parts oil of vitriol
Twelve parts of water.⁵³

Rupp claimed that by using his specially designed apparatus chlorine water could be used safely for bleaching cloth. However, the advantages of dissolving the gas in alkali solution had been established before Rupp's paper was published:

⁵⁰ Rupp, *op. cit.* (20), pp. 298-9.

⁵¹ *Ibid.* p. 299.

⁵² *Ibid.* p. 300.

⁵³ *Ibid.* p. 301.

...an addition of alkali to the liquor deprived it of its suffocating effects, without destroying its bleaching powers. The process then began to be carried out in open vessels. ...This advantage is unquestionably great; but it is diminished by the heavy expense of the alkali which is entirely lost..., that the alkali which is added to the liquor, though it does not destroy its power of bleaching, may diminish it;... that the oxygenated muriatic acid will lose its power of destroying the colouring matter of vegetable substances, in proportion as it becomes neutralized by an alkali.⁵⁴

The cost of alkali was the main disadvantage to its use, worsened by the fact that the bleaching power though not destroyed was in fact reduced. Rupp's experiments confirmed these opinions. In these analyses, he attempted to stabilise his chlorine water by using a darkened glass bottle fitted with a ground glass stopper. The method was as follows:

I weighed, first of all, a bottle filled with the colouring substance which I meant to employ: I then weighed, in a large and perfectly colourless bottle, half an ounce of the acid, to which I immediately, but very gradually, added of the colouring substance contained in the former bottle, till the acid ceased to destroy any more of its colour. The bottle with the colouring substance was then weighed again, and the difference between its present and original weight was noted.⁵⁵

In all these experiments, half an ounce of the oxygenated muriatic acid was used and the amount of colouring solution which was decolourised by the acid (chlorine solution) determined by weighing. The acidity of the indigo, being usually in sulphuric acid as a means of obtaining complete dissolution, was taken into account; Rupp used an 'acetous solution of indigo', explaining in a footnote:

This method [using an acid solution of indigo] was inadmissible in these experiments on the comparative strength of the bleaching liquor, with and without alkali; because the sulphuric acid would have decomposed the muriat of potash, and thereby produced errors. I therefore added to a solution of indigo in sulphuric acid, after it had been diluted with water, acetite of lead, till the sulphuric acid was precipitated with the lead. The indigo remained dissolved in the acetous acid.⁵⁶

In experiments I. II. and III., Rupp showed that on average, 162 grains of the indigo solution were decolourised. In experiment IV, 8 drops of pure potash was added. This quantity was sufficient to remove the noxious odour (free chlorine) but only 150 grains of indigo solution were then decolourised. Experiment V, confirmed the result given by the previous test. The amount of added alkali was increased to 10 drops in experiment VI, and the decolourising power fell to 125 grains. 15 drops of alkali were added in experiment VII, this reduced the decolourising further to only 120 grains. Four more determinations were made, but using a decoction of cochineal instead of indigo, and this established the same trend.

From these ten reported laboratory experiments, Rupp showed that increased additions of potash to his standard chlorine water, reduced its bleaching strength proportionally. Whilst these results appear valid it cannot be assumed that the same reductions in bleaching strength would have occurred in experiments using different ranges of concentration.⁵⁷ This illustrates the danger of limited chemical

⁵⁴ *Ibid.* p. 302.

⁵⁵ *Ibid.* p. 303

⁵⁶ *Ibid.* pp. 303-4.

⁵⁷ The same experiments are reported in *Encyclopaedia Britannica*, vol. 3 (1815) 5th editⁿ., p. 692.

experiments using different ranges of concentration.⁵⁷ This illustrates the danger of limited chemical understanding and laboratory investigation. There was no clear understanding regarding the formation of potassium chlorate and hypochlorite, although as mentioned above Berthollet had some insight into the complexity of the chemical reactions involved.⁵⁸

Because of the measured loss in bleaching strength, and the expense of the added alkali, Rupp designed a machine in which pure oxygenated muriatic acid, dissolved in water, could be used conveniently and safely. The remainder of his paper consists of a detailed description of the proposed apparatus, its mode of operation and the cost saving by using chlorine water.

Whatever criticism Rupp had laid against the value of chemistry and chemists, he had clearly used analysis to prove his own claims by using Descroizilles's method in measuring the effect of alkalis on bleaching liquors; unfortunately he drew misleading conclusions. Nevertheless this example, and that of Roe, clearly point to a general knowledge of analytical testing based upon the decolourising effect of chlorine.

VII. Further Observations regarding the Indigo Blue Test and the work of F A H Descroizilles (1751-1825)

Thomas Thomson's description of the 'indigo test', in the section on Bleaching in *Encyclopaedia Britannica* is worth noting:⁵⁹

The strength of this liquor is determined by means of the graduated glass tube, figured in the margin, which is known by the name of the **Test-tube**. The method is as follows: One part of the best indigo is dissolved in nine parts of strong sulphuric acid, and the solution is mixed with 990 parts of water, making a solution one thousandth part of which is indigo. Of this liquid a quantity is to be poured into the test-tube, so as to fill it up to 0, or the commencement of the scale. The bleaching liquor, whose power is to be tried, is then to be dropt gradually in and mixed with the blue liquor, by shaking the tube from time to time, till the blue is changed into a clear brown. As soon as this takes place, the degree of the scale to which the mixture reaches is observed, and the figure marked at that degree indicates the strength of the steep-liquor. The lowest on the scale is, of course, the strongest in bleaching power, being capable of destroying most colour. The liquor, whose strength is thus ascertained, is denominated Steep-liquor, of 1, 2, 3, 4, 5, and 6 degrees; the last of which is the weakest ever used for any kind of goods.

A satisfactory bleaching strength is one which would bleach effectively without damage to the cloth, and would in this test read four degrees.⁶⁰ Contrary to Descroizilles's original instruction, Thomson followed the description given by Berthollet in dropping the bleach solution of unknown strength into the standard volume of indigo. The method was not without weakness in that commercial indigo was of variable composition and the speed at which the test was carried would also affect its accuracy.

A less detailed entry had appeared in the 1815 fifth edition of *Encyclopaedia Britannica* describing Descroizilles's method of testing and similarly suggesting its industrial application at that time. Also mentioned is the suggestion by Watt to use cochineal instead of indigo but this is discussed later in this

⁵⁷ The same experiments are reported in *Encyclopaedia Britannica*, vol. 3 (1815) 5th editⁿ., p. 692.

⁵⁸ Smith, *op. cit.* (12), p. 145.

⁵⁹ *Encyclopaedia Britannica*, vol. 2 (1824), supplement to 4th, 5th, and 6th edits. p. 331.

⁶⁰ Duval, *op. cit.* (30), p. 514.

chapter. The method provided a useful working measure, particularly if the technique of conducting the determination remained consistent.

According to Descroizilles's own report a saturated chlorine water would usually show a strength of 8 degrees on the 'bertholimeter'.⁶¹ Both Madsen and Smith have commented on the possible strengths of chlorine waters shown by Descroizilles's method.⁶² Madsen points out that a truly saturated solution would theoretically contain 0.9% of chlorine and calculates that this would give a 'bertholimeter' reading of about 20-30 degrees. More realistically, Smith worked with a figure of 0.45% chlorine content as a more likely solubility for chlorine at the temperature of 10 degrees Reaumur which Descroizilles indicated.⁶³ We cannot be certain that Descroizilles's saturated solution was in fact fully saturated, but 'bertholimeter' results of 4 degrees and less would have given bleaching strengths comparable with recent modern practice. Madsen has gone so far as to calculate the proportional amounts of reactants in a typical titration which show that convenient volumes of titrant to titrator would occur.⁶⁴ Informative though this may be, its value must be questioned in the light of other variable unknown factors in the method, some of which have been discussed earlier. For example, the poor so-called end point which is partly supported by the above author's experimental testing,⁶⁵ but put more simply, errors would have occurred depending upon the speed of titration. Also of course, depending on which solution is taken as titrator or titrand, so the proportional ratios would be reversed with further consequent errors. Descroizilles's method was probably satisfactory as a control procedure and proved of great value to practising bleachers. In this test the indigo, in the soluble sulphonated acid form or salt,⁶⁶ becomes one of the reactants and is decolourised or bleached by the measured quantity of chlorine water being used in the test. Descroizilles's end point was therefore the point at which the indigo ceased to be decolourised. This would be the point at which a small trace of unbleached indigo, combined with the fawn colour of the bleaching products, would give the solution an olive green colour, as Descroizilles had described.⁶⁷

The same coloured products of reaction would not have occurred when testing alkaline bleaches. Indigo Carmine, as the disulphonic acid or sodium salt, can act as a true chemical indicator, in that at pH 11.6 it gives a blue colour while at pH 14.0 it is yellow.⁶⁸ It seems surprising that this was not reported by Descroizilles or Berthollet when testing alkaline solutions of chlorine. Descroizilles speaks of the saturation point being seen as a pale olive green, but under alkaline conditions this would not be so.

If the title, 'inventor of volumetric analysis', given to Descroizilles by Duval⁶⁹ is justified, it remains obvious that Descroizilles never set out to invent anything other than a simple quantitative test to satisfy an immediate industrial need. The test was both quick and easy and its limited accuracy was no serious

⁶¹ Descroizilles, *op. cit.* (32), p. 263.

⁶² Madsen, *op. cit.* (3), p. 146; Smith, *op. cit.* (12), p. 152.

⁶³ Smith, *op. cit.* (12), p. 152, ref. 115, citing Sconce, . S. *Chlorine: Its Manufacture, Properties and Uses* (New York, 1962), p. 33.

⁶⁴ Madsen, *op. cit.* (3), p. 146.

⁶⁵ *Ibid.* Experimental checking showed wide variations in results.

⁶⁶ Indigo Carmine, i.e. indigo disulphonic acid or its disodium salt, the chemistry of which was not understood before 1841.

⁶⁷ Descroizilles, *op. cit.* (32), p. 262.

⁶⁸ Tomicek, O. *Chemical Indicators* (London, 1951), trans. by A. R. Weir, p. 54.

⁶⁹ Duval, *op. cit.* (30), pp. 508-19, an account of the life of Descroizilles, as a chemist, pharmacist and inventor whose discoveries have been taken over by others. 'He is indubitably the inventor of volumetric analysis', p. 508.

disadvantage to practical bleaching operations. Descroizilles's efforts were clearly successful but it seems somewhat exaggerated to lay the entire discovery of volumetric analysis with him in the light of so much other independent achievement by, for example, Lewis and others described in earlier sections of this thesis. His importance lies not so much in his 'discovery' of volumetric analysis but in his popularising of it, a point not often emphasised.

It was through the so-called 'Blue Test' that titrimetry became widely known. Descroizilles remained the most important person associated with titrimetric development in the period between the end of the eighteenth century and beginning of the nineteenth. The earlier work of Francis Home and Joseph Black, with whom this dissertation began, also directly connected with bleaching although before the introduction of chlorine, should not be under-valued.

With firm origins in the bleaching experiments of Berthollet, it was Descroizilles who developed the means of determining the strength of chlorine solutions and thereby provided a practical means of analytical control so necessary in the use of this very active gas. Rancke Madsen summarises the method thus:⁷⁰

Titrand: Indigo dissolved in dilute sulphuric acid

Titration: Chlorine water (alternately a hypochlorite solution)

Indication: Change of colour.

The determination of quantity is volumetric, a graduated cylinder being used as a measuring apparatus.

Even with the analytical control provided by the indigo test the bleaching of linen and cotton, using alkaline leys and chlorine solutions, retained an empirical basis. It will be shown in the next chapter how James Watt provided explicit instructions to McGrigor regarding analytical testing, but pointed out the value of simple tests on samples of linen or cloth prior to full scale bleaching. This hardly placed analysis at the heart of bleaching liquor application. Nevertheless, analytical control became of increasing importance particularly when chlorine liquors were used in 'clearing grounds' where printed patterns were to remain unbleached.

Rupp had shown the effect of alkali content on bleaching capacity (and which he had wrongly interpreted) but without knowing the actual chemical reactions and the prevailing pH conditions. During bleaching the pH falls, i.e. the alkaline conditions change to acid conditions unless sufficiently buffered by an excess of alkali. At the neutral point, pH 7, bleaching is very effective but degradation and yellowing of the cloth, caused by certain by-products of the reaction, can also occur. It seems very possible that these unexplained aspects may have induced some wariness of chlorine bleaching which could account for its rather slow acceptance by the industry. A comprehensive account of the influence on bleaching by the use of alkaline medium in France is given by Smith.⁷¹ Whatever concepts existed about acid or alkaline bleaching conditions, there was no understanding of the chemical reactions involved, but this did not apparently retard industrial progress.

⁷⁰ Madsen, *op. cit.* (3), p. 131.

⁷¹ Smith, *op. cit.* (12), pp. 153-155.

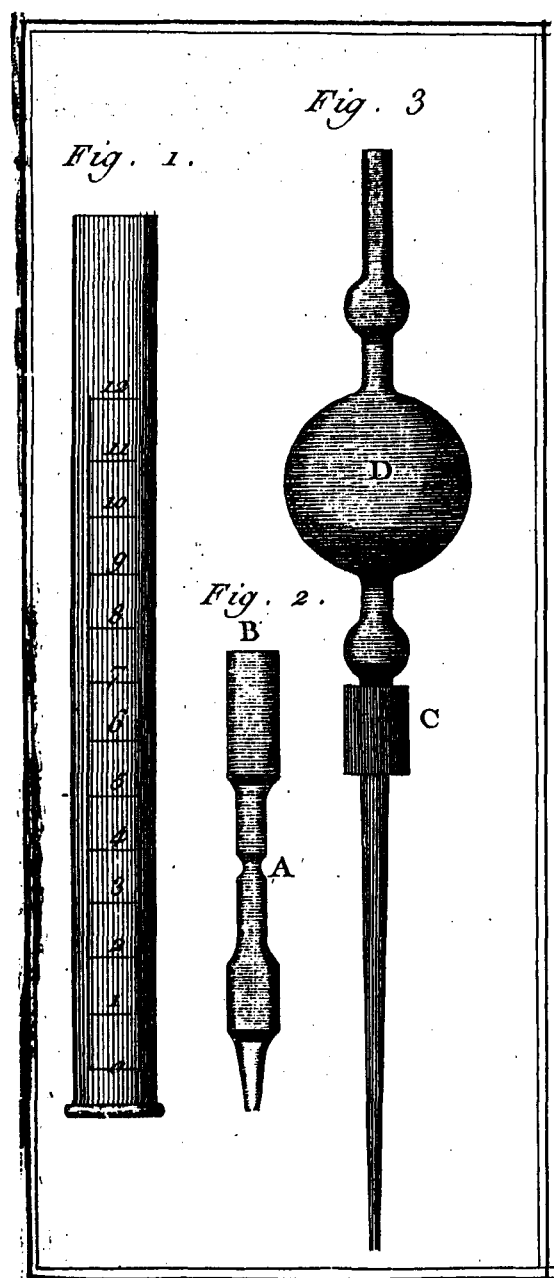


Fig. 3. Descroizilles's first burette and pipettes (reproduced from the original publication of 1795). 'La figure première est un tube verre du diamètre intérieur de six lignes au moins et de huit au plus [a little under $\frac{3}{4}$ inches]; il est fermé à la lampe par un bout.'

As mentioned above, Descroizilles's method was published in 1795: 'Description et Usages du Berthollimètre. Ou instrument d'épreuves pour l'acide muriatique oxigéné liquide, pour l'indigo et pour l'oxide de manganèse; avec des observations sur l'art de graver le verre par le gaz acide fluorique'.⁷² This fully explained how the method, though designed to determine bleaching strength, could also be made to measure the quality of manganese dioxide.⁷³ The apparatus designed by Descroizilles is shown on the opposite page; described as the 'Berthollimeter' it resembles a modern measuring cylinder and it was in this graduated vessel that the titration was observed. Szabadváry has suggested that the method 'was in use by the end of the century in almost all bleaching plants in Western Europe'.⁷⁴

⁷² Descroizilles, *op. cit.* (32), pp. 256-276.

⁷³ *Ibid.*, p. 264.

⁷⁴ Szabadváry, *op. cit.* (35), p. 212.

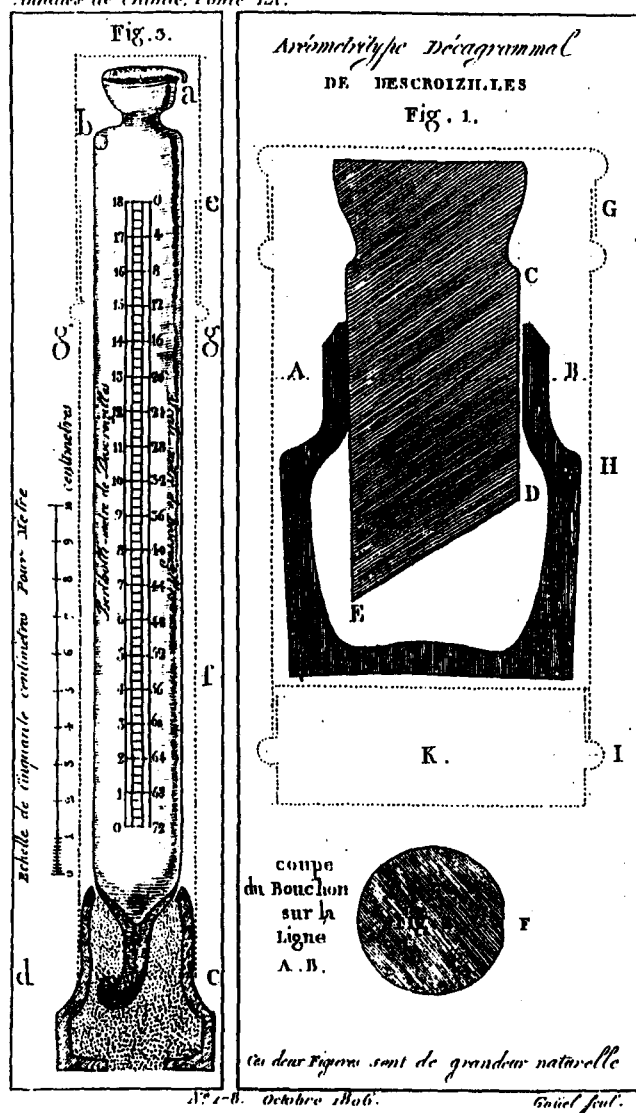


Fig. 4. Descroizilles's alkalimeter (left inset) taken from *Annales de Chimie*, 60 (1806).

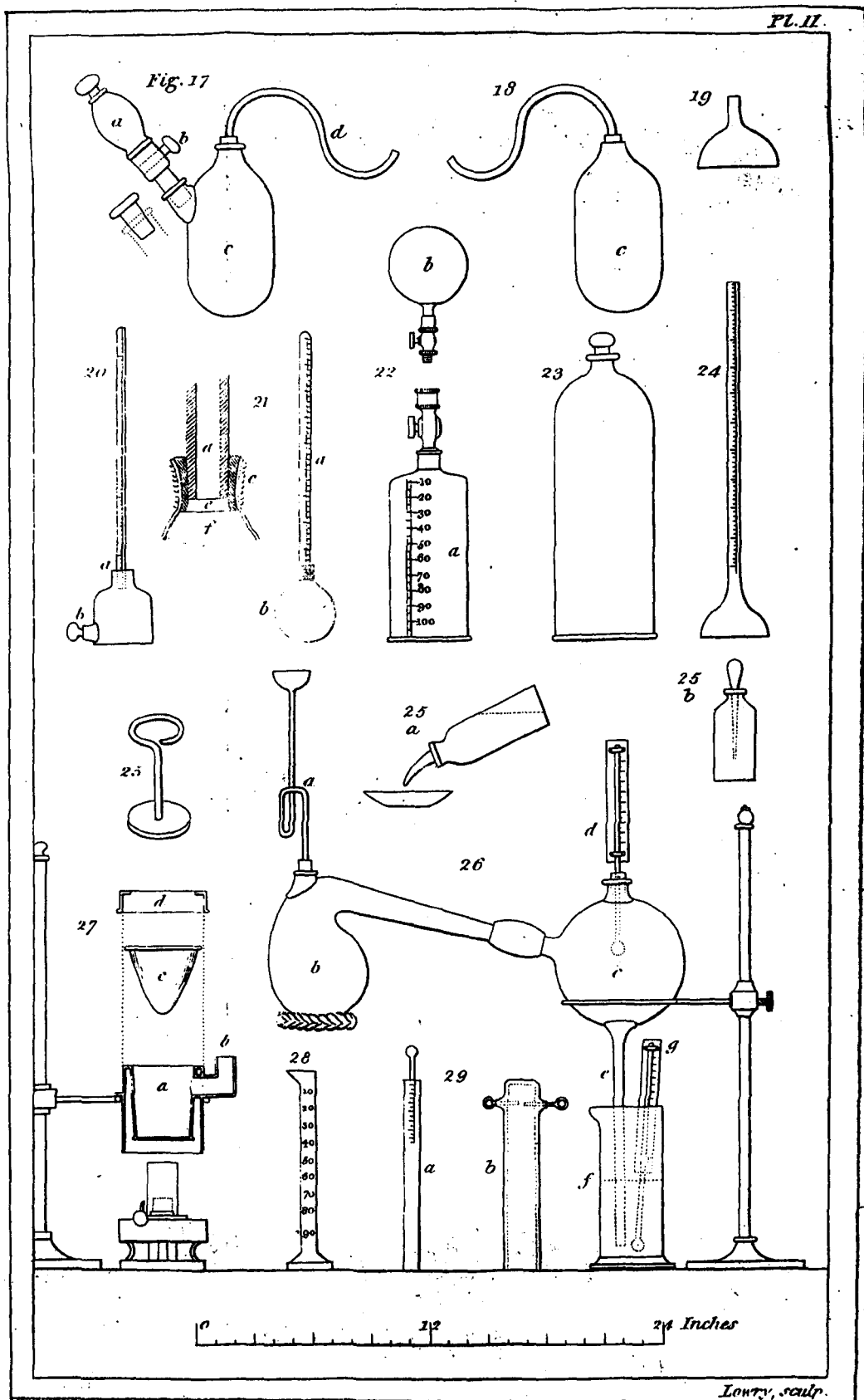


Fig. 5. William Henry's graphic representations of chemical apparatus in *Elements of Experimental Chemistry* (1818) 8th edit., plate ii.

VIII. Descroizilles's Alkalimeter: William Henry's account of Ure's Alkalimeter

In 1806 Descroizilles published his method for the examination of potash by reaction with acid in which his alkalimeter was described (see fig. 4).⁷⁵ By this method the results remained comparative, but were nevertheless sufficiently useful for everyday manufacturing purposes. For example if a 10g sample of potash required 55 volumes of sulphuric acid for saturation (the end point shown by the change in colour of syrup of violets), then the potash sample was acceptable for factory use; a point often acceptable in industrial processes to recent times. The acid used was of known density and the 'alkalimeter' of course functioned very much as a modern burette, indeed, by engraving two different scales, the tube or 'burette' (about 8 inches high) could be used for both chlorine strength and acid/alkali determinations. The top of the tube is funnel-shaped with a pouring lip and a small finger hole to assist controlled pouring. Clearly the tube would act as a modern burette and the titration reaction taking place in a separate container or drinking glass. Madsen has described Descroizilles's article as 'a milestone in the development of titrimetry', while Szabadváry claims that the modern burette evolved directly from the alkalimeter.⁷⁶

In William Henry's *The Elements of Experimental Chemistry* (1818) there is a section entitled 'Improved Alkalimeter and Acidimeter'.⁷⁷ It is this text of which Ure complains in his *Dictionary* of 1821, that Henry's description was nothing more than a replication of information passed in confidence to Henry, probably in 1816.⁷⁸ The personal feelings of Ure in this matter are of no concern here (see Appendix II), however, Henry's text is of interest although it shows little advancement of Descroizilles's earlier alkalimeter. Both Ure and Henry agree on the shortcomings of reporting alkalinity or bleaching strength as degrees in terms of the instrument, in this case 'degrees by Descroizilles's alkalimeter'. Henry states:

... he [Descroizilles] has proposed an instrument, which shall, at once, and without calculation, declare the true proportion of alkali in 100 parts of any specimen.⁷⁹

Henry's comment reveals a growing concern on how quantities, expressed in whatever units of the period, demand an expression indicating the amount present relative to the total amount of material. Obviously the term 'Descroizilles's units' had a quantitative meaning whereas parts per hundred is a way of stating percentage composition. Ure's or Henry's alkalimeter would provide this data.

The tube, as will be seen later, was referred to by Faraday as the test tube;⁸⁰ this description through countless lexicographic changes has indicated measuring cylinder, burette, and at present, the modern test tube. The dimensions of the tube are given as $9\frac{1}{2}$ inches long and $\frac{3}{4}$ inches internal diameter, it has a pouring lip and some kind of glass foot for standing upright. This tube (shown opposite as inset fig. 28) will hold a little more than 1000 grains of water and it is into this amount that the whole is subdivided in

⁷⁵ Descroizilles, F. A. H. 'Notices sur les alcalis du commerce', *Annales de Chimie*, **60** (1806), pp. 17-60. See also Descroizilles, 'On the Alkalies of Commerce, and on the least expensive Process for ascertaining their commercial Value by Means of the Instrument called the Alkali-meter', *Philosophical Magazine* (London), **28** (1807), pp. 171-178, 244-252, 311-316.

⁷⁶ Madsen, *op. cit.* (3), p. 195, and Szabadváry, *op. cit.* (35), p. 214.

⁷⁷ Henry, W. *The Elements of Experimental Chemistry*, vol. 2 (London, 1818), p. 512, 8th edit

⁷⁸ Ure, A. *A Dictionary of Chemistry* (London, 1821), p. xxi (Introduction); see also a letter from Ure in *Quarterly Journal of Science* **11** (1821), pp. 401-2.

⁷⁹ Henry, *op. cit.* (77), p. 512.

⁸⁰ Faraday, M. *Chemical Manipulation* (1830), p. 272, New Edition.

10 grain divisions having first established some graduations by weighings and others by dividing compasses. When the 1000 grain amount has been weighed into the tube and the line marked, this is designated as zero, the tenth below this as 10 and so on.⁸¹

There were differing opinions about the 'standard' sulphuric acid used in the test. Ure advocates acid of one uniform strength (*viz.* of sp. gr. 1.060) for all kinds of alkalis, while Henry recommends differing strengths for different alkali determinations using only one scale of 'equivalents parts'.⁸² In practice the actual acid dilution is carried out in the tube by addition of water - Henry points out that his starting acid no longer generates heat on further dilution and will therefore not invalidate volume readings. His 'test acid' is one part of acid of sp. gr. 1.849 diluted with four of water giving a sp. gr. of 1.141. There seems little to choose between these two other than the complexity of scale markings or graduations and other data on the glassware.

For the analysis of any particular alkali, reference is made to Wollaston's Scale of Equivalents to see how many grains of acid (as oil of vitriol) are needed to neutralize 100 grains of whatever the unknown alkali is thought to be.⁸³ This simple directive only remained valid provided the unknown sample contained no other carbonates or hydroxides which would interfere with the result. Modern day volumetric analysis uses synthetically produced sensitive indicators operating at known pH changes allowing titrimetric differentiation between different salts.

The entry for potash in Ure's *Dictionary* (1821) is noteworthy insofar as it states that potash does not effervesce with dilute sulphuric acid, suggesting therefore its chemical state is K_2O and not the normal carbonate. The latter was designated as sub-carbonate of potash or pearl ash if reasonably pure. There are no specific details of his alkalimeter, but its use is referred to under individual alkali subject headings. For example:

As 100 parts of subcarbonate of potash, are equivalent to about 70 of pure concentrated oil of vitriol, if into a measure tube, graduated into 100 equal parts, we introduce the 70 grains of acid, and fill up the remaining space with water, then we have an alkalimeter for estimating the value of commercial pearl ashes, which if pure, will require for 100 grains one hundred divisions of the liquid to neutralize them.⁸⁴

This is in good agreement with an equation using modern atomic weights. Oddly, Ure's *Dictionary* gives no indications of how the determination should proceed, whereas Henry's earlier text of 1818, whether or not this is gleaned from Ure's confidential essay, is a descriptive piece of analytical direction.

Confusion about the chemical constitution of potash and related alkalis is seen in Ure's *Dictionary*:

When the alkalimeter indications are required in pure or absolute potash [meaning K_2O], such as constitutes the basis of nitre, then we must use 102 grains of pure oil of vitriol, along with the requisite bulk of water to fill up the volume of the graduated tube.⁸⁵

⁸¹ Henry, *op. cit.* (77), p. 513.

⁸² *Ibid.* pp. 513-14.

⁸³ See below chap. 7, sec. IV and Ure's 1821 *Dictionary*, under 'Equivalents'.

⁸⁴ Ure, *op. cit.* (78), entry for potash.

⁸⁵ *Ibid.* same paragraph.

It should be noted that what is being measured is the total amount of alkali whether as hydroxide or carbonate or any other substance capable of reacting with the acid. None of the above analytical manipulations actually confirm the presence of the substance being reported. What we now see as a distinct weakness of titrimetric analysis may account in part for the low esteem given to titrimetry in chemical areas other than industrial settings. Whatever volume of acid was used in any titration, this could be interpreted as the amount, in percentage terms, of any substance thought to be present. Clearly the method, without any modification or reliance on some other analytical facts, simply gave the chemist a quantifying method of expressing the presence of any salt of his choice provided an 'equivalent' figure was available from Wollaston's scale or some other data source. In alkali analyses it is possible that one difficulty was overcome by determining the carbonate separately by weight loss, i.e. liberation of carbon dioxide. There are examples to suggest this method was sometimes used but it must have proved a slow and cumbersome route.⁸⁶

It is clear from Henry's instructions, albeit influenced by Ure, that titrimetry was developing. From a simple tube emerged a piece of graduated chemical glassware acting almost as a modern burette and from which a direct reading of percentage composition could be made. Another progressive stage will be examined later in the Binks burette.

Henry knew (from Wollaston) that 100 grains of subcarbonate of potash (potassium carbonate) are equivalent to 71 grains of concentrated oil of vitriol. To obtain 71 grains of acid, Henry weighed 355 grains of his diluted acid spec. grav. 1.141 (this consisted of one part sulphuric acid to four parts of water) into the tube and suggested that the level be marked for future determinations. The tube was then made up to the zero mark with water. This 100 measures of diluted acid was therefore equivalent to 100 grains of sub-carbonate of potash and each individual graduation on the tube was equal to one grain of sub-carbonate. In this example Henry supposed a representative sample of 200 grains dissolved in two ounces of water which when divided allowed for a repeat titration.

Instructions are given about the actual titration and the removal of liberated carbonic acid which would otherwise distort the result. At the completion of the neutralization (Henry does not use the word saturation) the level of remaining acid in the tube was read off as direct percentage of sub-carbonate of potash. According to Henry, thirty per cent had been a commonly recorded content but there is nothing to suggest that he saw these results as expressing actual contents of substance as named. What had been determined was merely an alkalinity which corresponded to the stated amount if expressed as a certain substance and which had been determined by the alkalimeter as if it was that same substance. This interchange, based on Wollaston's equivalents, appears to be implied when:

... supposing the pearlash to contain 80 per cent. of sub-carbonate, that number being set to sub-carbonate of potash on the scale, the equivalent in pure potash is at once seen to be 55.⁸⁷

This is in reasonable agreement where sub-carbonate is K_2CO_3 and pure potash is K_2O .

⁸⁶ Kirwan, R. 'Experiments on the Alkaline Substances used in Bleaching', *Transactions of the Royal Irish Academy*, 3 (1789), p. 6. See above, Samuel Parkes, chap. 1, sec. IX.

⁸⁷ Henry, *op. cit.* (77), p. 515.

At the end of this chapter in Henry's textbook of 1818 there is an entry regarding the quality and adulteration of manganese (dioxide). He implies that bleachers who generate their own chlorine were inconvenienced by the frequent presence of chalk in manganese raw materials. These carbonates, carried over from the reaction still, caused excessive effervescence. If this material was found mixed with the manganese, it could be detected by reacting a small amount with nitric acid to observe any effervescence, and then removed by adding a sufficient amount of potash solution (meaning K_2CO_3 in this instance) to precipitate the lime which could be washed and weighed as a means of analysis.

Descroizilles's name and method of alkalimetry remained in common use for a considerable time. This is evidenced by Faraday⁸⁸ who describes the use of Descroizilles's 'tube' in the determination of free alkali in potash samples by means of reaction with sulphuric acid of known strength to end points based on 'blue cabbage liquor' or an 'infusion of litmus' in the form of test papers. Whilst the method shows no great advance on Descroizilles's recommendations of some thirty odd years earlier, the concepts of 'standardisation' and purity appear. In these, Faraday suggests that the acid should be standardised against a known weight of pure potash - obtained by fusing potassium bicarbonate in a platinum vessel, dissolving the residue of pure potash in water and neutralized quantitatively by the acid from the 'tube' (Descroizilles's). Rather surprisingly there is no mention of the use of indigo as a chemical indicator or for use in determining chlorine strength. Henry claimed that Descroizilles's alkalimeter 'was in use by several persons in this country and in common use in France'.⁸⁹

It would be fitting and convenient to end this section regarding the introduction of chlorine into bleaching and the simultaneous development of titrimetric analysis, to show inter-dependence. Details of the 'blue test' appeared in Robert Kerr's translation in 1790 of Berthollet's work.⁹⁰ The next chapter will show that James Watt was using the test in 1788. Whilst the value of analytical control to industry cannot be questioned, it is tempting to assume that chlorine bleaching only developed because of the controlling value of analysis. The following two chapters will attempt to confirm this.

The definitive work of Musson and Robinson⁹¹ does not emphasise the role of chemical analysis but it must be recognised that titrimetric analysis developed concurrently with the introduction of chlorine bleaching. Descroizilles contributed enormously to this development. The following chapter will show Watt's understanding of chemistry associated with bleaching and is based mainly upon primary source material in the now fully consolidated archive collection in Birmingham City Archives (BCA).

⁸⁸ Faraday, *op. cit.* (80), p. 272.

⁸⁹ Henry, *op. cit.* (77), p. 512.

⁹⁰ Kerr, R. *Essay on the New Method of Bleaching by means of Oxygenated Muriatic Acid...from the French of Mr. Berthollet* (Edinburgh, 1790), published by Order of the Trustees of the Linen and Hemp Manufacture. The 'indigo blue test' is attributed to Descroizilles and is described fully on pp. 80-81. See also Musson and Robinson, *op. cit.* (14), p. 312, which suggests Kerr's translation was widely read; see also Partington, *op. cit.* (4), p. 507.

⁹¹ Musson and Robinson, *op. cit.* (14), pp. 283-4, describes the 'indigo test' and Watt's recommendation to use cochineal.

CHAPTER FOUR

SOME CHEMICAL AND ANALYTICAL CONTRIBUTIONS OF JAMES WATT

Musson and Robinson have provided a wide ranging history and contextual setting about the introduction of chlorine bleaching in Scotland including its priority of application.¹ These authors obtained evidence of Watt's achievements in this field from the Boulton and Watt papers and other archives then available. This chapter draws on the newly acquired collection which includes manuscript evidence on Watt's involvement in chemical aspects of bleaching with chlorine. Many of the manuscripts used in this chapter were not available to Musson and Robinson, indeed, one important letter by Watt, in which he describes Berthollet's method of making the gas, was thought not to have survived.² These recently acquired letters have made it possible to reveal Watt's practical and theoretical approaches to chemical aspects of bleaching. The usefulness of the indigo test and his interest in analytical control using cochineal as an improved indicator are discussed in this chapter.

Watt and Boulton visited Berthollet in Paris towards the end of 1786 and were shown the experimental evidence of chlorine bleaching.³ The effect of chlorine water was demonstrated - Berthollet had used earlier a series of Woulfe bottles as a means of dissolving the gas in water - but he had abandoned interest in alkaline chlorine solutions by the time of their visit.⁴

The practical difficulties Watt experienced in generating chlorine and dissolving it in either water or potash solution, is now difficult to determine. That he succeeded in making useful bleaching solutions is shown in various letters mainly to James McGrigor his father-in-law who was a bleacher in Glasgow.⁵ One of these letters, dated 19 March 1787, refers to a sample of bleaching solution sent to McGrigor with directions for its use and comments regarding costs and Watt's concern for proper reward to:

the Gentleman who has contrived it. And at the same time every precaution must be taken to maintain secrecy therefore it must not be shown to any chemist. my honour is pledged to the inventor for that.⁶

When James McGrigor replied to this by letter dated 19 April 1787 it appears he had clearly run into all kinds of difficulties and disappointments in his trials with chlorine solutions. He had noticed Watt's remarks about costs and from these Musson & Robinson infer a connection with Watt's idea of using sulphuric acid, instead of the more expensive hydrochloric acid, when generating the gas.⁷ This is now confirmed in the new archive.⁸ According to Eason, a Manchester physician and industrial chemist

¹ Musson, A. E. and Robinson, E. *Science and Technology in the Industrial Revolution* (Manchester, 1969), pp. 251-261.

² *Ibid.* p. 272, refers to Watt's letter of 17 June.

³ See a letter from Watt to Berthollet, March 1788, Matthew Boulton Letter Book, 1780-9, loc. BCA.

⁴ Musson and Robinson, *op. cit.* (1), pp. 263-4.

⁵ Birmingham City Archives, (BCA), see JWP, Letter Book (LB), no. 1, May 1782 - April 1789. See Page, F. G. 'Birmingham City Archives: James Watt's Chemical and Bleaching Interests', *Chemical Heritage*, 14 (1996-7), p. 18. Also Kingsley, N. *Catalogue of the Papers of James Watt at Doldowlod House* (Birmingham Library Services, 1993).

⁶ Watt to McGrigor 19 March 1787, JWP, LB/1, 196, BCA; Watt is referring to Berthollet.

⁷ Musson and Robinson, *op. cit.* (1), p. 267.

⁸ Watt to McGrigor 17th June 1787, JWP, LB/1, 208, BCA.

reporting five years earlier, the cost of hydrochloric acid was then less than that of sulphuric.⁹ Watt made a more definite reference to the cost of producing chlorine in a letter to one Mr. Middleton:

I have made some experiments on the whitening liquid. I found the quantity necessary would prove much too expensive but have by another process made it much cheaper.¹⁰

This must surely refer to his method of using vitriol on salt and manganese dioxide instead of the direct reaction between hydrochloric acid and manganese dioxide. This point is confirmed in another letter to McGrigor:

the liquor is made by distilling 6 oz. of spirit of common salt [hydrochloric acid] from [*sic* with] one oz. of a mineral called manganese and making the elastic vapour which it produces pass through 6 quarts of water. This is the inventors method but I have found a speedier one which is to make the liquor at the same time as I make the Sp of Salt by distilling comn Salt manganese and oil of vitriol together which succeeds.¹¹

It is in the same letter that Watt refers to alkaline solutions and the effect on bleaching strength:

The liquor I sent you last was made by receiving the gas in caustic alkali but that diminishes the strength and effect but I yet know no other method of making it portable. the first sent you was the simple acid liquor nearly of its utmost strength for water only admits a certain quantity of it...¹²

This is also a clear statement regarding solubility of chlorine in water compared with the greater solubility in alkaline solution and the greater stability in this medium.

Concerns about the costs of bleaching solutions are prominent in Watt's letters; similarly there is constant reference to his hopes that the inventor is properly rewarded:

No satisfactory plan has yet been thought of to make it profitable to the inventor... I must own it is one of the most surprising things I have met with in Chemistry and if paid as it deserves should have a high reward.¹³

The high esteem held by Watt for Berthollet is expressed more eloquently in a letter dated 27 April 1787 (reproduced in Appendix III).¹⁴

In extensive and undated instructions Watt describes methods of preparing the gas and the use of the alkaline solution in practical bleaching.¹⁵ Clearly he had researched both aspects in detail and whilst it seems possible for Watt to have carried out many laboratory preparations of chlorine, one is tempted to ask how he came to have the necessary resources to carry out lengthy, even if small-scale, bleaching trials. The letter, presumably to the well established bleacher Mr McGrigor, contains Watt's sketch of the suggested apparatus and emphasises thorough sealing of the glass joints by alchemists' well-established luting media. Apart from the serious absence of ground glass joints (these first appeared in laboratory

⁹ Eason, A. 'Observations on the Use of Acids in Bleaching of Linen', *Memoirs of the Literary and Philosophical Society of Manchester*, 1 (1785), pp. 240-2, (read 1782).

¹⁰ Watt to Middleton 3 April 1787, JWP, LB/1, 198, BCA

¹¹ Watt to McGrigor 17 June 1787, JWP, LB/1, 208, BCA.

¹² *Ibid.*

¹³ Watt to McGrigor, 8 April 1787, JWP, LB/1, 198, BCA.

¹⁴ Watt to McGrigor, 27 April 1787, JWP, LB/1, 202, BCA.

¹⁵ Watt to McGrigor (presumed), JWP, LB/1, 212. Reproduced in Appendix IV.

apparatus in the 1920s) the arrangement of apparatus is similar to that found in most nineteenth- and twentieth-century chemistry textbooks.

The instructions regarding equipment to generate chlorine illustrate fully the difficulties of constructing apparatus, particularly where air tight joints were demanded.¹⁶ Lutes were a kind of cement with which to make leak free joints in chemical apparatus; the material had to be flexible enough to allow for expansion and contraction under heating and cooling conditions. Chemists hoped that their glass apparatus and luting material were sufficiently inert to not adversely affect their results - this could not be taken for granted. Watt's emphasis on effective luting should not be taken lightly, for it was clearly of serious concern at that time.¹⁷ Watt then gives instructions (to McGrigor) on the amount of chlorine liquor to be used in practical bleaching operations while retaining many of the established practices of alkali washes, steepings etc. On a very empirical level Watt suggests: 'The liquor [chlorine solution] may be used repeatedly till it produces no effect on the cloth'.¹⁸

In another section of this undated manuscript Watt continues:

To impregnate caustic alkali with the 2d [here, Watt uses a symbol] whitening liquor take 8 oz. of Pearl Ashes make them caustic by boiling them with water and lime filtre them and add more water to the lime until you have extracted all the caustic alkali from it put the caustic alkali into a clean iron pot and boil away the water until you have only about a pint [illegible] of liquor left; put that liquor into the 2nd receiver putting water in A as before fill all the other receivers with water or with weak caustic alkali Let the water in the earthen vessel BB be filled only a little above the surface of the caustic alkali, put into the retort A a double dose of the ingredients and distil as before When the materials in retort cease to give air remove the [illegible] retort [illegible] and empty it but have all the receivers in their places with the liquors they contain having washed the retort replace it and lute it again Then put into a second time a double dose of the ingredients and distil it as has been directed When the distillation is over, separate all your vessels. the strong alkaline liquor in the 2d will be fully impregnated with the acid and the 3d partly, so that it may stand in its place for another distillation. As the alkaline liquor has absorbed the acid which should have made 24 quarts or 48 lbs of liquor it ought to bear being diluted with so much water but I have found that the whitening properties of the liquor are so much hurt by the alkali that it can only bear about 18 quarts of water nevertheless the process may have its utility I have hitherto used only alkali of pearl ashes but think it well worthwhile to try alkali of Barillas which perhaps may not impair its virtues so much - Lime totally destroys its virtues.¹⁹

Watt wrote to Annie (Mrs Watt) in October 1787 about the construction of a simple laboratory valve:

In order to prevent the water sucking back into your apparatus you may take a slip of glove leather about 3 or 4 inches long and a little broader than the tube is in diameter and tye it on the end of the last tube, putting the double over the end of the tube and tying the two ends to the tube with a waxed thread about an inch or less say $\frac{1}{2}$ inch from the end thus (a) is the tying (b) the bow which is over picture here the open end of the tube t the tube.

This thin leather when wet will act like a valve and will permit the air to go out but will not let the water come in but it should not be tyed too close over the end lest it do not let the air out freely.²⁰

¹⁶ *Ibid.*

¹⁷ See entry regarding Lute in Macquer, P. J. *A Dictionary of Chemistry*, vol. 1, (1771), pp. 385-386, trans. by James Keir from *Dictionnaire de Chymie*, 1st edit. (Paris, 1766).

¹⁸ Watt to McGrigor (presumed), undated, JWP, LB/1, 214, BCA

¹⁹ *Ibid.*

²⁰ Watt to Annie, 12 October 1787, JWP, LB/1, 226, BCA.

In another letter to Annie, Watt shows continuing concern for her father's (McGrigor) chlorine bleaching results and the effect on the cloth:

In order to preserve the strength of the Cloth, you must put more mild alkali in the liquor and that alkali should be both very mild and perfectly free from any sulphureous matter as the [symbol for chlorine gas] decomposes the sulphur and converts it into vitriolic acid - If the liquor is used very weak as I directed by Mr Berthollets last receipt, though no alkali be put into it the Cloth is not weakened. If after all, the cloth is still hurt there seems no remedy but the distilling it into caustic Alkali, but that much lessens its whitning power. The small quantity of liquor in the first Bottle may be used but should be well dosed with alkali as it contains some common spirit of salt which is very corrosive and no whitner.²¹

The remainder of this letter concerns Watt's instructions regarding dimensions and materials for the receiver or vessel in which the chlorine water is formed; clearly the process has been enlarged, 'I think your father should lose no time in getting a large one made say 6 feet diameter and 18 inches deep'. This was to be made of wood although Watt had obviously considered the merits of using lead vessels and pipework.

In another letter to Annie on the following day, Watt speaks of enlarging the reaction vessel to contain 'ten or twelve double doses'.²² There seems little doubt that McGrigor was by now, using chlorine bleaching successfully; a letter to him provides the data for a much enlarged system of manufacture.²³

From several letters of this period, knowledge of the strength of bleach solution seems not to have been of paramount importance; Watt has been content to judge by rule-of-thumb methods, particularly in the bleaching test conducted by himself. He does however give a method for preparing the indigo test solution in a letter to McGrigor:

The best trial of strength I can advise is take say 10 grains of the best Indigo in fine powder put it in a balanced tin cup, drop in 40 grains weight of strong OV stir them until they are thoroughly dissolved, then add 4 oz pure water mix well & preserve the clear for use perhaps more water may be necessary but of that I will inform you upon trial take an oz measure of the acid liquor you want to try, drop in gradually as many drops as it will uncolour in some given time, say 10 minutes, & that liquor which can uncolour most is the strongest - -If the liquor be mixt with OV I believe this test is not so accurate I shall make this expt, & report the strength of my liquor.²⁴

In the following letter to McGrigor dated 18 Feb 1788, having found the end point colour change using indigo not entirely satisfactory, Watt sets out the results of his testing method using cochénille (cochineal):

I have found however what I believe will do I dissolved 20 grains of cochénille ground to powder in 3 oz of strong brandy and set it in a warm place to extract the colour. I poured some of this into a thin glass tube about three eighths inch diam and added the liquor to be tryed gradually until the red disappeared and became yellow I found that 83 grains of the test liquor was uncoloured by 118 of the liquor I have used in my late experiments. I am not certain as this test was only made today whether the brandy had extracted all the colouring matter from the cochénille so perhaps it may not be a decisive comparison

²¹ Watt to Annie, 19 October 1787, JWP, LB/1, 228, BCA.

²² Watt to Annie, 20 Oct 1787, JWP, LB/1, 229, BCA.

²³ Watt to McGrigor, 14 Nov 1787, JWP, LB/1, 229, BCA., reproduced in Appendix V.

²⁴ Watt to McGrigor, 15 Feb 1788, JWP, LB/1, 239, BCA.

between your liquor and mine....neither am I sure that all the cochenille contains the same quantity of colour, probably not. In order to try if it was a test of anything else but the whitening quality I dissolved 60 grains chrystallized mild alkali in 4 oz of the liquor which, to every other intent, made it perfectly neutral yet I found exactly the same quantity of liquor with the [symbol for fixed alkali] as without it uncoloured the test -The cloth that was steeped not boiled in [symbol for fixed alkali] comes on slowly but is nearly white, and the threads very much stronger than that which has been repeated boiled...²⁵

From the reply by McGrigor, of 5 April of the same year, he apparently had no cochineal available and had used the 'liquid Blue test' based on indigo. It is clear from this letter and other documents that the 'blue test' was found valuable in controlling bleaching strength.

James Watt's interest in laboratory testing of the strength of bleach developed further when it became apparent that the solution might be so carefully controlled as to allow the 'clearing of grounds' on already printed materials. With accurate control of the bleach solution it became possible therefore to 'clear' the whites, yet not harm the printed colours. In a letter to McGrigor in August 1788 there is a clear reference to this use:

Saw Henry at Manchester who was proposing to make [symbol for whitening liquor] for sale....Its use for clearing printed goods handkerchiefs with blue and red stripes, muslins with gold fringes and other fine goods...²⁶

It seems likely that Watt's response to Henry arose from this subject:

About testing [symbol for bleach solution]. Infuse 48 grains of good cochineal bruised in 6 oz weight of common plain malt spirits digest in gentle warmth 24 hours, filtre and preserve for use - take a thin glass tube about $\frac{1}{3}$ inch bore hermetically seal or cork one end (let the tube be of equal bore throughout) drop into the tube 30 grains weight of the test liquor and make a mark on the tube at its surface. then weigh in 30 grains water and mark again, then 30 grains more and another mark and so on until you fill the tube which should be six or 8 inches long, paste a narrow strip of paper lengthways of the tube divide each of the primary divisions into 10 divisions varnish the scale with some spirit of varnish and the instrument is made. to use it fill to the lowest mark with 30 gr of the test liquor then add slowly what you judge necessary of your liquor to be tried, frequently inverting and shaking the tube until the contents lose the red colour and acquire a greenish yellow and mark the strength by the number of small divisions which the liquor to be tried occupied the strongest I have made without alkali destroyed the test colour by four divisions and about 24 is a good strength for use.²⁷

James Watt was an engineer able to design and make chemical apparatus of good physical performance. The letters show his close regard for detail in constructing laboratory apparatus and of the practical problems of making gas tight joints by means of effective luting materials (a topic of wide concern at that time). Watt's description of a mechanical stirrer for the main receiver reflects the outlook of a proficient early chemical engineer²⁸ and he was later commended by Davy for his 'profound knowledge' of chemical matters.²⁹ His interest in determining the strength of acids and alkalis, by noting the point of saturation using colour indicators, is shown in his 1784 publication.³⁰ As mentioned earlier,

²⁵ Watt to McGrigor, 18 Feb 1788, JWP, LB/1, 240, BCA.

²⁶ Watt to McGrigor, 28 Aug 1788, JWP, LB/1, 253, BCA.

²⁷ Watt to Henry, Sept 1788, JWP, LB/1, 255, BCA.

²⁸ Watt to McGrigor, 29 Jan 1788, JWP, LB/1, 237, BCA.

²⁹ Davy, H. *The Collected Work of Sir Humphry Davy*, ed. John Davy, vol. 3, (1839-40), p. 141.

³⁰ Watt, J. 'On a new Method of preparing a Test Liquor to shew the presence of Acids and Alkalies in chemical Mixtures', *Philosophical Transactions*, 74 (1784), pt. 1, pp. 419-422.

when writing to McGrigor in 1788 he recommended the use of cochineal instead of indigo when determining bleaching strength. Watt realised the inadequacy of indigo in not giving an entirely satisfactory end point. Musson and Robinson suggest that he recommended cochineal because the indigo test was not sufficiently accurate in testing alkaline bleach solutions.³¹ Furthermore, after testing with cochineal he attempted to confirm the result by comparison 'with liquor of known strength, previously determined by direct experiment on cloth, thus providing a standard'.³² This point, together with other technical and chemical aspects of bleaching discussed in this chapter, confirms Watt's appreciation of the value of chemical analysis and his abilities to execute this as a practical chemist. The evidence provided by these recently discovered letters adds significantly to existing knowledge of Watt's chemical interests.

The extent to which the method of testing and control of bleaching strength developed beyond the simple indigo or 'blue test' and was routinely applied can only be ascertained from the publications and archives of individual bleachers and chemists. The following chapter considers some of this evidence.

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³¹ Musson and Robinson, *op. cit.* (1), p. 284.

³² *Ibid.*

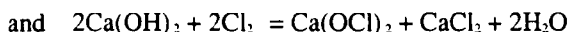
CHAPTER FIVE

THE CONTINUING DEVELOPMENT OF ANALYTICAL METHODS AND CONTROL IN THE EARLY CHLORINE BLEACHING INDUSTRY

I. Bleaching Powder

From the time when chlorine was introduced as a bleaching agent, until bleaching powder became available in commercial quantities, bleachers had to make the gas for themselves. The generation and handling of gaseous chlorine even at the smallest commercial level must have presented enormous problems. It is not surprising therefore to find commercial development taking place of the more expensive liquid alkaline bleach (eau de Javel). This was safer and more convenient to use than chlorine water and its greater stability made transportation possible. Smith suggests that because of the higher cost of liquid alkaline bleaching solutions, commercial users then looked more towards the newly developed bleaching powder and it is this aspect of bleaching history which follows.¹

Two Scottish names are directly associated with bleaching powder development: Charles Tennant (1768-1838) and Charles Macintosh (1766-1843). To the first, is attributed the development of a bleaching suspension made by passing chlorine gas through a slurry of slaked lime, Ca(OH)_2 (perhaps better described as a milk of lime suspension), instead of the more usual potash. Using present-day formulae this is represented:



At the time, this 'soluble' product was referred to as oxymuriate of lime, later, chloride of lime and today, calcium hypochlorite. But it was Charles Macintosh who found that chlorine could be directly absorbed by dry lime and who produced the first bleaching powder. This must surely have been an early, if not the first ever, example of a gas-solid reaction finding immediate commercial application.

In a Hurter Memorial Lecture of 1952, Hardie described the bleaching powder manufacturing process as:

...one of the simplest and certainly one of the most momentous inventions in the history of industrial chemistry,

and credited it to Charles Macintosh.²

As an early industrial chemist with flair in chemical manufacture it can be no surprise that Macintosh should be aware of the growing need to quicken the bleaching process. Also, if such a new development guaranteed the continued need for vitriol from the Prestonpans site in which Macintosh had an interest, so much the better. Indeed it is possible to view Macintosh as an outstanding chemically influenced entrepreneur, linking major fields of industrial expansion at that time. His invention and development of bleaching powder was, without doubt, his greatest offering to this early chemical industry, but it is difficult to identify possible pointers which led him to this particular and unexpected chemical invention.

¹ Smith, J. G. *Origins and Early Development of the Heavy Chemical Industry in France* (Oxford, 1979), pp. 156-160.

² Hardie, D. W. F. 'The Macintoshes and the Origins of Chemical Industry', *Chemistry and Industry*, (28 June 1952), p. 610.

Granted, Tennant had achieved considerable success with his chlorinated lime suspension insofar as this was a much cheaper product than alkali chlorine solutions of the eau de Javel kind, and could be transported conveniently. But why Macintosh chose a dry process while his chemical background to this time had developed mainly in wet processes may not be obvious. Why did he suppose that chlorine, a gas, should react with a solid? One possible answer lies in a closer scrutiny of Tennant's first patent; Musson and Robinson point out that in this patent there is no claim by Tennant to having discovered that chlorine could be absorbed by lime water.³ Instead, it describes a mechanical method of merely keeping the suspension agitated by mechanical means during the absorption of the gas. We cannot now be certain why Charles Macintosh investigated the reaction between powdered lime and chlorine and in so doing produced bleaching powder.

In 1797, Charles Tennant set up the St. Rollox works in Glasgow and it was here that his chlorine-lime suspension was made. He was joined by Charles Macintosh and others from the alum and sal ammoniac works and here the dry process of making bleaching powder was developed, although patented under the Tennant name.⁴ This new product removed the necessity for on-site production of chlorine by bleaching works, and the practical difficulties of handling this, or its solution in alkali or water, or indeed any liquid concoction to achieve more rapid bleaching. This suggestion is not supported by Higgins who quotes bleaching powder output figures for the St. Rollox site over the period 1799-1870 and infers that Tennant did not develop sales for this product very rapidly.⁵

Many bleaching works however still chose to make their own bleaching liquor by dissolving chlorine (the chlorine 'still' was a familiar piece of equipment at many bleach works) in a lime water suspension. Higgins gives a cost comparison showing that liquor produced from bleaching powder, as against the limewater suspension, was just a little cheaper, and could therefore be used to produce a slightly greater bleaching degree at the same cost:

In this way the strength of the liquor made was brought up from 39 degrees, by the old way [lime water suspension], to 54 degrees, by the new way [bleaching powder], in 1844, the degrees being obtained by the blue test.⁶

Whether the invention of bleaching powder, reduced the need for analytical control is difficult to determine, for, as a stable product, easily handled, a weighed quantity stirred into water would automatically yield a predetermined bleaching strength perhaps within acceptable practical limits. It seems very likely that as and when a chlorine still wore out, a bleacher would begin to use bleaching powder.

Modern bleaching powder contains about 37% available chlorine but Ure reported 22% to 28% based on an overall assessment of the analytical methods in common use in 1822.⁷ Clearly there were variations

³ Musson, A. E. and Robinson, E. *Science and Technology in the Industrial Revolution* (Manchester, 1969), pp. 322-3.

⁴ B.P. 2312/1799.

⁵ Higgins, S. H. *A History of Bleaching* (London, 1924), p. 90.

⁶ *Ibid.* p. 92.

⁷ See Ure, A. 'On the Composition and Manufacture of Chloride of Oxymuriate of Lime, (commonly called Bleaching-Powder,) and on the Atomic Weight of Manganese'. *Quarterly Journal of Science, Literature and the Arts*, 13 (1822), pp. 1-23.

in the quality of product, no doubt resulting from various factors such as accuracy of the method and of sampling and weighing.

II. Control by Analysis: The Evidence

Although the period of the works' quality control laboratory had not yet arrived, the initial needs for technical support and quality control were gradually coming into being. To what extent the 'blue test' found wide application is difficult to determine, but the following sections in this chapter will show that this test and other methods became of importance to the growing number of bleaching works. It has already been shown that the accuracy of this method depended upon how quickly the chlorine solution and indigo were mixed, but by consistent repetition of the same technique and procedure, a useful control was obtained. Madsen has examined the growth of Descroizilles's method in France and Germany⁸ during the first decade of the nineteenth century but offers little evidence of its routine use in industrial situations.

The crucial question must surely be, are there any extant primary source archives indicating that the 'blue test' was in common use in the period 1800-1810? Szabadváry claims the method was in use by almost all bleaching plants by the end of the eighteenth century, but, like Madsen, offers no supporting evidence.⁹ Research has found little of this much needed evidence; however, one highly authentic instance found in the archives of Marshall's, flax spinners of Leeds, is very noteworthy and proves the established use of the so-called 'Blue Test'.¹⁰

The scientific and commercial interests of John Marshall, fortunately supported by a considerable archive, have been used by Musson & Robinson to illustrate collaboration between scientific and industrial thought and activity. These authors have attempted to pin-point the origins of much of Marshall's scientific knowledge which included the making and use of chlorine in bleaching.¹¹ But it is a notebook written between 1797 and 1802, which is of relevance here:

Tried a cask of bleaching powder from Tennant Knox & Co - 42 lb. cost as much as making of our own & only bleaches 10 bundles therefore was 7 times dearer. Though it appeared as strong by the Hydrometer and the Blue test, it had much less effect on the yarn than ours, which we cannot account for but by supposing that the acid is so far neutralized by the chalk as to make it act weakly on the linen yarn. It could then [illegible] that this is not the case with respect to cottons, for the bleachers near Glasgow buy the powder & speak of it as being as cheap as the liquor they made themselves.¹²

This is proof that the 'blue test' was used in industrial situations also the document shows Marshall's broader interest in all aspects of bleaching particularly the comparative costs between using bleaching powder (which had only become available in the previous year) and his own chlorine or chlorine lime water mixtures.¹³

⁸ Madsen, E. Rancke. *The Development of Titrimetric Analysis till 1806* (Copenhagen, 1958), pp. 146-150.

⁹ Szabadváry, F. *History of Analytical Chemistry* (Oxford, 1966), pp. 212.

¹⁰ Marshall Papers MS200, held in the Brotherton Library, University of Leeds.

¹¹ Musson and Robinson, *op. cit.* (3), pp. 153, and 329-332.

¹² Marshall Papers, item 55, MS 200.

¹³ The transcript of pages 57 and 58 of Item 55, Marshall Papers, is reproduced as Appendix VI. This includes a formulation used for making chlorine to be dissolved into a lime water mix.

Musson and Robinson, and Rimmer¹⁴ state that Marshall found Tennant's new bleaching powder ineffective although Marshall reported only that 'it had much less effect on the yarn than ours', and 'it appeared as strong by the Hydrometer and the Blue test' as Marshall's own bleaching liquor. Rimmer also claims that chlorine bleaching had been in use since 1787 by cotton spinners, which was ten years before Marshall's experiments.¹⁵ The main difficulty in chemical bleaching was to obtain uniform whiteness throughout the batch but this was not so much a problem of controlling bleach strength as one of mechanical handling. Apparently Marshall had consulted Rupp's publication (see chap. 3 sec. VI.) on this subject.

The importance of the 'blue test' probably grew as it was realised that the strength of the bleaching liquor must be adjusted according to the different materials being bleached. Acceptable production costs were sought by controlled dilution of the bleaching solution and by producing their own chlorine but the entire bleaching process remained uncertain and expensive, involving a mixture of techniques using potash and chlorine with some traditional exposure in fields. Such was the situation at Marshalls into the second decade of the nineteenth century.

The monograph by Morris and Russell,¹⁶ *Archives of the British Chemical Industry 1750-1914 A Handlist*, shows nothing associated with analysis by bleaching companies during the period 1800-1820. The extensive United Alkali collection held at Chester Record Office contains material of only peripheral relevance to industrial analysis associated with the bleaching industry in the same period.¹⁷ Fortunately other archival sources remain as important proof of early analysis and it is on these that this chapter has drawn. They show that Descroizilles's test and other analytical methods contributed to the development of bleaching materials and the continued expansion of the textile industry.

As a primary source, the comments by James Sheridan Muspratt, son of James Muspratt (perhaps the greatest early alkali maker to use the Leblanc process in England), are worth noting. He attributes the indigo test to Welter and in 1860 commented, 'Indeed the indigo test, although much used by practical bleachers, is at best a very unsafe one', basing this opinion on the poor keeping qualities of indigo solution, the variations depending on how quickly the reacting solutions are added and mixed, and the difficulty in observing the 'end point'.¹⁸

III. The Estimation of Bleaching Powder by Analysis (Dalton 1813)

The true chemical composition and structure of bleaching powder has received attention over a long period of time. A survey of the researches and discoveries of this aspect of bleaching powder is not given

¹⁴ Rimmer, W. G. *Marshalls of Leeds Flaxspinners 1788-1886* (1960), p. 53, and Musson & Robinson, *op. cit.* (3), p. 331.

¹⁵ *Ibid.* pp. 51-3.

¹⁶ Morris, P. J. T. and Russell, C. A. edit. Smith J. G. *Archives of the British Chemical Industry 1750-1914 A Handlist* (Faringdon, 1988), BSHS Monograph no.6.

¹⁷ UA16/105 and 106. 'Notes and Memorandum (Charles Tennant Co of St Rollox Glasgow)', one vol., now held in conservation, and 'Daily Analyses of raw materials, products and residues (soda manuf) (Charles Tennant Co of St Rollox, Glasgow)'. The latter contains a reference to a Mr Black (presumably Joseph Black) about his manufacture of bleaching liquor, and lists raw material costs and making formulation. Location, Chester RO.

¹⁸ Muspratt, Sheridan. *Chemistry, Theoretical, Practical, and Analytical, as applied and relating to the Arts and Manufactures*, vol. I (London, 1860), p. 333-4.

here and it would be difficult to show a relationship between these academic researches and the industrial production of this product.¹⁹

One practical method of analysis was described by Dalton in 1813²⁰ although this was not favoured by Ure.²¹ Dalton's method for determining chlorine content was to add a solution of ferrous sulphate, presumably of known strength, to a given amount of oxymuriatic acid until the smell of chlorine was no longer present:

As soon as green sulphate of iron comes in contact with oxymuriatic acid solutions, the black oxide is converted into red, at the expense of the oxygen of the oxymuriatic acid; if the sulphate is deficient [not enough added] a strong smell of oxymuriatic acid accompanies the mixture; whence more sulphate must be added, till the mixture, on due agitation, ceases to emit the fumes of oxymuriatic acid: if too much sulphate is put in, then more of the acid liquor [the bleach solution] must be added by degrees, till its peculiar odour is developed.²²

While the method contained the essential basic theory of what was later to become a standard method of analysis, the use of the human nostrils to detect the completion of reaction, the end-point or point of saturation, places doubt upon its accuracy. The method depended upon the presence of 'oxygenated' hydrochloric acid to bring about the transfer of Fe^{2+} ions to Fe^{3+} ions (see also Crum's methods²³ and the description by Muspratt²⁴ of the ferrous sulphate method). Clearly Dalton still held the view that oxymuriatic acid (chlorine) was a compound of muriatic acid and oxygen.

In the final paragraph Dalton claims his test is easy to use and compares it with the blue indigo test:

It requires little or no skill in the application, and can always be commanded of the same strength; whereas coloured solutions are not easily obtained of the same strength, and are liable to decay.²⁵

Higgins claims that the 'blue test' continued in common use into the 1840s and that in 1845 the bleaching powder used by the firm of Sykes of Stockport, was tested by 'titrating with sulphate of iron until the liquor changed red to yellow prussiate of iron'.²⁶

IV. An Original Commentary by James Rennie

Birmingham City Archives hold a manuscript book written by James Rennie (1787-1867) probably in 1816-17.²⁷ It is a descriptive commentary on contemporary bleaching practices and also contains a

¹⁹ Ure, *op. cit.* (7), p. 1, and 14, in which Ure denies any definite composition of bleaching powder '...feebleness of affinity between the constituents of chloride of lime which leaves the quantities of each indefinite, and makes it resemble rather a mixture... than a true atomic compound.' Partington, J. R. *A History of Chemistry*, vol. 3, (London, 1962), p. 821, interprets Dalton's view (Dalton, J. 'On the Oxymuriatic of Lime', *Annals of Philosophy*, 1 (1813), pp. 15-23.) of a more definite compound of hydrate of lime with oxymuriatic acid (chlorine) or 'hyperoxymuriatic of lime'. However, Dalton's analytical figures clearly point to an unstable compound (p. 20).

²⁰ Dalton, J. 'On the Oxymuriatic of Lime', *Annals of Philosophy*, 1 (1813), pp. 15-23.

²¹ Ure, *op. cit.* (7), pp. 1-4.

²² Dalton, *op. cit.* (20), pp. 17-18.

²³ Crum, W. 'On Chlorimetry, and a new mode of Testing weak Solutions of Bleaching Powder', *Proceedings of the Philosophical Society of Glasgow*, 1 (1841-2), pp. 17-23.

²⁴ Muspratt, *op. cit.* (18), p. 334.

²⁵ Dalton, *op. cit.* (20), p. 23.

²⁶ Higgins, *op. cit.* (50), p. 93.

²⁷ Rennie, James. 'An Essay on the Improvements in the Art of Bleaching by the Application of the Principles of Chemistry', unsigned and undated MS probably written 1816-17. A pencil insertion states 'By James Rennie A.M.' Location BCA., JWP/C4/C8.

detailed account of Dalton's method of determining bleaching strength. Rennie has chosen to use the term oxymuriate pointing out his preference for the name chlorine although 'this has scarcely yet come into use even among Chemists.'

The *DNB* states that Rennie was a naturalist who became professor of natural history at King's College London in 1830. In this field he published very considerably but it is not clear from where his experience in bleaching was gained other than his tribute to Home, Des Charmes, Parkes, Higgins, Berthollet, and Chaptal. It is not clear whether his manuscript was published,²⁸ but it is this document which shows his extensive knowledge on matters concerning the use and preparation of chlorine in bleaching.

According to Rennie, bleaching powder or oxymuriate of lime, which he called Tennant's salt, was impossible to obtain by crystallization and could only be made by using 'oxy hydrate of lime.' The importance of reliable analysis is noted:

But I am not aware that any method has come into general use among Bleachers, by which the quality of a given quantity of this substance can be ascertained.²⁹

He differentiates between analysis used prior to immersion of the textiles and that necessary to show the quality of the purchased bleaching salts:

...which is commonly done by an indigo test, and in this way by observing the quantity of salt and the proportions of water used they may make a crude guess concerning the strength of the salt when purchased, but this at best must be an inaccurate method of proceeding.³⁰

Recognising certain deficiencies in the 'indigo test', this author claims that the remedy lies with 'the ingenious Mr. Dalton' and his 'test of easy application for ascertaining the purity of Oxymuriate of lime.'³¹ He is of course referring to the paper by Dalton in 1813,³² and merely rewrites the numbered experiments. It is the fourth experiment based on the reaction between the bleaching liquid and ferrous sulphate which Dalton so strongly advocated but which depended upon detecting any residual chlorine by smell after several attempts to find exact saturation. Later in this manuscript, Rennie appears to hesitate in his recommendations and admits:

the indigo test does tolerably well in ascertaining the strength of the diluted liquor, and as it is very generally used, I cannot well omit detailing the manner of its application.³³

The method of preparing the indigo solution is given followed by instructions for carrying out the test and there is a comment about Watt's suggestion of using cochineal instead of indigo:

²⁸ Musson and Robinson, *op. cit.* (3), p. 261: 'Rennie wrote a series of "Essays on Bleaching" in the Glasgow Mechanics' Magazine, Vols. III and IV (1829).' This has been confirmed. The Royal Society catalogue of scientific papers contains nothing by Rennie.

²⁹ Rennie, *op. cit.* (27), pp. 137-8.

³⁰ *Ibid.* p. 138.

³¹ *Ibid.*

³² Dalton, *op. cit.* (20), pp. 15-23.

³³ Rennie, *op. cit.* (27), p. 144.

From what I can learn however, this has not been found so convenient in practice as the indigo test: Mr. Dalton's test from sulphate of iron will soon, I imagine, supersede all others.³⁴

Whatever misgivings Rennie held about the 'blue test' in 1816, methods were to change as industrial bleaching processes made greater demands on analytical services. The transition of what now appears to be a very unrefined control method into a distinct branch of science occurred through the later work of Joseph Gay-Lussac. He stated that the accuracy of the 'blue test' depended on the rate of addition of the chlorine solution to that of the indigo and he pointed to the necessity of standardisation of reactants and technique. Indeed, Gay-Lussac raised the status of titrimetry in general; from mere 'works control' to a specialised science. To support this view Szabadváry cites a paper by Gay-Lussac which refers to the earlier work of Descroizilles and the analysis of commercial potash.³⁵ The same author (Szabadváry) considers that Gay-Lussac achieved an 'absolute' method in determining the amount of alkali in the commercial product (presumably on the assumption that vitriolic acid of 1.84 specific gravity was in fact 100% acid).³⁶

Molecular formulae represented by symbols, together with knowledge of atomic weights, provide a means of expressing 100% purity by calculating the ratios of individual elements or groups of elements (radicals); such knowledge had yet to occur, but its absence did not hinder the practical work of industrial chemists of the period. There is little evidence to show that the absence of this knowledge retarded either the development of analysis or the manufacture of chemical products.

V. Gay-Lussac, Berthollet and Welter: Graduated Glassware

In the second edition of Berthollet's *Éléments de l'art de la teinture* (1804)³⁷ there is reference to the analysis of commercial alkalis and the work of Francis Home; also shown is the laboratory apparatus in the familiar form of a pipette, measuring cylinder, and beaker, this being Welter's (1763-1852) analytical apparatus. This is shown in the illustration opposite and has been taken from Rancke Madsen.³⁸ Szabadváry has used the same illustration taken from the 1804 publication by Berthollet; this diagram does not appear in either the 1791 French edition or the translation by Ure of 1841.³⁹

Welter was briefly assistant to Berthollet (in 1787-8) and was an early pioneer of chlorine bleaching in France.⁴⁰ Like Descroizilles, he was a true industrial chemist and laboratory innovator of the period insofar as his analytical method was clearly tied to the needs of the manufacturer;⁴¹ these were usually speed and reproducibility without too much emphasis on accuracy and 'absolute' values.

³⁴ *Ibid.* p. 145.

³⁵ Gay-Lussac, J. L. 'Essai des potasses du commerce', *Annales de Chimie et de Physique*, **39** (1828), p. 337, cited by Szabadváry, *op. cit.* (9), p. 222.

³⁶ Szabadváry, *op. cit.* (9), p. 222.

³⁷ Berthollet, C. L. and A. B. *Éléments de l'art de la teinture, Avec une description du blanchiment par l'acide muriatique oxigéné* 2nd ed., 2 vols. (Paris, 1804), (not seen). 1st ed., 1791, trans., by Andrew Ure, *Elements of the art of dyeing and bleaching* (London, 1841).

³⁸ Madsen, *op. cit.* (8), p. 190.

³⁹ Szabadváry, *op. cit.* (9), p. 213.

⁴⁰ Smith, *op. cit.* (1), pp. 175-6.

⁴¹ *Ibid.* p. 163, Welter invented the anti suck-back tube which became an essential safety feature of apparatus used to dissolve chlorine gas into liquids, and to this day is commonly employed in laboratory methods.

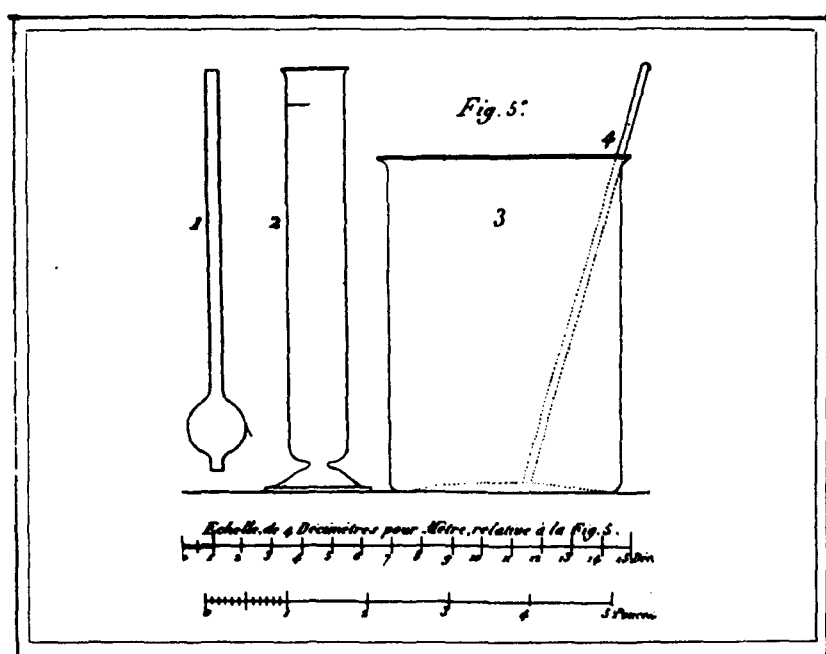


Fig. 6. Welter's analytical apparatus reproduced from Rancke Madsen (1958); a graphic reproduction of a beaker, cylinder etc., from Berthollet's *Éléments de l'art de la teinture* (2nd edn. 1804). The pipette on the left probably had a capacity of one-fiftieth of that of the measuring cylinder.

The apparatus shown in fig. 6 was used thus: A certain volume of soda solution containing a known weight was poured from the cylinder into the beaker, into which a known pre-determined volume of dilute sulphuric acid was also poured. If a spot test using litmus did not turn red, more acid was added, apparently using the pipette, until neutrality was finally reached. The method was truly empirical and volumetric. Although using acid of constant strength, he does not appear to need to know its concentration, for he reports the results numerically against the number of further additions by means of the pipette of alkali or acid. Clearly he was not measuring absolute values, these being probably unnecessary to the industrial requirements of the time.

The question whether a density of 1.84 actually proved 100% purity has been asked above, but perhaps this was not a common enquiry at that time and Welter did not need this information. His method apparently gave a satisfactory empirically useful result without this knowledge. It is very probable that a tacit assumption was held that 100% purity existed, for example in those substances obtained by crystallization, but this was a concept not based on chemical symbols, formulae, molecular structure or weights to which we now refer. The early analysts, some considered earlier in this study, did not concern themselves with 100% purity; many of the alkali determinations related to the kelp industry, depended for their accuracy by comparison with the most pure grade of alkali known at the time.

Szabadváry possibly overstates the existing knowledge of purity by claiming that Gay-Lussac devised an analytical method giving absolute values.⁴² There can be little doubt about his contribution to titrimetry and that he raised this method of industrial testing to a distinct branch of chemical analysis. The method reported was as follows:

Gay-Lussac prepared a solution of 100g of sulphuric acid (sp. gr. 1.84) and diluted this to 1l. (i.e. approx. 2N). He found that 50 ml. of this solution are required to neutralize 4.807g of potassium carbonate. This acid he referred to as normal acid (*acide normal*), and on his burette 100 divisions correspond to this 50ml. Therefore, by weighing 4.807g of the potash sample the acid titre gave a direct reading for the alkali carbonate content.⁴³

The method was thus modified in order to give a direct reading of content for the convenience of the operator or chemist; of all branches of analysis none was so easily modified for the sake of convenience and has remained a characteristic to recent times.

Was Gay-Lussac convinced that 1.84 acid and the potassium carbonate were representative of 100% pure compounds? The modifications in the above method, allowing a direct reading of the component being sought, were probably common at that time particularly where a rapid result was needed and where the accuracy consistently lay between predetermined acceptable limits.

It is in a later paragraph from the same original paper by Gay-Lussac that we see a description of a classical titration:

Using a pipette, transfer a known amount of alkaline solution into a beaker. Add sufficient litmus (tincture of tournesol) to give a definite blue colour. Place the beaker over white paper in order to see better the colour change of the litmus. Fill the burette with normal

⁴² Szabadváry, *op. cit.* (9), p. 222.

⁴³ *Ibid.*

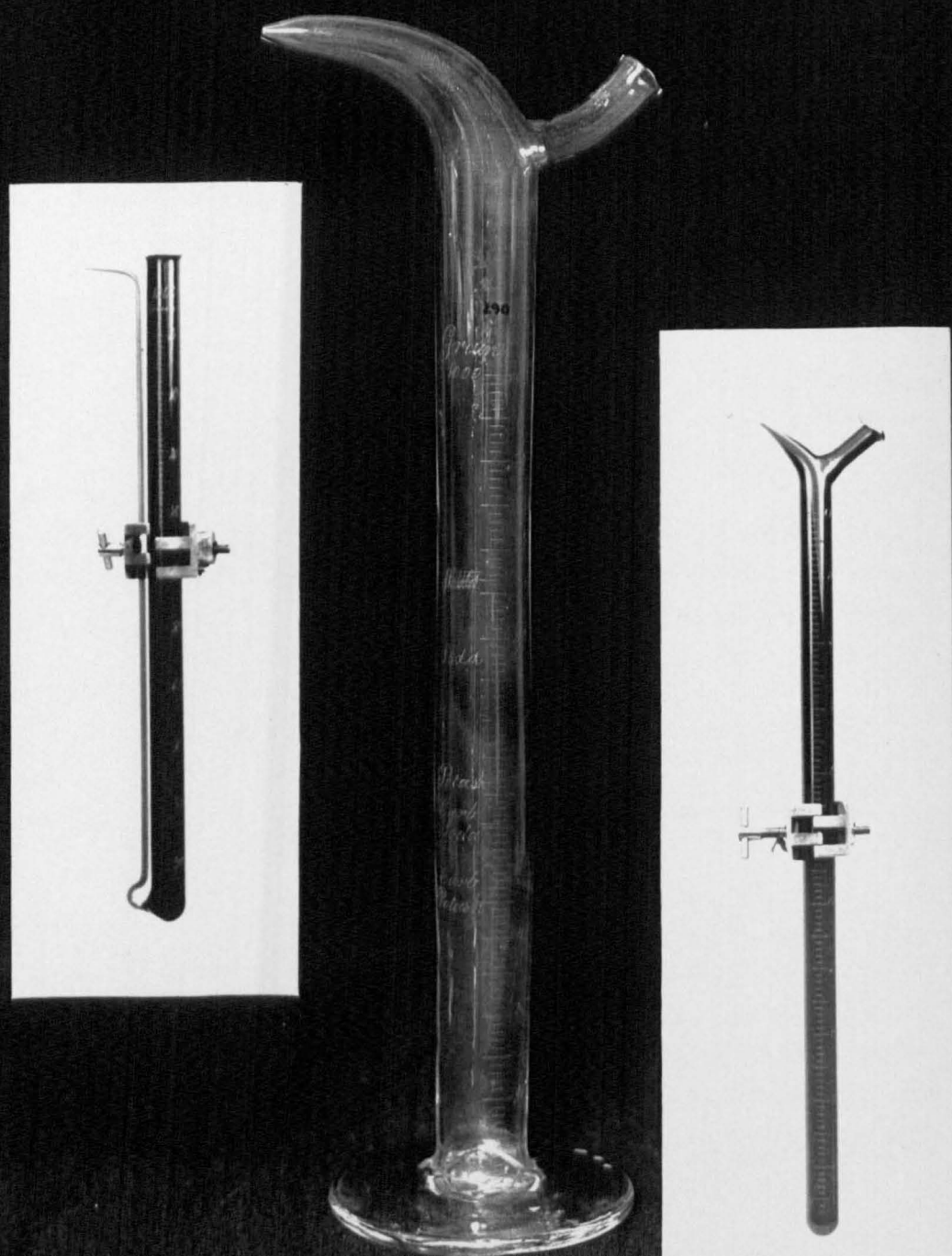


Fig. 7. Early burettes of Gay-Lussac and Christopher Binks. The left inset is by Gay-Lussac and right inset by Binks; courtesy of W. A. Campbell. The robust central model with glass foot is by courtesy of the Museum of History of Science, Oxford, cat. no. 290. This is calibrated as an 'alkalimeter'.

acid to the zero mark. Hold the burette in one hand and the beaker in the other. Run the acid slowly into the alkaline solution, mixing well. The blue colour does not change at first but when just over half of the saturation [neutralization] has taken place, if it is potassium carbonate which is being tested, the colour turns to wine-red due to the liberated carbonic acid in solution. Care must be taken to avoid passing the saturation point. If when the acid is added this only causes a slight bubbling, then continue the addition of the acid dropwise, testing after each addition and using a glass rod or matchstick soaked in the liquid, apply a trace to the blue litmus paper. As the saturation point is passed, the wine colour of the solution turns to onion skin red, and the colour of the paper turns to red, and remains at this colour...⁴⁴

Four years earlier, in 1824, Gay-Lussac described the use of what he referred to as a burette; the figures opposite are various burettes of this kind; the more robust apparatus thought to have been used and designed by Christopher Binks, a Sunderland alkali maker is also shown (see following section). A description has been given by Campbell:

The burette was used after the manner of a pipette, by closing the air-hole with the thumb and tipping. Careful control of the air-hole allowed the liquid to emerge drop by drop. This burette continued in use until the end of the nineteenth century in spite of invention of the modern form by Mohr as early as 1853.⁴⁵

It is in the 1828 publication by Gay-Lussac, regarding the analysis of commercial potashes, that he described a titrimetric method to determine sulphate content, these salts often being present in potash. His method lay in adding a solution of barium chloride of known strength to the clear potash solution and observing the precipitation of barium sulphate; the end point being when no more precipitate was formed; clearly not a very convenient method.

Of far more importance was Gay-Lussac's determination in 1835 of chlorine strength in solution by a method different from the indigo blue test. In recognising that any one of three substances could be used in a titrimetric method, arsenious acid, potassium ferrocyanide, or protonitrate of mercury, he chose the first, arsenious acid, possibly because of the sharpness of its transition or end point. Indigo still found use in this method but without the disadvantages present in the 'blue test'.

More accurate though this was, the simpler 'blue test' remained in use in industrial settings. Gay-Lussac's practical developments in the field of titrimetric analysis are noteworthy improvements but did not present a generalised ordered scheme of analysis. Whilst referring to 'normal' or 'standard' solutions, he was not using these terms in our present day understanding based on stoichiometrical chemical equations. His solutions therefore were specific to particular analyses and similarly his graduated burette, like that of Binks, was calibrated within the same limitations.

VI. Christopher Binks : A Practical Burette

Analytical chemistry cannot be conducted without laboratory equipment needed for the various operations such as weighing, heating and measuring of liquid volume. Francis Home in 1756 found it necessary to use a teaspoon as a crude measuring device in a simple analytical procedure. It has been shown that the need for a practical method of measuring volume developed further through the work of

⁴⁴ Gay-Lussac, *op. cit.* (35), pp. 346-7. My translation.

⁴⁵ Campbell, W. A. *Century of Chemistry on Tyneside 1868-1968* (1968), for the Newcastle upon Tyne Section of the Society of Chemical Industry, pp. 36-37.

2737. FOOT FOR BINKS'S BURETTE, Fig. 2738, stained wood, small size, slight. 8d.

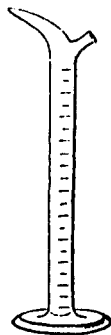
2738. FOOT FOR BINKS'S BURETTE, Fig. 2738, large size, mahogany, loaded with lead. 1s. 6d.

2739. BINKS'S BURETTE with FOOT, in one piece of Glass, stout, for the use of workmen :—

1. 100 Septems in $\frac{1}{2}$ 4s.
2. 100 Decems in $\frac{1}{2}$ 4s.
3. 50 Centimetre Cubes in $\frac{1}{2}$ 4s.
4. Burette for Testing Ammonia in Gas Liquors. 100 Septems in 16° each in $\frac{1}{2}$ 5s.

TESTING OF AMMONIA IN GAS LIQUOR.—The instrument No. 4 is used at gas works to estimate the value of ammonia liquor, according to the number of ounces of oil of vitriol which saturate one gallon. The acid is formed by diluting with water 2 ounces by weight of oil of vitriol to a pint of test acid. 100 Septems of ammonia liquor being acted upon, the number of degrees of test acid used to neutralize it according to the scale, shows the ounces of oil of vitriol per gallon. Blue litmus paper is used as the indicator. See No. 2807.

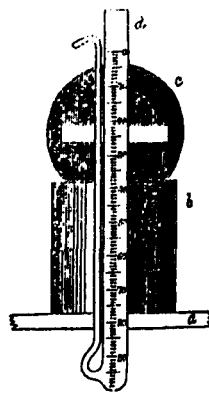
This method of testing indicates only the free ammonia. What is combined with an acid is not recognised. A more accurate process consists in mixing the gas liquor with milk of lime, distilling it in the apparatus No. 2867, receiving the ammonia as a flask containing water, and testing this distillate, which contains, not only the free ammonia of the gas liquor, but that which is liberated by the lime.



2739.



2738.



2740.

APPARATUS FOR CLARK'S WATER TEST.

315

CLARK'S WATER TEST.

The Commissioners of Woods and Forests require, as one of the indispensable conditions to a Bill for supplying water to a town being presented by them to Parliament, that there shall be given, in reference to the waters already supplied to the town, as well as in reference to the waters proposed to be supplied, —

“A statement of the quality of the water as exhibited by chemical analysis, specifying its adaptation for domestic and manufacturing purposes, and its degree of hardness with reference to the Tests and Scale of Dr. Clark.”

The water-works sanctioned by the Board of Health have all the waters submitted to the same tests.

The process invented by DR. CLARK for DETERMINING THE HARDNESS OF WATERS is of easy execution, and of such extreme precision as to rank among the most exact and delicate operations of chemical analysis. The circumstances above referred to render this process of great interest, not only to professional chemists, but to engineers, manufacturers, and the public.

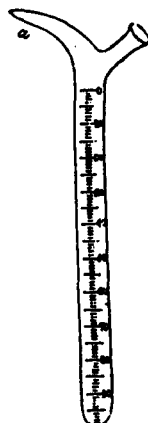
2872. SOLUTIONS AND APPARATUS FOR CLARK'S WATER TEST.—
Made in strict accordance with Dr. Clark's instructions.

1. FOR TESTING THE HARDNESS OF WATER.

1. SOAP TEST, standard strength, 4s. per pint, in a bottle.
2. STANDARD SOLUTION, WATER of 16° of HARDNESS, 2s. per pint, in a bottle.
3. GRADUATED BURETTE, for measuring the quantity of Soap Test, or the Test for Alkalinity, used in each analysis. Graduated into Test Measures, (each = 10 grains of water), and every Test Measure (degree) divided into $\frac{1}{10}$ ths, form of Fig. 2872, 3. *The following varieties :—*
 4. Contents, 16 Test Measures in $\frac{1}{2}$ ths, 3s. 6d.
 5. Contents, 20 Test Measures in $\frac{1}{2}$ ths, 3s. 0d.
 6. Contents, 32 Test Measures in $\frac{1}{2}$ ths, 4s.
 7. Mahogany Foot for the Graduated Burette, Fig. 2872, 7, 1s. 6d.
8. Pipette to deliver 100 Test Measures of Water (= 1000 grains,) Fig. 2872, 8, 1s. 0d.



2872, 7.



2872, 3.

chlorine.⁵¹ This suggests that Binks did not perhaps entirely appreciate the chemistry involved in bleaching, i.e. the liberation of oxygen by nascent chlorine. This particular patent is witnessed by A. Clapham, Junior. A local directory lists Christopher Binks as an experimental and manufacturing chemist residing at Friars Goose.⁵² In a personal communication, W. A. Campbell claims this was the Manager's house of Clapham's chemical works, but it can only be presumed that Binks held this post. In the same directory there is listed only one alkali and soda manufacturer at Friars Goose - Anthony Harrison & Co. These entries indicate that Binks was probably working and certainly living, in the Friars Goose area in the 1840s; less certain however is exactly what prompted him to develop his modification of Gay-Lussac's burette, supposing he was already familiar with this instrument and indeed whether his interest resulted from actual involvement with alkali testing. It is not certain if and when Binks joined the company or his position, other than that indicated by his occupation of the Friars Goose House. Harrison appears to have taken over the Friars Goose works from Anthony Clapham in about 1844-45.⁵³ The latter had owned the works since 1838 according to *Richardson's Directory*.⁵⁴ In about 1849 the works were again sold, this time to Gray & Crow; after almost ten years they became Jarrow Alkali/Chemical Company in 1858.⁵⁵

Two other references to Binks are worth noting; the burette was included in Griffin's *Chemical Handicraft*, but was not thought so convenient to use as Mohr's burette although claiming that any 'test' (meaning liquid) could be used.⁵⁶ Furthermore it was more resilient than Gay-Lussac's instrument in routine testing conditions. The instrument by Binks was offered with a range of graduations including Clark's Test Measures (see illustration opposite) and Degrees after Descroizilles. The item marked 2739, in this catalogue is of interest: 'BINK'S BURETTE with Foot, in one piece of glass, stout, for the use of workmen'. The glass foot or rim of this workman's burette was an idea already in use as a means of stabilizing tall pieces of glassware. A separate foot, in which the burette could be placed upright was also a common piece of additional equipment. The same burette was calibrated for use in gas works to estimate the value of ammonia liquors. The method used a 'standard' acid of 2 ounces oil of vitriol diluted to one pint placed in Binks's burette and run into 100 Septems of liquor using blue litmus paper as indicator. This of course only gave a direct reading of free ammonia. Ammonium salts had, at that time, to be determined by liberating the total ammonia by heating with lime and then titrating the solution into which the ammonia gas had dissolved.

⁵¹ Binks, Christopher. 'Manufacture of Chlorine, Chlorides, &c. (London, 1839), patent no. 7963.

⁵² *General Directory* (White & Co., Newcastle upon Tyne and Gateshead, December 1847).

⁵³ *The Gateshead Observer* 27 April 1844, p.1, col. 1, shows Anthony Clapham still at Friars Goose but in 1846 Harrison was advertising in various local directories. His son R. C. Clapham was author of 'An Account of the Commencement of the Soda Manufacture on the Tyne', *Transactions of the Newcastle Chemical Society*, 1 (1868), pp. 29-45.

⁵⁴ Richardson, M. A. *Directory of the Towns of Newcastle-upon-Tyne and Gateshead* (Newcastle, 1838).

⁵⁵ *The Gateshead Observer* 29 May 1858, p. 5. reported the sale to Mr. Williamson of Jarrow Alkali Works.

⁵⁶ Griffin, J. J. *Chemical Handicraft: a classified and descriptive catalogue* (Glasgow, 1866), pp. 293-4. There is no mention in the 1841 edition.

Other references to Binks can be found in the book by Richardson and Watt, *Chemical Technology*,⁵⁷ and according to W. A. Campbell,⁵⁸ Christopher Binks was known to Richardson. The burette appeared frequently in catalogues of apparatus into the 1900s.

VII. A Study of Walter Crum (1796-1867)

Many of the analytical examples assessed so far were not determinations of absolute content of alkali but rather its relative neutralizing power when reacted with an acid solution of known strength. Early industrial chemists saw that analysis represented a direct measure of commercial value whether in making or selling a product or in buying necessary raw materials. However, the deductions and the decisions which a modern industrialist draws from analytical results were perhaps not so apparent at the time of Home's and Black's work on bleaching. How and at what rate that change in vision occurred is difficult to assess but empirical judgements, whether or not based on analysis, clearly became interrelated with commercial success leading to a profit making ethos.

One important industrialist engaged in bleaching and calico printing who had the ability to apply chemical innovation, often based on chemical understanding and analysis, was Walter Crum. An obituary notice stated he was of Glasgow upbringing and education and was a distinguished student of practical chemistry under Thomas Thomson in 1818-19.⁵⁹ After this he gained a high reputation as a calico printer, this lasting for about forty years. Wise and Smith reported that:

Crum owned a whole town of cotton mills outside Glasgow, at Thornliebank, employing about 850 men, women, and children working twelve hours a day.⁶⁰

The obituary notice described his many improvements to the calico industry based on his chemical discoveries but there was no mention of his work in chlorimetry. The same topic is absent in Crum's entry in both the *DSB* and Partington.⁶¹ From his 1823 publication regarding indigo and the products formed by the action of sulphuric acid, it is clear he was extremely well-informed on this subject and would therefore be familiar with earlier methods of measuring chlorine strength by its decolourisation.⁶²

Before considering further the broader issues arising from his industrial life and his ready application of chemistry to contemporary industry, an assessment of his important publication on 'Chlorimetry' made in 1841 is appropriate.⁶³ This gives an historical survey of the main inventors and their methods for use in determining the strength of bleaching powder or other aqueous chlorine solutions and will be considered later.

⁵⁷ Campbell, W. A. Personal communication, 8 Dec. 1998 confirmed references to Binks in Richardson, T. and Watt, H. *Chemical Technology* (1867) edition which is now lost; page numbers not available. This edition is not recorded in the British Library catalogue.

⁵⁸ Campbell, W. A. Personal communication 1 May 1996.

⁵⁹ Anon., *Proceedings of the Chemical Society*, Report of the Anniversary Meeting, March 30th 1868, xvii-xviii.

⁶⁰ Wise, M. N. and Smith, C. 'Work and Waste: Political Economy and Natural Philosophy in Nineteenth Century Britain (III)', *History of Science*, **28** (1990), p. 225, extract taken from *The new statistical account of Scotland*, (London and Edinburgh, 1845), vol. 7, Renfrew-Argyle, p. 41.

⁶¹ Partington, J. R. *A History of Chemistry*, vol. 4 (London, 1964), pp. 249-50.

⁶² *Ibid.* p. 250, quoting *Annals of Philosophy*, **5** (1823), pp. 81-100, (not seen).

⁶³ Crum, *op. cit.* (23), pp. 17-23.

Just as the methods using the decolorisation of indigo to measure bleaching strength, which have been discussed earlier, were not strictly titrimetric, so the new method advocated by Crum was also outside this definition. Crum's method in fact borders on that of true colorimetry as commonly used in industrial laboratories to the middle of this century and illustrates a continuity from 'volumetric' origins. In specifying its application to weak solutions, Crum is applying a general principle of colorimetry where the method is well suited for measuring low concentration. Indeed the method was often used where the sought substance was present in a smaller quantity than could be determined by other volumetric or gravimetric methods. He is aware of the speed with which regular determinations can be made; again this is a general characteristic of this type of analytical method.

The method demands an assumption that, if two solutions of the same colouring agent in the same solvent have the same tint, they will have the same concentration. Hence if the concentration is known of one of the solutions against which the unknown has exactly the same colour, the concentration of the unknown will be the same.

Methods of observing the strength of colour have developed since Crum's time and now involve sophisticated optical principles but the method under review is very close to present day use of Nessler's Tubes. Considerable accuracy can be achieved with these; if the unknown colour is first judged between two close standards, a new range or series can be prepared within even narrower limits. Whether Crum was the originator of this method of analysis, has not been established in this study. Having described the methods previous to his own, he commented: 'Hence all the processes I have described are too delicate and tedious.'⁶⁴ If by this, we are to believe that Crum's new method offered ease and speed for repetitive analysis suitable for an ordinary artisan to carry out, then clearly he was offering something of great value to industrial laboratories:

...the testing is performed in an instant. It depends on the depth of colour of the peracetate of iron. A solution is formed of proto-chloride of iron [ferrous chloride FeCl_2], by dissolving cast-iron turnings in muriatic acid, of half the usual strength. To ensure perfect saturation, a large excess of iron is kept for some time in contact with the solution at the heat of boiling water. One measure of this solution, at 40° Twaddell, (spe. grav. 1.200) is mixed with one of acetic acid, such as Turnbull and Co. of Glasgow sell at 8s. a gallon. That forms the proof solution. If mixed with six or eight parts of water it is quite colourless, but chloride of lime occasions with it the production of peracetate of iron, which has a peculiar intense red colour.⁶⁵

The remainder of Crum's paper consists of two parts: the first describes the process of matching the bleaching solution of unknown strength against a prepared known series by aligning the degree of red colour resulting from the formation of ferric acetate; the second part is an explanation of how the numerical values obtained above are translated into useful instructions to adjust the bleaching strength of the steeping vessels. Both sections represent sound examples of technical chemistry being adapted, modified, and used to a useful end in an important industrial operation.

Twelve phials (tubes) were used, each containing a fixed known amount of 'proof solution', i.e. the solution of ferrous chloride in acetic acid. These are then filled up with bleach solutions of known but

⁶⁴ *Ibid.* p. 21.

⁶⁵ *Ibid.* pp. 21-22.

varying strengths determined by the Twaddell hydrometer.⁶⁶ For the unknown sample drawn from the bleaching plant, the same quantity as used in the comparison tubes is added to the standard quantity of test solution and the red colour is formed. This shade is then matched against the nearest shade in the series. The numerical value given to each tube corresponded to a twelfth of a degree Twaddell, and the range was one twelfth to twelve twelfths. The unknown sample when matched indicates by its number the strength in twelfths of a degree of the hydrometer. By reference to the ingenious tables prepared by Crum, the amount of fresh stock bleaching powder of six degrees needed to raise the strength of the entire steeping vessel to the desired strength is seen. This entire innovative method used little chemistry apart from an appreciation of the initial chemical reaction needed to produce an indicative colour related to concentration. Once this was established the method only depended upon laboratory manipulation and careful observation.

Hourly testing, and certainly every time fresh goods were to be treated, appeared to be the recommended practice in Crum's extensive works; he claimed that the range of safe bleaching concentration was not very wide particularly for cottons:

A solution standing 1° on Twaddell's hydrometer, (spec. grav. 1.005) is not more than safe for such goods, while that of half a degree is scarcely sufficient for the first operation of stout cloth, unless it is packed more loosely than usual.⁶⁷

The publication ends with a comment on the chemistry involved when bleaching solution acts upon 'protomuriate of iron'. Crum bases an explanation on an 'old' and new chemical understanding of bleaching powder composition and attempts to show the oxidation, ferrous to ferric. He suggests there is some advantage by using the proacetate of iron instead of ordinary ferric chloride which would be the case had no acetic acid been added. An acetate of iron known as 'red crystals of iron' has alchemical origins. Szabadváry makes very little mention of this method by Crum and merely cites its publication in Germany in which Crum again mentions the instability of ferrous chloride (Eisenchlorur) and refers to Dalton's Chlorkalk bleaching powder test.⁶⁸

As the scale of bleaching operations grew so the requirement for control and measurement of the various operations gained importance. Indeed it would seem that industrial progress, if viewed through the circumstances of Crum's activities, depended more upon relatively simple and reliable methods of control analysis, than upon full chemical and theoretical understanding. In the 1840s when it is possible that Crum's colorimetric method was in common use it is now difficult to see any significance in Dalton's atomic theory or the chemistry laws which this confirmed, although it allowed the concept of normal solutions which did find practical use in industrial laboratories. Of course had it been necessary to determine the absolute content of the element chlorine, a different way of calculating this would have been needed. Crum was only measuring bleaching strength. This was all that was needed to work his

⁶⁶ See Clow A. & Clow, N. L. *The Chemical Revolution* (London, 1952), p. 212. George Macintosh was supplied with a hydrometer for testing urine as a source of ammonia by an instrument maker named Twaddle (*sic*) although this is refuted by Hardie, *op. cit.* (2), p. 611. It provided a simple means of guaranteeing the genuine article. The Twaddell scale was devised as a mere convenience to the user and could be easily converted to real density if desired. See also Black's comments in Ramsay, W. *The Life and Letters of Joseph Black, M.D.* (London, 1918), pp. 131-2.

⁶⁷ Crum, *op. cit.* (23), p. 21.

⁶⁸ Crum, W. Dingler's *Polytechnisches. Journal*, 96 (1846), pp. 44-46, my translation. Also cited by Szabadváry, *op. cit.* (9), p. 264.

processes efficiently and his method no longer rested upon the uncertainties of the decolourisation of indigo by a bleaching solution.

The demands of the bleaching industry undoubtedly pushed forward analytical developments which in turn allowed the industry to expand and become 'chemically minded'; it did not make great demands on chemical and theoretical understanding however. As Wise and Smith point out, a constant theme amongst the members of the Glasgow Philosophical Society at this time (1840s) was that 'measurement was the foundation of progress, industrial and scientific, theoretical and practical' - but not absolute measurement.⁶⁹ This was not necessary to the industrialists of the period just as it was not essential to the early analyses by Hume and Black with which this study began. If absolute values were not essential, then the acid alkali balancing and analysis without weights (see chap. 1) were as valid as Crum's apparently sophisticated colorimetric method.

Crum's method did not depend upon knowledge of atomic weights or chemical formulae and a modern chemist's appraisal of the method, based upon better understood chemistry, would no doubt question the chemical reactions involved. For example it is doubtful if ferrous chloride (FeCl_2) alone was formed by reacting iron with hydrochloric acid, also the formation of an acetate and the stability of this proof solution, is open to question. The important point remains, that the method worked and satisfied an extremely important need in Walter Crum's bleaching empire. My own memory (1950s) of carrying out routine analyses using Nessler's tubes or simple open beakers in methods very similar to the above was the need for a very precise and well developed laboratory technique; this hardly supports Crum's claim that the 'testing is performed in an instant' although the speed with which a repetitive operation can be carried out is sometimes very surprising. The report suggests that the method had been in constant use for some years.

In Crum's assessment of other analytical methods for measuring bleaching strength he suggests that the one by Descroizilles is generally considered the oldest.⁷⁰ This has been assessed above, together with the part played by Welter which led to Gay-Lussac's further refinements of essentially the same method of indigo decolouration.

Crum also describes the method using potassium ferrocyanide which he states had been long used by Mr. John Mercer of Oakenshaw, Manchester.⁷¹ His comments about Dalton's method (1813)⁷² are of interest because Crum suggests that Graham's modification in detecting the end point by using a spot test of potassium ferrocyanide, makes 'the best and most easily executed of all the tests of bleaching powder'. Using a white stoneware plate, spotted over with drops of red potassium ferrocyanide, the end point is detected when a spot taken from the titration flask fails to produce a blue colour, that is, when no more ferrous sulphate (protosulphate) remains. There is no mention of using potassium ferrocyanide however in Dalton's original 1813 paper and Crum gives no source reference accounting for this change other than

⁶⁹ Wise and Smith, *op. cit.* (60), p. 225.

⁷⁰ Crum, *op. cit.* (23), p. 18.

⁷¹ *Ibid.*, p. 20.

⁷² Dalton, *op. cit.* (20).

it was Graham's 'arrangement'. Nevertheless he attributes to Dalton the use of ferrous sulphate in this instance.

One other industrial entrepreneur and chemist similar to Crum and already mentioned was John Mercer (1791-1866). His self-taught chemical knowledge and industrial achievements closely resembled those of Crum. Whilst Mercer's innovative and advanced dyeing developments are outside this study, it seems probable that his famous work on the 'mercerizing' process and other textile-chemical developments involving ferrocyanides may have led to the use of this chemical in determining chlorine content.

Because of his advanced chemical means of calico printing, leading to what became known as the 'mercerizing' process,⁷³ accurate and reliable control of bleaching processes became of paramount importance. Also, his careful observations of colour changes in dyeing processes surely pointed to the possible role of indicators in quantitative volumetric analysis.

According to Parnell, Mercer used the potassium ferrocyanide method to determine available chlorine from 1827 onwards, at a time when the quality of bleaching powder varied greatly.⁷⁴ His familiarity with red prussiate of potash clearly arose from its use in dyeing processes but from where his knowledge of its analytical use came we cannot now be certain. Parnell writes as a chemist himself,⁷⁵ and his terminology (1886) may not entirely reflect Mercer's true chemical knowledge in 1827. There is little doubt that Mercer maintained chemical solutions of known concentration but there is no indication by Parnell that these were standard solutions in the modern sense. Whilst he speaks of 'colour-shop solutions adjusted to a simple relation to their chemical equivalents',⁷⁶ and those solutions for analytical use 'are made of special strengths for special objects', these sentences suggest he merely maintained a range of solutions of known and convenient concentrations. The aspect of convenience, common in most industrial volumetric methods, is suggested by Mercer's measure to give a direct reading:

a 2½-ounce tube similar to the old alkalimeter, but with four graduated columns for refilling when necessary, each being marked with the percentage of pure 'chloride of lime'.⁷⁷

Mercer developed and used the potassium ferrocyanide method in an industrial setting, but his biographer, Edward Parnell, writing almost sixty years later almost implies an atomic understanding by Mercer in describing the analytical solutions - something more than mere reacting 'equivalents'. Nieto-Galan points to correspondence between Mercer and Playfair and cites a paper by Mercer which confirms his awareness of atomic concepts.⁷⁸ However this cannot be seen to suggest that in or around 1827 Mercer devised a method of determining chlorine in advance of current knowledge. His determination of the 'equivalents' of chlorine and lime was a common exercise at that time.

⁷³ See Travis, A. S. *From Turkey Red to Tyrian Blue* (Jerusalem, 1993-4), p. 53.

⁷⁴ Parnell, E. A. *The Life and Labours of John Mercer* (London, 1886), p. 44.

⁷⁵ See Parnell, E. A. *Applied Chemistry in Manufactures, Arts and Domestic Economy* (London, 1844), 2 vols.

⁷⁶ Parnell, *op. cit.* (74), p. 44.

⁷⁷ *Ibid.* pp. 47-8.

⁷⁸ Nieto-Galan, A. 'Calico Printing and Chemical Knowledge in Lancashire in the Early Nineteenth Century: the Life and "Colours" of John Mercer', *Annals of Science*, 54 (1997), pp. 1-28, on p. 20, notes (135) and (138).

Mercer has not received much attention by historians of science and Parnell possibly overstates Mercer's chemical understanding if not his actual achievements. The John Mercer Archives held by the Oxford Museum of History of Science (MSS North) contain no record of Mercer's analytical methods.

VIII. The Modern Burette of Mohr

Few analytical chemists of the twentieth century would recognise the so-called burettes of Descroizilles, Gay-Lussac or Binks. At what point therefore did burettes familiar to chemists of this century come into being?

Karl Friedrich Mohr (1806-1879)⁷⁹ is often associated with a simple mechanical device to close the flow of liquid or gas through rubber tubing (Mohr's clip) - it was this device which he used to finely control the flow of liquid from the lower end of a graduated tube and which became the now familiar burette. The top outlet used by Gay-Lussac and Binks, the reasons for which are not entirely clear, changed its position to the bottom of the tube and so required a control tap of some kind.⁸⁰ Whilst this change in design may not be entirely original to Mohr it is to him that the modern burette is generally attributed and on which volumetric analysis became so dependent.⁸¹

Analytical control of industrial processes rested very much upon volumetric analysis and accurate liquid measurement by means of burettes; this continued for the following hundred years or more. The earlier 'burettes' continued to be used long after Mohr's modifications. How Mohr's new burette came into use in this country cannot now be determined although J. J. Griffin's extensive importing activities may have played a part. We know Mohr's most important work on volumetric analysis was published in 1855-6 and it is reasonable to suppose that the burette became of interest to practising chemists.⁸²

Mohr's achievements in the modification and manipulation of chemical apparatus are too numerous to mention here, but those relevant to this study demand mention.⁸³ Oesper and Scot give the impression that Mohr was a contentious figure, although he managed a life-long friendship with Liebig such that the water cooled condenser designed by Mohr is commonly attributed to Liebig.⁸⁴ Mohr did not invent the idea of back-titration although he probably developed the idea further than Joseph Black. Also, while his use of normal solutions in volumetric work occurs frequently in his book, this does not prove that the practice originated from Mohr (see following chapter on Ure and Griffin). Oesper suggests that Mohr introduced two primary standards into analytical chemistry, oxalic acid and ferrous ammonium sulphate;⁸⁵ the latter compound found use in standardising solutions of potassium permanganate or dichromate and became known as Mohr's salt.

Farrar points out that Mohr's book brought titrimetry before a wider analytical public and that this method of analysis 'remained curiously unpopular until after the publication of the influential

⁷⁹ To avoid confusion with his father and son, also named Karl, he was often referred to as Friedrich or Doctor Mohr.

⁸⁰ Scott, *op. cit.* (47), p. 197, suggests ground glass stopcocks were used before Mohr's invention of the pinch clamp.

⁸¹ See Szabadváry, *op. cit.* (48), remarks about O. E. Henry.

⁸² Mohr, Friedrich. *Lehrbuch der chemisch-analytischen Titrimethode* (Braunschweig, 1855-6), 2 parts.

⁸³ Oesper, R. E. 'Karl Friedrich Mohr', *Journal of Chemical Education*, 4 (1927), pp. 1357-63; and Scott, *op. cit.* (47), pp. 191-203.

⁸⁴ Scott, *op. cit.* (47), p. 193.

⁸⁵ Oesper, *op. cit.* (83), p. 1360.

A HANDBOOK
OF
VOLUMETRICAL ANALYSIS.

BY
ROBERT H. SCOTT, M.A., T.C.D.,
SECRETARY OF THE GEOLOGICAL SOCIETY OF DUBLIN, AND LECTURER IN MINERALOGY
TO THE ROYAL DUBLIN SOCIETY.



LONDON:
LONGMAN, GREEN, LONGMAN, AND ROBERTS.
1862.

Fig. 9. Title page of Scott's book on volumetric analysis (1862).

Lehrbuch'.⁸⁶ The development of titrimetry probably came more from people such as Mohr and Gay-Lussac than those permanently engaged in industrial pursuit; Mohr made extensive contributions to the improvement of analytical apparatus and techniques sometimes assuming credit for ideas already existing. Works' chemists, perhaps not occupying a well-ordered laboratory but a simple shelf on which to carry out a rapid control test or check, were not the people to develop momentous forward steps in volumetric analysis. The practical influence of Mohr's book is now difficult to assess, but from it the application of normal solutions appears an accepted practice. Again, as can be seen in other instances of his inventive mind, his ability to develop further the ideas of others is apparent. Certainly he influenced the growth of interest in volumetric analysis, very probably through this almost first ever text book. Curiously, it was never translated into English.

IX Conclusions

Consistent and reproducible results have always been important requirements of volumetric analysis. We know that with the introduction of chlorine into bleaching processes, regular and frequent analytical control became essential. This could often be hourly depending on processing rates etc. However, the viewpoint of Oesper that volumetric analysis or measurement by volume was retarded by inadequacy of suitable glassware, is without foundation;⁸⁷ similarly there are no grounds to believe that the Gay-Lussac or Binks burettes were difficult to handle (because there was no apparent means of standing them upright) and did not give results of high accuracy. We cannot now assess either of these points and it is wrong therefore to suggest that Mohr's modification was the most important turning point in titrimetry. It is quite wrong to attach importance to modifications, as in this instance, simply because the result is more familiar to modern eyes. We do not complain of the modern burette because it does not stand upright without a burette stand. There is no reason to believe that Binks's burette was less accurate and more difficult to handle than the later Mohr model, particularly when in the hands of a skilled operative.

The idea that Mohr's *Lehrbuch* influenced volumetric analysis more than the gadgets and modifications now associated with his name is surely more plausible; after all, the book was very nearly the first of its kind and was therefore likely to be received enthusiastically. As such, this was a milestone in volumetric analysis and by virtue of its timing, innovative and authoritative nature, it seems to have set the pattern and approval for this kind of analysis which lasted for the following hundred years.

According to Szabadváry, a book on titrimetry was published in Germany by Schwarz in 1850 and it was the first in this field.⁸⁸ The first publication on the same subject in Britain occurred in 1863 with Sutton's *A Systematic Handbook of Volumetric Analysis*; in this, Sutton states: 'with the exception of a small and somewhat exclusive book, written by Mr. Scott, of the Trinity Office, Dublin, there has been no English text-book on the subject.'⁸⁹ Scott's title page is reproduced opposite; its publication was in 1862,

⁸⁶ Farrar, W. V. 'The Origin of Normality', *Education in Chemistry*, 4 (1967), p. 279.

⁸⁷ Oesper, *op. cit.* (83), p. 1357.

⁸⁸ Szabadváry, *op. cit.* (9), p. 239, cites Schwarz, H. *Praktische Anleitung zu Maassanalysen* (Braunschweig, no date). The correct title for the first edition is: *Über die Maassanalysen, besonders in ihrer Anwendung auf die Bestimmung des technischen Werthes des chemischen Handelsproducte wie Potasche, Soda, Chloralk, Braunstein, Säuren, Arsenm, Chrom, Eisen, Kupfer, Zinn, Blei, Silber &c.* (Braunschweig, Vieweg, 1850). The title page reproduced by Szabadváry is that of the enlarged second edit., 1853.

⁸⁹ Sutton, *F. A Systematic Handbook of Volumetric Analysis* (London, 1863), preface, v.

one year before Sutton's textbook. Robert H. Scott, though never a member of staff at Trinity College, became Secretary of the Geological Society of Dublin and lectured in mineralogy to the Royal Dublin Society.⁹⁰

If it is accepted that it was Mohr's book which gave wide publicity to the use of standard solutions and the concept of normality, from where did he gain this knowledge? This is not easily answered particularly in this case where Mohr's transient interests and enthusiasms covered such a wide variety of subjects. He may have known about Griffin's work on standard solutions (see below, chap. 7),⁹¹ also, the earlier book by Schwarz (1850) had stated that these could be made up so that for a one gram sample the burettes reading would indicate percentage composition.

After the publication of Mohr's *Lehrbuch* apparatus and standard solutions and many of the methods suggested by him remained essentially the same until the recent 1950s and possibly to this day in some industrial laboratories. This does not place Mohr as the 'Father of Volumetric Analysis'⁹² but rather as one occupying a particular chronological spot in a continuing process of analytical development.

Standard solutions certainly marked him as an important turning point, interestingly without much reference to the atomic theory of Dalton. Sodium hydroxide and acids remained the most used although due emphasis on the need for primary standard solutions was becoming evident which promoted new methods for their preparation. For example greater use was made of hydrochloric acid prepared from its constant boiling fraction. Perhaps the most important forward step in titrimetry came with the introduction of synthetic indicators such as phenolphthalein (in 1877) and methyl orange in the following year; their synthesis depended on developments in organic chemistry. The complete understanding of titrimetry was provided by physical chemists through theories of hydrogen ion concentration. Afterwards 'titrimetry came into its own',⁹³ but the divisions of chemistry, organic and physical, are outside the limits set for this study.

⁹⁰ Scott, R. H. *A Handbook of Volumetrical Analysis* (London, 1862). Published with assistance of Trinity College and printed by Dublin University Press.

⁹¹ Szabadváry, *op. cit.* (9), p. 246, mentions that a later edition of *Lehrbuch* speaks of Griffin. This is probably the 7th edition of 1896, edited by A. Classen (not seen).

⁹² Scott, *op. cit.* (47), p. 191, article title. The phrase probably originated from Sutton (1863).

⁹³ Brock, W. H. *The Fontana History of Chemistry* (London, 1992), p. 184, suggests some areas of volumetric analysis were curtailed during the nineteenth century by the absence of satisfactory indicators.

CHAPTER SIX

EARLY ALKALI MANUFACTURE : CHEMICAL AND ANALYTICAL ASPECTS

I. Synthetic Alkali

There were chemists who, prior to the adoption of the Leblanc process, attempted to discover methods of obtaining alkali from common salt. According to Gittins,¹ writing over thirty years ago, the efforts of these chemists received little attention by historians before the publication of an article in 1945 by A. and N. L. Clow.² However, the broad outline history of this early period of alkali making has received attention more recently.³

Earlier chapters in this thesis have shown that by simple analytical means the alkali content of 'ashes', obtained from certain plants, was found to be fairly low. The imported ash made from the barilla plant (*salsola soda*) rarely contained more than 20% of alkali, while kelp from seaweed, often less than 5%.

The approximate chemical composition of potash, barilla and kelp according to Gittins is thus:⁴

		Potash %	Barilla %	Kelp %
Alkaline Salts	KOH	20		
	K ₂ CO ₃	35	65	
	Na ₂ CO ₃	10	17	4
Neutral Salts	K ₂ SO ₄	15	10	
	KCl		5	10
	NaCl		10	10
Other Salts			10	5
Insoluble Residue and Water		15	50	50

The fluctuations in price and availability and the low alkali content from naturally occurring sources shown above adversely affected such industries as soap, glass and textiles.⁵ Wide variations in composition of the ash obtained from barilla and kelp resulted from such factors as location of the seaweed, season of collection and how long the plant was exposed to rain;⁶ this represented an unsatisfactory commercial position for those expanding industries which were becoming more and more dependent on alkali. The answer lay in the possibility of home-produced synthetic soda of high alkali content and free from the uncertainties described above.

¹ Gittins, L. 'The Manufacture of Alkali in Britain, 1779-1789', *Annals of Science*, **22** (1966), no. 3, pp. 175-190.

² Clow, A. & N. L. 'Vitriol in the Industrial Revolution', *Economic History Review*, **15** (1945), pp. 44-55.

³ Padley, R. 'The Beginnings of the British Alkali Industry', *University of Birmingham Historical Journal*, (1951), pp. 64-78; Clow, A. and N. L. *The Chemical Revolution* (London, 1952); and several papers by Gittins, although confined to specific periods of time.

⁴ Gittins, L. *The Development and Location of the Soap Manufacturing Industry in Great Britain, 1700-1850* University of London Ph.D. Thesis, 1962, pp. 279-282.

⁵ Gittins, *op. cit.* (1), pp. 175-190.

⁶ Hendrick, J. 'The Value of Seaweeds as Raw Materials for Chemical Industry', *Journal of the Society of Chemical Industry*, **35** (1916) no. 10, pp. 565-574; part of Table VIII has been reproduced in Appendix VII, see also a tabulation of analytical results of kelp from various sources in Appendix VIII, by kind permission of Dr. L. Gittins.

II. Synthetic Alkali before Leblanc: James Keir (1735-1820) Alkali Maker

The early legal skirmishings surrounding attempts to make synthetic alkali are described in the 1780 *Journals of the House of Commons* and it is from this primary source that much of what follows has been drawn.

Some background details of James Keir have been given in an earlier chapter regarding his chemical analysis of alkali (fossil alkali from Bombay). His industrial interests, based in the Midlands, led Moilliet and Smith to use the soubriquet 'Mighty Chemist' in their 1982 'shortened version of a life of James Keir'.⁷ Keir was well-fitted to take a place amongst Lunar Society members of that time; his introduction to the Society through Erasmus Darwin dates from about 1767. In this select group there were members who were distinctly interested in the possibility of synthetically produced alkali if only because the supply of natural alkali was becoming questionable.⁸ Also, it was already known that a relation existed, between common salt, hydrochloric acid, and caustic soda either as free caustic or soda ash.

Moilliet and Smith provide an explanation of the possible thinking by chemists of the period particularly that which might have led Keir to investigate the use of slaked lime. However, it seems probable that the cheapness of lime and its property for causticisation influenced this choice. Keir was not alone in this pursuit. James Watt had been approached by Joseph Black and Roebuck⁹ to investigate the possibility of producing alkali from salt which seemingly created some internal tension within the Lunar Society involving William Small.¹⁰ The commercial benefits of chemically produced soda for use in pottery and glass making were very clear to Keir and Josiah Wedgwood also a member of the Lunar Society. Moilliet's account of what he believes were the chemical reactions which Keir unknowingly employed in attempting to make synthetic alkali are so intriguing that their consideration is included here. Moilliet is a direct descendent of James Keir and whilst his researches on this ancestor provide only secondary source material, his findings are noteworthy.

He points firstly to the likely testing by Keir of the reaction between salt and slaked lime which must have given an immediate negative result assuming that the reactants were reasonably pure. Such a reaction would not proceed - our modern day law of mass action demands removal of one of the reaction products - a serious difficulty where both products are soluble. This desire to find the right chemical reaction to produce alkali from salt was taking place at a time of high duty on this raw material and yet Keir and other Lunar Society chemists were apparently seeking a financial return on a process using it. Their petitions to gain exemption from this tax were unsuccessful.

Lime or slaked lime was a common and cheap material; it was known that by reacting slaked lime with a mild alkali (such as soda) the solution became caustic. Home and Black had given a more

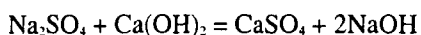
⁷ Moilliet, J. L. and Smith, B. M. D. 'A Mighty Chemist, James Keir of the Lunar Society: Scientist, Technologist, Industrialist, Soldier, and Political Commentator', (privately printed, 1982).

⁸ Gittins, *op. cit.* (1), p. 180.

⁹ See Musson, A. E. and Robinson, E. *Science and Technology in the Industrial Revolution* (Manchester, 1969), p. 353; Gittins, L. 'The Alkali Experiments of James Watt and James Keir, 1765-1780', *Transactions of the Newcomen Society*, 68 (1996-97), pp. 217-29, ref. 4.

¹⁰ Coley, N. G. 'James Kier, F.R.S. (1735-1820) Soldier, Chemist and Gentleman', *West Midland Studies*, 4 (The Polytechnic Wolverhampton, 1970-71), pp. 1-22, on p. 3.

'scientific' explanation (see chap.1.) but they, like Keir, could only direct their theory and research on the basis of known chemical raw materials the trivial names of which were not always indicative of potentially useful chemical reactions. Salt was a common commodity but heavily taxed and clearly it did not readily react with slaked lime. Another common substance having origins in common salt was Glauber's salt (sodium sulphate) and this in fact reacts with slaked lime to produce caustic soda:



Sodium sulphate was a well known substance and became a commercial by-product in the production of hydrochloric acid;¹¹ it was freely available and could be seen to originate from common salt since the latter is merely reacted with sulphuric acid in order to generate hydrochloric acid and sodium sulphate. Moilliet and Smith postulate that this is what Keir did.¹² What might have been a single stage reaction became instead two stages; firstly, sodium sulphate was made which produced a saleable by-product, and the sulphate was then reacted with slaked lime to produce caustic soda (as in the reaction given above). The process remained one based on salt only - if a little indirectly. Their account is based on the reporting of a House of Commons enquiry (1780) entitled, 'Keir's Manufactory of Marine Acid', implying that Keir was making hydrochloric acid, and clearly finding an outlet for the otherwise waste sulphate.

According to Moilliet and Smith the only explicit confirmation that caustic soda was being made by this process is that given by Keir's daughter, Amelia, in *Sketch of the Life of James Keir*.¹³

At a date which cannot be accurately assigned, but apparently about the year 1780, Mr. Keir engaged in a business with Mr. Blair. Mr. Blair was the only other brother officer in the Army whose friendship Mr. Keir had the good fortune to secure. They established works at Tipton, near Dudley, for the manufacture of alkali, for the use of the soap-makers, from the sulphates of potash and soda. The method of extraction proceeded on a discovery of Mr. Keir's, contradicting a point in the doctrine of elective affinities held by the Chemists of the day. Their experiments seemed to show a stronger affinity of sulphuric acid for either of the two fixed alkalis than for lime. Mr Keir found that - by presenting the salts in exceedingly weak solution, and by calling in the aid of a chemical agent [for which he always professed the highest respect, and the functions of which in natural operations were, he thought, greatly underrated] Time - the rule of election was reversed. By passing the weak solution *slowly* through a thick body of lime, the sulphates were decomposed, the sulphuric acid uniting with the lime, and leaving the alkalis disengaged. The liberated alkali had then only to be brought into a concentrated form for sale.¹⁴

The absence of primary material regarding these alkali developments may lie in Keir's desire for secrecy and it is suspected that many records were lost in the serious fire at Keir's home, Abberley Hall in Worcestershire in 1845.

¹¹ Glauber's Salt was used by apothecaries from as early as 1648 and was known as Sal Mirabile throughout the eighteenth century. See Clow, *op. cit.* (3), chapter IV for an account of sodium sulphate in the early developing chemical industry.

¹² Moilliet and Smith, *op. cit.* (7), p. 24.

¹³ The citation in Moilliet and Smith, *op. cit.* (7), p. 78, is as follows: 'Moilliet, Amelia. and Moilliet, James Keir; *Sketch of the Life of James Keir, Esq., F.R.S., with a Selection from his Correspondence*, privately printed in 1868. The date of publication is not made clear, and it is given as 1859 by some writers. Entries in the *Notebooks* [cited as an incomplete set of manuscripts in Amelia Moilliet's handwriting and other transcripts by James Keir Moilliet] suggest that this book was published for the Lunar Society centenary in 1868.'

¹⁴ [Moilliet, Mrs Amelia] *Sketch of the Life of James Keir, Esq., F.R.S., with a Selection from his Correspondence* (London, nd. [1868]), pp. 75-76. Author and date are hand written insertions; see previous footnote.

Using the information in Amelia's text, Moilliet¹⁵ in 1966 attempted to reconstruct Keir's method using additional data obtained by Neumann and Karwat.¹⁶ Their reconstruction and Moilliet's more recent work suggested that Keir's empirical methods succeeded.

No evidence has been found to suggest Keir's use of any quantitative analytical means in developing his alkali process; there is no mention in his earlier paper, on the analysis of Indian alkali, that analysis might be of value in future alkali developments.¹⁷ Moilliet's assessment of Keir's and Neumann's and Karwat's work highlights the depth of chemistry needed by Keir's process; one in which Keir must have been the 'empiricist supreme', considering the mistakes made by these almost modern day chemists, operating admittedly 140 years after the event. Later, it will be shown that a similar, hugely empirical appreciation of the Leblanc process existed for a very long time.

Moilliet's and Smith's criticism of Neumann and Karwat is influenced by the assumption that Keir's method of making alkali depended upon the slow percolation of a weak solution of sodium sulphate through a bed of slaked lime thus allowing the reaction to go to completion. The removal of unconverted sodium sulphate by fractional crystallization, necessary to this process, was familiar to Keir; this demanded carefully controlled concentration and by these means the backward reaction, to re-form the sulphate and lime, was inhibited. This was not taken into account in Neumann's and Karwat's reconstruction. Why Keir adopted his method of slow percolation using a weak solution of sulphate is not obvious. Moilliet suggested the necessity of evaporating the liquor to a caustic soda content of 14% determined by titration,¹⁸ but as Gittins pointed out 'whether he [Keir] was able to determine 14% caustic soda content by titration of a solution containing caustic soda and slaked lime is a matter of conjecture.'¹⁹

Keir's method was so far in advance of contemporary chemical reasoning that one is tempted to believe that his invention was one based on the most finely tuned empiricism. Why such a weak solution of sodium sulphate? Was this because he compared sulphate solubility with the sparing solubility of calcium hydroxide - information no doubt gleamed from Joseph Black, in particular his experiments using lime water and carbon dioxide which show the process of this reversible reaction. Clearly there would be no significant reaction between solid sulphate and slaked lime; making a slurry of both materials would have been an obvious step (not one based on atomic or molecular distances) and perhaps application of heat might have sensibly been tried. But no, Keir used a weak sulphate solution dripping through a bed of slaked lime and seems to have exactly pitched the concentration to fit the precise percolation time:

...and by calling in the aid of a chemical agent (for which he always professed the highest respect, and the functions of which in natural operations were, he thought, greatly underrated) Time - ²⁰

¹⁵ Moilliet, J. L. 'Keir's Caustic Soda Process - an Attempted Reconstruction', *Chemistry and Industry*, (5 March 1966), pp. 405-8.

¹⁶ Neumann, B. and Karwat, E. 'Die Kaustizierung von Natrium Sulfat', *Zeitschrift für Elektrochemie und Angewandte Physikalische Chemie* 27 (1921), p. 114, quoted by Moilliet, *op. cit.* (7), p. 28, and *op. cit.* (15), pp. 406-7.

¹⁷ Keir, J. 'On an Analysis of Imported Indian Fossil Alkali sent by Mr. Hellenus Scott', *Transactions of the Society for the Encouragement of Arts, Manufactures and Commerce*, 6 (1788), pp. 133-148

¹⁸ Moilliet, *op. cit.* (15), p. 407.

¹⁹ Gittins, L. 'The Alkali Experiments of James Watt and James Keir 1765-1780', *Transactions of the Newcomen Society*, 68 (1996-97), p. 222.

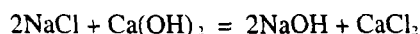
²⁰ Moilliet and Smith, *op. cit.* (7), p. 27.

This gave the best result though, as Keir recognised, it appeared to contradict the contemporary concept of elective affinity. With modern understanding of the chemistry involved it seems surprising that such a process developed empirically; the law of mass action was not stated generally until 1864 (Guldberg and Waage) although Berthollet's observations in 1799 anticipated it.²¹ But Keir was encountering its implications before 1780 and carrying out the necessary modifications in order to satisfy a law which had not yet come into being. His process was based on a reversible reaction which as Padley pointed out 'is a curious foreshadowing of what a century later came to be known as the law of mass action.'²²

We do not know for certain whether Keir's ideas for alkali production were considered by other members of the Lunar Society before 1780 (the year suggested by Amelia in which Keir 'engaged in a business with Mr. Blair'). That the subject was of interest to the Society is proved by a letter from Watt to Small dated 5 July 1769:

Both Dr. Black & I am busy with large experiments on the Alkali & Black is forthwith to solicit a patent under the title of [having invented] the art of making an Alcaline salt from common salt and lime.²³

James Watt's attempt to develop a commercial alkali process by reacting salt with lime (calcium hydroxide) failed, although the small amounts of alkali he obtained led him to believe his reaction was possible. In an appendix, Musson & Robinson²⁴ have reproduced a previously unpublished contribution by W. V. and K. R. Farrar. These authors suggest that in trying to reproduce an experiment in the study of its history it is impossible to know for certain the degree and effect of impurities current at the time. The same point has been expressed in this thesis, particularly when concerning analytical results. In Watt's attempts to produce alkali by the reversible reaction:



it is possible that the sulphate impurities present in his reacting salt were indeed responsible for some alkali formation.

III. Analytical Aspects

The analysis of Keir's alkali is referred to in the *Journals of the House of Commons*²⁵ and also by Schofield,²⁶ who reports that Boulton received a shipment of Keir's alkali in July of 1781. In September of the same year, Wedgwood also had a supply for a comparison with common fossil alkali.²⁷ No other records of sales to Lunar Society members have been found.²⁸

²¹ Partington, J. R. *A History of Chemistry*, vol. 4 (London, 1964), p. 576, cites Berthollet's publications in 1801-2 regarding the action of mass on chemical equilibrium.

²² Padley, *op. cit.* (3), p. 74.

²³ Watt to Small, 5 July 1769, in Papers JWP, 4/24 1769, BCA.

²⁴ Musson and Robinson, *op. cit.* (9), pp. 369-71.

²⁵ *Journals of the House of Commons*, (1780), vol. 37, p. 914.

²⁶ Schofield, R. E. *The Lunar Society of Birmingham* (Oxford, 1963), p. 340.

²⁷ See Wedgwood, J. 'J. W. Experiments 1781-1793', MS E26-19121, Trustees of Wedgwood Museum, Barlaston, now held in Special Collections and Archives, University of Keele.

²⁸ Musson and Robinson, *op. cit.* (9), p. 367, reports a sale of 'one pound of crystals of Mineral Alkali' to Boulton and Fothergill and refer to a communication, Richard Edwards to Boulton, 13th June 1781. This MS has been examined, present location, Keir Box, MBP. 319/68 BCA.

The analysis by Wedgwood²⁹ is of interest because Keir's material was found to be three-quarters as alkaline 'in power of saturating acids' as the fossil alkali; in the same proportions it could be used to vitrify ground flint. Some technical aspect of the glass produced, using Keir's alkali, seemed to indicate it contained sea salt.

Wedgwood's analytical figures were possible, so argue Moilliet and Smith, only if Keir had allowed a long percolation time for the reaction to reach equilibrium.³⁰ Also, since his filtrate would then be virtually free of calcium salts, the liquor could be concentrated without creating the reverse reaction to form lime and sodium sulphate. Schofield³¹ believes that part of the above manuscript ('J. W. Experiments 1781-1793') is not by Wedgwood and originates from the collected work by Chisholm for William Lewis, before the former joined Wedgwood. How Wedgwood came to know about the method of quantitative assessment of an unknown alkali by saturating with an acid of known strength would be difficult to discover. Some of Lewis's analytical developments appear in the handwritten notes made by Chisholm³² but to what extent Wedgwood used this source of chemical knowledge is difficult to determine; certainly such information was easily accessible to him, and it is possible that this raised his experimentation from a mere run of disconnected facts to that having a truly scientific basis.

Schofield places emphasis on the influence of Thomas Bentley, this friendship arising through an introduction by a Liverpool surgeon, Matthew Turner, and suggests that Wedgwood's empirical approach, shown in the hundreds of experiments he carried out, appears to become more scientific at the time of this new friendship. Wedgwood's first letter to Bentley, in 1762,³³ contains an isolated reference to 'Acids, & Alcalies [sic] - Precipitation - Saturation &c'. In the full context of this otherwise trivial letter, these chemical references cannot be taken to confirm Wedgwood's familiarity with the topics named therein.

The legal wranglings by the several early alkali makers in applying either for patents or removal of salt duties³⁴ are discussed by Musson and Robinson³⁵ and the Clows³⁶ who have drawn upon *Journals of the House of Commons* (1780). Reference to this source is made here:

...a Copy of a Caveat [a warning, or a court process to suspend proceedings], entered the 14th of February 1771, by Mr James Keir, against any Person obtaining a Patent for an Invention by which Alkali may be extracted from Common Salt, from Sea Water, or from the Water of Salt Springs,³⁷

Various witnesses were called before a Committee of the House of Commons including Mr. Moore [sic] Secretary to the Society of Arts. Such questions as to the suitability of Keir's alkali for the glass and soap

²⁹ Wedgwood, *op. cit.* (27).

³⁰ Moilliet and Smith, *op. cit.* (7), p. 28.

³¹ Schofield, R. E. 'Josiah Wedgwood, Industrial Chemist', *Chymia*, 5 (1959), pp. 180-192, on p. 186.

³² Brit. Lib. Dept. of Manuscripts, Additional Mss., 1739-1776, 28309-28318, ten bound volumes bearing the Wedgwood book plate, presumably purchased by Wedgwood at the time of Lewis's death (not seen, location confirmed).

³³ Wedgwood to Bentley, 15th May 1762, MS Collection, 18048-25, former location, Wedgwood Museum, Barlaston, now held in Special Collections & Archives, University of Keele.

³⁴ 36 shillings per hundred weight at that time, but Gittins, L. *op. cit.* (1), states £20 per ton and 'this would have been a crippling burden for an infant industry to bear'.

³⁵ Musson and Robinson, *op. cit.* (9), pp. 360-4.

³⁶ Clow, A. and Clow, N. L. *The Chemical Revolution A Contribution to Social Technology* (London, 1952), pp. 96-7.

³⁷ *Journals of the House of Commons* (1780), vol. 37, p. 914.

industry, and whether the alkali had been made solely from common salt were frequently made to these witnesses. More claimed he had examined the alkali and found it was suitable, but the sample had been in a 'state of solution' and was strongly alkaline. His methods of confirming it as alkali were by taste, and its reactions with sal ammoniac, alum, and Epsom Salts. More does not state any quantitative measurements. Another witness, Matthew Boulton claimed:

he had compared its [Keir's alkali] strength with Barilla, and it was superior to it in Quality, in the Proportion as 20 to 14.³⁸

Exactly how this comparison was made seems problematic for if it was merely a solution of alkali in water, how could Boulton make this quantitative assessment?

Later in the same examination where a Mr. Fordyce enters, Boulton mentions 'a milder form [of alkali] from being exposed to the Air'. He could be referring to the concentrate from the end of Keir's process, i.e. caustic soda, and not mild soda. Boulton then admits to taking equal weights of Keir's solution and comparing these against equal weights of Barilla to find the amount of acid needed to neutralize the two alkali samples; thus, Keir's alkali saturated 20 (units unknown) and the Barilla, 14. Again, this appears to be an invalid quantitative method of comparison.

More was asked to establish that the alkali could be used in glass making while its use in soap manufacture was entrusted to a Mr. John Adams, but it is More who is the disinterested witness and it is here he remarks:

That he was a chemist, and acquainted with the Science of Chemistry; that he was bred a chemist, and has always made the Arts that depend on chemistry his particular study.³⁹

More had carried out tests on an alkaline salt from James Adam using the same acid/alkali balancing procedure as described above, but in addition, tried its use in making flint glass in which it did not perform as well as the same proportion of pearl ashes. Questions arose about the 'shelf-life' of Adam's alkali; of two samples submitted, both were affected by storage in contact with the air and were probably caustic solutions rather than soda. It was asked if the alkalinity arose perhaps from it being a volatile alkali, but Adam ruled this out and confirmed 'it to be a fixed alkali; but when exposed to the Air, Alkali loses its strength'. Clearly there is misunderstanding here, for if the sample was in fact a caustic solution, then exposure would reduce its strength by absorption of carbon dioxide, but if the sample was a 'fixed alkali' as Adam stated then no amount of exposure to air would alter its strength so long as water of crystallization or occluded water were taken into account. It may be that Adam is misusing the term fixed alkali or a mixture of free caustic and soda is involved.

The caveat was granted on 14 February 1771.

Samuel More was again called, this time in connection with a petition made by John Collison. The latter had given a sample of alkali to More requesting his opinions. Again, these were based only on qualitative tests such as taste and reaction with sulphuric acid to make Glauber's salt. He was convinced it

³⁸ *Ibid.*

³⁹ *Ibid.* p. 915.

was good fossil or mineral alkali. In other samples from Collison, who was claiming production of alkali from sea salt, More commented on the presence of sea salt, but, 'That he never met with any without some - And that they are as pure as those Salts generally are'.

Joseph Fry⁴⁰ was another petitioner and he claimed that Collison's alkali was 'half as good again as Barilla; and will answer the Purpose of Barilla in making soap and Glass - That he [Collison] has made many Tons, and converted it into soap'. The same text suggests that Collison produced hydrochloric acid during the process of making alkali from sea salt, which apparently he saved as a saleable by-product.⁴¹ There is no indication here by what method the soda was finally produced from the sulphate stage.⁴² Clearly the production of hydrochloric acid suggested that the process involved reacting sulphuric acid with sea salt. Collison's attempts to find sales for his product are confirmed in a letter to George Goldie.⁴³ Having made some Glauber's salt from a sample of Collison's alkali More stated it was 'a good kind of fossil alkali'. No other qualitative or quantitative test had been used.

John Collison's alkali was analysed by Joseph Black in 1782:

I have examined the ash prepared by Collison & Co. & find it to be very strong and powerfull, It contains more alkali than the best Alicant barilla in the proportion 68 to 44, and more than the best kelp, in the proportion 68 to 10... and there is no need to use lime in drawing the leys from it as it is already in a Caustic State.⁴⁴

Earlier authors, in reporting these analytical results in this condensed form, appear to have drawn on Ramsay's account;⁴⁵ a transcription of the draft reply made by Black to George Goldie of the Edinburgh Linen Hall is given as Appendix X. Another letter shows that Goldie acted as an intermediary between Collison and Black.⁴⁶ It seems likely that Collison's product contained a real sodium carbonate content of not more than 50%. Black's selective (and therefore unrepresentative) method of sampling should be noted:

I made my Essays, on the black or grey Ash the bits of white ash appeared much weaker, but too little of it for an Essay.⁴⁷

In support of a Petition from Watt, Matthew Boulton was questioned about Watt's and Black's discovery of extracting mineral alkali from sea salt. Boulton claimed that 'Mr. Keir's process was also invented by Mr. Watt in conjunction with Dr. Black; but that Mr. Watt has also invented another process, which he apprehends is equally as good, if not better'.⁴⁸ Another contributor to Watt's petition was Joseph Black's brother, James Black, who claimed that Dr Black and James Watt had shared in the invention.

IV. Reflections on Keir's Contribution

⁴⁰ Fry and Collison held jointly an alkali works in Battersea; alkali products were used in Fry's soapworks in Bristol.

⁴¹ *Journals of the House of Commons*, (1780), vol. 37, p. 930.

⁴² See comments by Ramsay, W. *The Life and Letters of Joseph Black* (London, 1918), pp. 67-8, on Collison's patent.

⁴³ John Collison to George Goldie, 7 February 1782, Edin. Univ. Lib., Gen. 875/II/42,43. Part of this letter is reproduced in Appendix X.

⁴⁴ Black to George Goldie (soon after 19 March 1792), Gen 873/II/47, EUL. Transcription reproduced in Appendix X

⁴⁵ Musson & Robinson, *op. cit.* (9), p. 365, cite Clow, *op. cit.* (36), p. 98, for this extract. Clow cites Ramsay, *op. cit.* (42), p. 67, who gives no archive location.

⁴⁶ John Collison to George Goldie, 7 February 1782, Gen 875/II/42,43 EUL. Reproduced in Appendix IX.

⁴⁷ Black to Goldie, *op. cit.* (44).

⁴⁸ *Journals of the House of Commons*, (1780), vol. 37, p. 930

Keir's process for making alkali, foreshadowed a great law of chemistry which came into being much later and became known as the law of mass action. This was to have great relevance to the future chemical manufacturing processes.

How Keir came to devise such a method and what guided him in this particular direction is unanswered. There are no extant notebooks or other archives to show what practical research tests were made before arriving at a workable process; one in which the concentration of reactants and velocity of reaction appear critical. We do not know to what extent, if any, chemical analysis was used by Keir; it is known that chemical testing of his alkali was carried out by others, pointing the way for future raw material quality control.

The various Parliamentary episodes considered above, led to some relaxation of salt duties but these were followed by new taxes upon finished products. The removal of the salt tax was followed by legislation allowing government inspectors to enter chemical works and this perhaps foreshadowed the Alkali Acts of 1863.

The *House of Commons Journals* show that there was little dependence upon analytical chemistry; the role of Samuel More's consultancy however is highlighted and presumably that of the Society of Arts which he represented. From a modern viewpoint, his lack of quantitative analysis is disappointing in view of the contemporary work of Lewis. More's dependence upon forming sodium sulphate crystals as a test of alkali quality is very surprising. There is nothing to indicate that Keir or Watt received an award from the Society of Arts. The full understanding of the chemistry of alkali, either as caustic soda or soda, or a mixture of both seems confused, and the lack of emphasis on analysis is surprising when this would have provided answers to the many repetitive questions posed in these official enquiries.

We do not know what motivated Keir to offer his analytical services to the Society of Arts in 1786. The need for synthetic alkali and chemical analysis appears in Collison's comments:

Finding by our partner Joseph Fry that the Bleachers and Callicoe printers in North Britain complain that the adulteration of Pot & Pearl Ashes is now become so universal as to render a genuine article exceedingly scarce & almost impossible to be procured we have now entered into the Manufacture of such Alkaline Salts...⁴⁹

The urgency for reliable analysis, as a means of combating deliberate adulteration thereby defining market value, was thus becoming apparent in the 1780s.

V. Charles Tennant's contribution to the determination of Alkali

In 1817 Charles Tennant published his method of determining the strength of 'Soda, either free or combined with Sulphur or Carbonic Acid'.⁵⁰ The letter was addressed to Thomas Thomson who was perhaps the most prominent chemist in Scotland at that time. The analytical details within this letter are now considered.

⁴⁹ Collison to Goldie, *op. cit.* (46).

⁵⁰ Tennant, Charles. 'A Table showing the Quantity of Soda (either free or combined with Sulphur or Carbonic Acid) contained in the Specimen under Trial with Sulphuric Acid containing 10 per Cent. real Acid', *Annals of Philosophy*, **10** (1817), pp. 114-15.

Tennant emphasises the use of sulphuric acid at a concentration of 10 per cent which allows a precise end point to be observed. As in other descriptions of methods examined in this study, this author gives no information about the initial strength of the acid or indeed the meaning of his term real acid. Presumably the acid used was of the St. Rollox works production and was merely concentrated chamber acid. This would routinely give 93-95% acid, but this cannot be proved and in fact makes little difference to the principles used in the method.

Between the analytical work of Keir and Tennant there lies a considerable time span and if we assume that Tennant's method was one in general industrial use, it suggests there had been little progress in alkali testing within the period of 1786 to 1817. Tennant clearly used some kind of burette. 'I use the acid measured by a glass tube graduated into five grain divisions'. The more sophisticated alkalimeter of Descroizilles had been reported in 1806 but Ure's self-claimed better model was not described until William Henry's ill-judged publication in 1818 (8th edit.) (see chapter 3, sec. VIII). Chemical industrialists such as Tennant devised their own routine methods of analysis and whilst employing volumetric principles, tended to modify their methods to suit particular needs such as speed, ease and simplicity of operation.

The details given in Tennant's letter summarise many of the important aspects of volumetric analysis although, as stated above, these showed little advance on the chemical reasoning behind acid/alkali balancing. He makes only one weighing in the method and the acid solution is made up by volume measurement only. Using the factor 0.8 (being the mean of Dalton's and Wollaston's figures) as the unit amount of soda equivalent to 1.0 of sulphuric acid, it becomes a simple matter to read off from his prepared table the amount of soda present. The single weighing is that of the 100 grain sample. On the basis of this amount, Tennant's paper includes a table from which the number of grains of acid used are read off as percentage content of soda. He mentions other tables for potash and ammonia determinations. Interestingly he claims not to have found alkali contents greater than 24.48% even in the best barilla although Robison had reported 24.8 and even 26.5 in the best Alicante barilla.⁵¹

The report is a useful landmark in establishing the progress, however small, of useful analysis particularly in industrial situations. His reference to other stock solutions is a reminder that to overcome the necessity for a whole range of these solutions, against which individual substances could be measured, there developed through the later work of Ure and Griffin the concept of normality (see chap. 7). This, as will be shown, was based on concentrations related to atomic weight following Dalton's important theory.

To simplify matters further, Tennant could have reverted to the simpler operation of strict acid/alkali balancing (see chap. I p. 29) without using weights although a mechanical balancing device remained a requirement. Oddly, no precise details of this procedure have been found in searching original literature in this study, perhaps because the method was so simple it was thought unworthy for publication by

⁵¹ Robison, J. (editor) *Lectures on the Elements of Chemistry, delivered in the University of Edinburgh; by the late Joseph Black, MD.*, vol. 1, (Edinburgh, 1803), pp. 375-377. The same table shows Alkali made in Liverpool contained 49%.

learned chemists. Nevertheless one can imagine its usefulness on the simple laboratory bench of an industrial chemical processing factory.

VI. Sulphuric Acid and the Leblanc Process

Of the few chemicals being commercially produced in the early eighteenth century, sulphuric acid was the most important. The names of Joshua Ward (1685-1761) and John White, whose joint patent of 1749 so directly associates them with early acid making, are seen as prefacing the transition of laboratory scale to industrial scale production which resulted in lower selling prices.⁵² Its new application in the bleaching industry beginning with Home has been considered in earlier chapters.

In order to make sulphuric acid before the more productive lead chamber method came into being, a charge of nitre and sulphur contained in an iron dish and standing on an earthenware pot was placed inside a large (fifty gallon) glass globe, positioned so that its neck lay horizontal. The mixture was ignited and the fumes of acid dissolved in a small amount of water contained in the glass globe. The reactants could be replenished and the process continued until the acid was thought to be of such strength as to justify concentration by distillation.⁵³ In 1747 Roebuck and Garbett used a lead chamber for the reaction and thus created a truly industrial process. However, any extant archives about their work and other early vitriol makers listed by Mactear have not been examined in this thesis for reasons of space and time.⁵⁴ Throughout Mactear's paper on the history of sulphuric acid the use of hydrometry as a means of determining the acid strength is claimed. A Mr. Foy (probably Hugh Foy who at one time was associated with Charles Tennant)⁵⁵ is mentioned by Mactear in connection with a particular set of hydrometers at a time when the strength of commercial acid received much attention.⁵⁶ It is very clear from Mactear's paper that analytical control was confined to specific gravity measurements; not only were these values used as a means of determining the appropriate selling price of the acid but also as a means of arriving at the optimum conditions and amounts of reactants, temperatures, and flow conditions to give the best acid yield. The understanding of the part played by potassium nitrate was confused but empirical observation showed the optimum chamber conditions and reaction mixture to produce the greatest yield of sulphuric acid. The concentration of weak acid by evaporation was not an easy process: it was much simpler to adjust other variables in the process and so obtain the desired density. When in the 1840s the burning of pyrites replaced that of sulphur, the dependence upon density measurement continued; an on-site method of analysis such as this could be applied easily and quickly with the same convenience as simple titrimetry. Mactear records that in 1813 or 1814, with the introduction of steam into the lead chamber, as a means of improving the rate of acid condensation, the acid strength which had previously been about 50° to 60° Twaddell rose to 100° to 120° Twaddell. From these same observations the optimum use of raw materials in acid making was made apparent. Smith points out that after Lavoisier's explanation of the nature of sulphuric acid (as an oxidation product of sulphur) its quantitative composition received

⁵² Clow and Clow, *op. cit.* (2), pp. 44-5.

⁵³ Campbell, W. A. 'Portrait of a Quack: Joshua Ward (1685-1761)', *Newcastle Medical Gazette*, (June 1964), pp. 118-122.

⁵⁴ Mactear, J. 'History of the Technology of Sulphuric Acid', *Proceedings of Glasgow Philosophical Society*, 13 (1881), pp. 409-427: a year earlier, Mactear published a paper entitled 'Action of Concentrated Sulphuric Acid on Lead' reprinted in *Chemical News*, (1880 May 21), pp. 236-7.

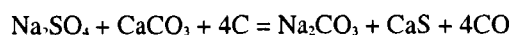
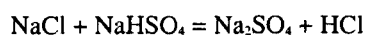
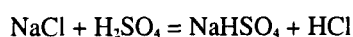
⁵⁵ Higgins, S. H. *A History of Bleaching* (London, 1924), p. 88.

⁵⁶ Mactear, *op. cit.* (54), p. 419.

considerable attention ultimately enabling manufacturers 'to measure the chemical efficiency of their operations in precise and absolute terms, and assess the room remaining for improvement.'⁵⁷

Sulphuric acid was essential for the growth of the chemical industry particularly in the Leblanc process for the manufacture of alkali. Leblanc's process was perfected in 1791 and in this, salt and sulphuric acid were reacted together using heat.⁵⁸ This produced hydrochloric acid fumes and sodium sulphate (salt cake). The latter was then mixed with calcium carbonate (limestone) and charcoal and heated to produce a mixture of sodium carbonate and calcium sulphide (black ash). The soda in this mixture, being water soluble, could be leached out (lixivated), concentrated and crystallized. The unpleasant residues became known as alkali waste and these together with the liberated hydrochloric acid became the first major pollutants of the chemical industry. Such was the severity of this pollution that government intervention became necessary which led to the Alkali Acts.⁵⁹

Leblanc's main contribution in this chemical process is properly confined to his use of limestone to complete an otherwise already known reaction; using modern nomenclature the reactions involved are:



To modern eyes the process involves considerable chemistry and the above equations merely represent the main chemical reactions. The chemistry was imperfectly understood both before Leblanc and for several generations after; this perhaps accounts for the absence of archival evidence showing analyses of the reaction products at different stages. According to Gillispie no records remain of Leblanc's researches (begun in 1784) and it is impossible to know whether he employed any kind of chemical analysis.⁶⁰ The state of knowledge about the process in the late 1870s is discussed by Kingzett and others,⁶¹ and they show that contentious issues arose, in early alkali making, from the interpretations of analytical results. Kynaston's paper of 1859 clearly illustrated disagreements between eminent chemists in their interpretation of analyses of black ash, in particular the composition of insoluble calcium sulphide.⁶² His opening remark points to the incomplete understanding of other aspects of the Leblanc process:

The process of Leblanc, although so extensively and so successfully pursued is, nevertheless, as to several of the products of decomposition, not even now, *after the lapse of nearly sixty years*, thoroughly understood.⁶³

⁵⁷ Smith, J. G. *The Origins and Early Development of The Heavy Chemical Industry in France* (Oxford, 1979), p. 73.

⁵⁸ Gillispie, C. C. 'The Discovery of the Leblanc Process', *Isis*, 48 (1957), pp. 152-170. See also Padley, *op. cit.* (3), pp. 64-78, and Gittins, L. *op. cit.* (3), pp. 175-190.

⁵⁹ Macleod, R. M. 'The Alkali Acts Administration 1863-84: The Emergence of the Civil Scientist', *Victorian Studie*, (1965, December), pp. 85-112. See also 'Injury from Noxious Vapours', *Minutes of Evidence, Select Committee of the House of Lords*, July 1862. This led to the actual Act, 'An Act for the more effectual condensation of Muriatic Acid Gas in Alkali Works', 26 & 27 Vict. c. 124., and became law on 1 January 1864.

⁶⁰ Gillispie, *op. cit.* (58), p. 167.

⁶¹ Kingzett, C. T. *The History, Products, and Processes of the Alkali Trade* (London, 1877) p.102-3; Lunge, G. *Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali* 3 vol. (London, 1880).

⁶² Kynaston, J. W. 'On the Composition and Analysis of Black Ash or Ball Soda', *Journal of the Chemical Society*, 2 (1859), pp. 155-165. Kynaston was a consulting chemist in Liverpool who had connections with the Muspratt alkali works.

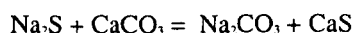
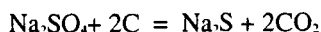
⁶³ *Ibid.* p. 155.

Analysis had shown wide differences in alkali content of barilla depending on its source (see Appendices VII and VIII), similarly there were variations in the alkali produced by the Leblanc process which could have been explained by better applied chemistry and analysis. Kingzett states:

Analyses of black ash necessarily differ widely, as it is not a pure chemical individual; moreover, the analyses of the different samples of the same ball often differ considerably.⁶⁴

In support Kingzett quotes some analyses by G E Davis which show a range from 28% to 32% but points out that these figures merely serve as comparisons, 'while, in many instances, the actual results obtained are not to be trusted'.⁶⁵ Kynaston's own comprehensive analysis (1859) reported a sodium carbonate content of 36.9%. Reactions at the high temperatures used in forming the salt cake and black ash followed by leaching with water clearly challenged chemical knowledge of the time. The value of analytical results from the Leblanc process depended upon the understanding of the conditions and chemical changes taking place; these were not always apparent and consequently results could sometimes be misleading.⁶⁶

The formation of sodium sulphide is not shown in the above chemical equations but is assumed to occur as an intermediate product of the reduction of the sulphate by heating with coke or charcoal to give sodium sulphide and carbon dioxide. This sodium sulphide on heating with chalk (calcium carbonate) forms calcium sulphide, which is insoluble. Mixed with this was the newly formed soda which was removed from this solid mixture by leaching with water followed by various processes of concentration and crystallization. That the reaction occurred in two stages is shown in these equations:



Because there are no extant records showing the use of analysis, either to improve or understand better the reactions involved in the early developments of the process, it is tempting to assume that progress was empirically based. In Gillispie's account of the discovery of the Leblanc process he comments on Leblanc's third rate standing as a chemist, and points out that the role of the limestone (which was the essential substance in the process), was apparently not investigated.⁶⁷ Also, the full understanding of the chemical reactions were not 'properly described until near the end of the nineteenth-century, sometime after the Leblanc process had already begun to go out of use'.⁶⁸ Gillispie's view that the practice of a process and its full understanding rarely occur concurrently seems very apposite to the early years of the Leblanc process.⁶⁹ Smith disputes Gillispie's views to some extent and points to the conjectural content of the latter's alternative account to that given by Leblanc's industrial partner Dizé in

⁶⁴ Kingzett, *op. cit.* (61), p. 102.

⁶⁵ *Ibid.* p. 103.

⁶⁶ For a survey of the various theoretical and practical issues which arose from the early years of the Leblanc process see Lunge, G. *A Theoretical and Practical Treatise on the Manufacture of Sulphuric Acid and Alkali, with the Collateral Branches*, vol. 3, (London, 1880), pp. 427-482.

⁶⁷ Gillispie, *op. cit.* (58), p. 170.

⁶⁸ *Ibid.*

⁶⁹ *Ibid.*

1810.⁷⁰ The strong evidence in the documents of partnership between Dizé and Leblanc, in which Leblanc's true ownership of the process is stated, are cited by Smith.⁷¹ The development of the process appears to have truly belonged to Leblanc and further, it was not the result of naive empiricism as described by some authors. Chemical analysis of the different stages in the Leblanc process must have proved almost impossible considering the reaction conditions in such a fusion process; this perhaps accounts for the absence of such records. However, this does not necessarily imply that the process was not understood by late eighteenth- and early nineteenth century chemists. Their explanations, of course, 'were merely interpretations based on casual observation rather than elaborated theories built on detailed study [or analysis]'.⁷²

The initial reaction between salt and sulphuric acid produces hydrochloric acid gas which in the early years of the process went to waste. At the final stage of the process another waste product remained, this became known as alkali waste and consisted mainly of insoluble calcium sulphide. The unpleasant aspects of these waste products demanded both chemical analysis and research and created important new roles for industrial chemists.

The safe disposal of waste products is not a twentieth-century phenomenon, for in 1863 the first Alkali Act was passed.⁷³ This limited the disposal by alkali works (here we have the first public definition of alkali works) of hydrogen chloride gas. Of course, as in all legislation, its value depended upon the means of execution and in this instance, that of chemical analysis.

VII. Chemical Analysis and the Alkali Acts

It can be argued that the influence of analytical chemistry during the Industrial Revolution found no greater place of application than in providing the means for the enforcement of the Alkali Acts. Furthermore, because of the chemical aspects of this legislation, the creation of civil scientists occurred.⁷⁴ A private bill in March 1863 proposed that all alkali works be subjected to a fixed standard of ninety-five per cent condensation of hydrochloric acid vapours emitted into the atmosphere. It further suggested penalties of £50 and £100 for first and subsequent offences and that the Board of Trade should be directed to appoint an inspector with powers to prosecute. The Act came into being on 1 January 1864 and was to remain for a period of five-years; in 1868 the Act was renewed and made perpetual.

Robert Angus Smith,⁷⁵ was appointed Inspector assisted by four sub-Inspectors one of whom was Alfred E. Fletcher. Some of the early apparatus used in sampling and determining the acid content of chimney gases was devised by Fletcher.

Before the date of enforcement most alkali makers had by some means or another reduced acid emissions. Gossage condensing towers⁷⁶ came into being by which the acid vapours were turned into

⁷⁰ Smith, *op. cit.* (57), pp. 210-215, 280-285, on p. 213.

⁷¹ *Ibid.*

⁷² *Ibid.* p. 283.

⁷³ MacLeod, *op. cit.* (59), pp. 89-90.

⁷⁴ *Ibid.* pp. 85-112; for another examination of 'civil scientist' see Kargon, R. H. *Science in Victorian Manchester* (Manchester, 1977), who discusses R. A. Smith.

⁷⁵ *DNB* (1909), pp. 520-22.

⁷⁶ Anon., 'Industrial Celebrities: 1, William Gossage', *Chemical Trade Journal*, 2 (1889) p. 111. Condensation in the strict sense of distillation was not the main objective but absorption into water. According to Fletcher, A. E. 'Modern Legislation in

hydrochloric acid which soon found outlets in bleaching powder manufacture but nevertheless the need for accurate analysis of chimney gases remained.

Legislation which prescribes precise parameters demands the means of accurate measurement; the necessity of measuring the acid content of a moving volume of gas in a chimney must have presented difficulties. The creation of these very tall chimneys had arisen in order to remove offensive vapours to the furthest possible height away from the work's site,⁷⁷ and were not designed for easy sampling by a not too welcome government representative.⁷⁸ Experiments with various kinds of aspirators were made and in 1865, Smith reported⁷⁹ widespread introduction of the 1863 Alkali Act based upon analytical controls. These resulted in the reduction of average escape of HCl to 1.28%, well within the five percent maximum. All the registered works (64) reported figures of less than 5% while 33 of these were achieving 100% condensation or not more than 0.1% emission.⁸⁰ Of course Smith realised early the limitations of the Act and that even a 1% allowance became meaningless as the number of alkali works grew; consequently over the next few years he pressed for full prohibition on HCl emission and the inclusion of copper works within the Act. The term 'noxious gas' would include sulphuric and sulphurous acid, nitric acid and oxides of nitrogen, hydrogen sulphide and chlorine.⁸¹

In the early period of the 1863 Act samples of flue gases were obtained by using aspirators which depended upon the controlled run-off of a known volume of water, the space then being filled by the vapours drawn from the sampling point. Initially this was a cumbersome and probably inaccurate method because of the solubility of the HCl in aspirator water. The technique nevertheless illustrates a continuity from the early 'pneumatic chemists' but appears to have soon been modified by Fletcher who devised a collapsible aspirator or bellows.

The Alkali Acts encouraged the employment of chemists as stricter controls and methods of chemical measurement were demanded and many firms appointed their own chemists to make daily analytical checks. From here onwards a whole new area of analytical chemistry grew; two names became famous in this field, Ferdinand Hurter of Widnes and Georg Lunge⁸² who came to Tyneside in the 1860s presumably intending to find employment in the growing alkali industry. It is in one of Lunge's many publications, *The Technical Chemists' Handbook* of 1910 that the details of Fletcher's aspirator are

Restraint of the Emission of Noxious Gases from Manufacturing Operations', *Journal of the Society of Chemical Industry*, (20 Feb. 1892), pp. 120-124, the efficiency of Gossage towers influenced the adoption of a 95% absorption standard by the 1863 Act.

⁷⁷ See Campbell, W. A. *The Chemical Industry* (London, 1971), pp. 40-41.

⁷⁸ MacLeod, *op. cit.* (59), p. 93, argues that alkali works came to depend upon the advice of such men as Smith and Fletcher who were frequently acting in a useful consultative capacity at the expense of the State. See also Gittins, L. 'An Inspector Calls', *Chemistry in Britain* 29 (1993), no. 8, pp. 684-6.

⁷⁹ Smith, R. Angus, *Alkali Act. 1863. First Annual Report by the Inspector of his Proceedings during the year 1864* (London, for HMSO, 1865). Also contains details of analytical methods and results, see pp. 32-62.

⁸⁰ Anon., *Chemical News*, 11 (1865), p. 252.

⁸¹ An Amendment Act of 1874 [37 & 38 Vict. c. 43.] set a volumetric standard of hydrochloric acid gas escape of 0.2 grains per cubic foot; this did nothing to alleviate the nuisance from alkali waste heaps emitting hydrogen sulphide because of the loose ruling to alkali makers to use the 'best practicable means' to prevent the escape of all other noxious gases; quoted by MacLeod, *op. cit.* (59), p. 97.

⁸² 'The Life and Work of Ferdinand Hurter PhD', edited by members of the Liverpool Section of Society of Chemical Industry, *Journal of the Society of Chemical Industry*, 17 (1898), pp. 406-411; also Hardie, D. W. *A History of the Chemical Industry in Widnes* (London, 1950), pp. 164-179; G. Lunge, editorial obituary notice, *Journal of the Chemical Society*, 123 (1923), pp. 948-50, and *DSB*, vol. 8 (1975), p. 553; and 'Two Immigrants', editorial, *Chemistry and Industry*, (22 April 1967), p. 627.

given;⁸³ a book which shows very strongly the application of volumetric analysis in industrial or technical analysis.

VIII. Determination of Hydrochloric Acid in Chimney Gases

In recalling the short history of the Alkali Act, Fletcher comments about the apparatus used for withdrawing the gas sample:⁸⁴

It took the form of a collapsible cylinder constructed of ebonite and vulcanised rubber, in size capable of holding one-tenth of a cubic foot. The solvent for the acid or other body contained in the air aspirated was introduced into the collapsible aspirator, where on agitation it was brought well into contact with the contained gas. Thus armed with anemometer and collapsing aspirator and a few bottles of standard solutions, it was in the power of an inspector rapidly to determine from his own observations what proportion of the hydrochloric acid produced in an alkali works was allowed to pass through the smoke flues and chimney into the air.

Lunge gives directions for calibrating the Fletcher aspirator and thus determining the number of aspirations from the flue gases which must be made in order to obtain one cubic foot.⁸⁵ The gas is withdrawn from the chimney through a glass tube of a half inch diameter, reaching well into the inside. 100 or 200 cc. of distilled water are put into the bellows and after each aspiration the gas is washed (dissolved) by shaking vigorously. After the appropriate number of aspirations, the tube is washed and all the liquid is transferred to a beaker standing on a white tile ready for titration. Any soot or other discolouration is removed by filtration. All of the apparatus is made chloride free before the test which involved, titrating with decinormal silver nitrate solution using potassium chromate. The test solution may first be oxidised with potassium permanganate, any excess being removed with a trace of ferrous sulphate then neutralized with pure sodium carbonate. In true 'volumetric' practice Lunge gives the necessary calculation to find the number of grains of HCl per cubic foot of gas. From this the percentage of escape into the atmosphere could be calculated given that the following data was available:

1. The velocity of the rising gases at 60° F. in feet per second.
2. Diameter of the chimney in feet at the sampling point.
3. The number of tons of salt decomposed assuming 93% NaCl, per twenty four hours.

Clearly the co-operation of the alkali works' personnel was necessary to obtain this data and was probably achieved by the high standards of negotiation set by Angus Smith and his sub-Inspectors; the success of the Act did not arise from numerous prosecutions. Whatever misgivings Smith held about the 1863 legislation he always attempted to develop and push forward a more encompassing legal requirement although Lunge's text as used above, based on a 1906 Alkali Act, still speaks of a 95% condensation and 0.2 grains muriatic acid per cubic foot, requirement.

IX. Conclusions

This chapter has shown that the attempts to find successful methods of making synthetic alkali were not dependent upon analytical chemistry and perhaps this accounts for the lack of primary source material on

⁸³ Lunge, G. *The Technical Chemists' Handbook* (London, 1910), pp. 147-8.

⁸⁴ Fletcher, *op. cit.* (76), pp. 120-24.

⁸⁵ Lunge, *op. cit.* (83), p. 147.

this subject. Keir's pioneering attempts to produce synthetic alkali were based more upon intuition and practical empirical observation than on fundamental chemistry or analytical results. From a modern viewpoint, better chemical knowledge, aided by analysis, could have brought improved commercial success to his process.

It has been shown how the introduction of the Alkali Acts in 1863-4 demanded accurate analytical procedures. By this time analysis had become more refined, but it was the legislative power of the Acts which gave industrial analysis a major forward push and created the demand for professional analytical chemists. It was of course the Leblanc process which created the need for legislative powers to control its polluting waste products and led to the appointment of industrial analytical chemists or civil scientists. The role of analysis changed dramatically however, with the establishment of the Alkali Acts. The chapter has shown that the Leblanc process did not develop entirely from an empirical base. Furthermore, its full chemical understanding was possibly retarded because of the practical difficulties of analysing and interpreting a fusion process involving secondary chemical reactions.

Analysis involves chemical measurement and the enactment of the Alkali Acts could not be dependent for legitimate quantification upon the results of simple laboratory tests such as acid alkali balancing however well this principle had served in the past - something more fundamental was needed and this is explored in the following chapter.

CHAPTER SEVEN

STANDARDISATION THROUGH NORMAL SOLUTIONS

I. Introduction

As a practising consultant chemist John Dalton carried out analyses of mineral waters in 1814 and in describing his analytical methods he used the term 'test solution' to indicate a solution of known concentration. This idea was not entirely original to him; other instances of its use have been noted in earlier chapters where a solution of pre-determined concentration has been used in a titration in order to determine the amount of another constituent.

This chapter will show that in the years following Dalton's atomic theory, solutions of known concentration became the means of quantifying chemical reactions, particularly in volumetric analysis. This practice placed analysis on a new and more definite basis, and gave greater convenience to the analyst. These developments will be seen through the work of Andrew Ure, Thomas Thomson and W. H. Wollaston, ending with the concept of 'normality in solutions' in the work of J. J. Griffin and Friedrich Mohr.

This thesis began by examining the analytical achievements of Francis Home and Joseph Black, followed by detailed assessments of other eminent chemists engaged in analytical attempts. No general laws of chemistry or analysis evolved from their activities although a cumulative tacit knowledge resulted which provided a basis for chemical analysis. Industrial analytical chemists found it unnecessary to give theoretical explanations of their methods which perhaps suggested that their success rested upon tacitly held chemical rules. Their methods often consisted of balancing and measuring the performance of an unknown substance against one thought to be of acceptable quality; in this, no strict quantitative units were needed. Furthermore, they were often not seeking a full compositional analysis of the unknown substance or raw material. Both of these aspects of course are of the highest priority in modern day analytical operations.

Exactly how early analysts perceived the chemical reaction taking place in an analytical determination is now almost impossible to envisage. The explanation of the acid/alkali reaction given by Bryan Higgins (1736-7 to 1820) though dependent upon an atomic theory predating that of Dalton, postulated that these substances could only combine in certain proportions in which each atom of the same kind repels its own but attracts the other kind.¹ Any excess of one or other substance was unable to combine in the absence of a compensating attractive force. The idea that some kind of interaction occurred is indicated by the early affinity tables,² unfortunately there is little evidence to show that these tables made any practical contribution to analytical developments and by the beginning of the nineteenth century their value had all but disappeared. Thomas Graham's comment on affinity tables is worth noting:

Tables of this kind when accurately constructed may convey much valuable information of a practical kind, but it is never to be forgotten that they are strictly tables of the order of

¹ Higgins, B. *A Philosophical Essay Concerning Light* (1776), pp. 201-5, quoted by Partington, J. R. *A History of Chemistry*, vol. 3, (London, 1962), pp. 732-3. See also Gibbs, F. W. 'Bryan Higgins and his Circle', *Chemistry in Britain*, 1 (1965), pp. 60-65.

² See Klein, U. 'Experimental Practice and Layers of Knowledge in Modern Chemistry I.' in *Preprint 25*, (Max Planck Institute for the History of Science, 1995), pp. 73-101.

decomposition and of the comparative force or order of affinity in one set of circumstances only.³

We now predict and calculate chemical reactions through written equations from which reliable analytical methods can be devised. This chapter examines the changes in techniques and understanding which are commonly thought to have depended upon the atomic theories of John Dalton. From these it became possible to make chemical calculations based on atomic weights instead of equivalents or other empirically obtained combining proportions such as those found by acid/alkali balancing. It will be seen that the initial step in bringing this mathematical approach into being was through the work of Richter.

Many of the analyses assessed in this thesis, whether acid-alkali balancing or some variation using coloured indicators to show the reaction's completion, were comparisons made against another substance thought to be of acceptable purity, or, an empirically obtained equivalent weight. This left little need for any other ideas based on an atomic theory. Industrial analysts were not waiting in eager anticipation for an atomic theory although it allowed their otherwise tacitly held views about the constancy of composition of compounds to be publicly expressed. The indestructibility of matter and the widely held view by early analysts that compounds were formed by the combination of constant amounts of their constituents had, at last, through Dalton, a valid means of quantified expression.

Of course Dalton's atoms could not be seen or weighed, but through laboratory based experiments it was possible to measure the relative weight of known elements taking hydrogen, the lightest known, as unity. The theory of atoms could thus be expressed in measurable tangible reality.

J. B. Richter (1762-1807) had for a long time pursued the idea that mathematical relationships existed in chemistry which,⁴ by further development of the evidence available from existing simple analytical concepts, provided a basis for the terms equivalent and combining ratio in chemical reactions. In so doing he coined the word stoichiometry, but it was Ernst Fischer (1754-1831) who in 1802 took the subject further and produced a table of equivalent weights of acids and bases related to sulphuric acid to which he gave a value of 1000.⁵

Bases		Acids	
Alumina	525	Fluoric	427
Magnesia	615	Carbonic	577
Ammonia	672	Muriatic	712
Soda	859	Sulphuric	1000
Potash	1605		

From this it can be seen that 859 parts of soda or 1605 parts of potash react with 1000 parts of sulphuric acid, or 672 equivalents of ammonia neutralize 712 of muriatic acid. But this remained an empirically devised table which undoubtedly provided a useful aid to chemical analysis.

It was seen later that Dalton's atomic theory provided a rational explanation for these observations and the relationships within chemical reactions. Analytical chemistry of the time was not hindered by the absence of this knowledge; indeed the understanding, if only implicit, appears to have existed before the

³ Graham, T. *Elements of Chemistry* (London, 1842) p. 187; also cited by Duncan, A. *Laws and Order in Eighteenth-Century Chemistry* (Oxford, 1996), p. 170.

⁴ Partington, J. R. 'Jeremias Benjamin Richter and the Law of Reciprocal Proportions', *Annals of Science*, 7 (1951), pp. 173-198.

⁵ Partington, J. R. *A History of Chemistry*, vol. 3, (London, 1962), pp. 678-9.

researches of Richter and Fischer. Industrial chemists, satisfied with analysis based on empirically obtained proportional ratios, were not seeking theoretical explanations of their methods, a point perhaps which might explain the slow entry of Dalton's theory into industrial analysis. Greenaway's comments on Dalton's theory as 'a theory of structure, not a theory of proportional composition... Dalton's atomism had to subserve stoichiometric theory', do not suggest radical changes in analysis were about to occur.⁶

II. Dalton: The Atomic Theory

The chapter is an attempt to identify any changes in early chemical analysis which developed from Dalton's atomic theories.⁷ Analysts could have made use of the work by Richter and Fischer and continued using their established methods without the rationale given by Dalton. The usefulness which modern analysts find in atomic and molecular weights was not immediately evident to Dalton.

His theory emerged only slowly, often from the discussion and promotion of others. This is illustrated by the part played by Thomson and Ure for example, in having the wit to apply Dalton's theory in ways which he himself perhaps did not visualise at the time.⁸ For example we know that given a molecular formula and reliable analytical data, the atomic weights of the compound's constituents can be calculated. Or, if the atomic weights are known, it is possible to work out the molecular formula. Industrial analytical chemists at the time of Dalton's atomic theory had little of this perception and were therefore unlikely to pursue these new approaches on which future analysis might be based.

There are three main assumptions in Dalton's atomic theories:

1. All matter consisted of solid and indivisible atoms.
2. In a chemical reaction, these atoms retain their individual identities and are indestructible.
3. The assumption was made that there were as many different kinds of atoms as there were elements.⁹

In a totally unexpected direction, Dalton then proposed, as Brock puts it:

to rid metaphysical atomism of its intangibleness by fixing a determinable property to it, that of relative atomic weight.¹⁰

His immediate problem was to make the right assumptions regarding how atoms combine to form new compounds, for it was on this that the determination of relative atomic weights by analysis would depend. In what he called the *principle of simplicity* Dalton suggested that where two elements A and B form only one 'compound atom' then this contains one atom of A and one atom of B. If a second compound exists, its 'compound atom' will consist of two atoms of A and one of B. A third compound will consist of one atom of A and two of B, and so on. He knew that hydrogen and oxygen combined to form water and from analysis it was known that 87.4 parts by weight of oxygen combine with 12.6 parts of hydrogen. This ratio of 12.6 to 87.4 must also be the ratio of the individual weights of hydrogen and oxygen atoms making up the binary atom of water. Adopting hydrogen as the lightest known element, this was given

⁶ Greenaway, F. *John Dalton and the Atom* (London, 1966), p. 150.

⁷ *Ibid.* pp. 201-2. See also Guerlac, H. 'Daltonian Doubts', *Isis*, **52** (1961), pp. 544-54.

⁸ Mauskopf, S. H. 'Thomson before Dalton: Thomas Thomson's considerations of the issue of combining weight proportions prior to his acceptance of Dalton's chemical atomic theory', *Annals of Science*, **25** (1970), pp. 229-242.

⁹ This follows the summary given by Brock, W. H. *Fontana History of Chemistry* (London, 1992), p. 136.

¹⁰ *Ibid.*

(244)
 Observations
 on the ultimate particles of Bodies,
 & their combinations.

1803

Characters of Elements. —

- Hydrogen
- ⊙ Oxygen
- ① Azote —
- Carbon — *page charcoal.*
- ⊕ Sulphur

(245)

At. wt. Hydrogen	1.00
Oxygen	8.00
Azote	5.00
Carbon (Charcoal)	5.00
Carbon	5.00
Ammonium	17.00
Nitrous Gas	44.00
Nitrous Oxide	46.00
Nitric Acid	62.00
Sulphur	16.00
Sulphurous acid	64.00
Sulphuric acid	80.00
Carbonic Acid	44.00
Oxide of Carbon	28.00

Fig. 10. Dalton's first tables of Symbols and Atomic Weights (from Roscoe & Harden, 1896, page 27).

the value of one, whence the relative atomic weight of oxygen must be 7 (Dalton always rounded numbers up or down to the next whole). He thus proposed that water consisted of one atom of hydrogen united to one of oxygen. This was a wrong hypothesis for it implied that the atomic weight of oxygen must be the weight of it found experimentally to combine with unit weight of hydrogen. This serious difficulty led to controversy and the continued use of equivalent weights or combining proportions. By similar processes of analysis and calculation he produced a table of atomic weights in which symbols were used (see fig. opposite of Dalton's symbols and weights).

Both Dalton's graphical representation of atomic symbols and Berzelius's later system of symbols and notation tended to be ignored by practical chemists.¹¹ Indeed, in Dalton's own paper in 1813 (chap. 5, sec. III) there is no recourse to his or any other symbolic notation. Crosland¹² points out that given an accurate set of atomic weight, which Berzelius provided in 1830, by 1840 these were still largely ignored by practising chemists. It seems that chemists placed reliance on the use of equivalents determined by relatively simple experimental evidence; a view supported by the researches of this present study and illustrated in the acid alkali balancing method from whence the concept had some origins. As early as 1767 Henry Cavendish published a paper showing that a given quantity of lime could be considered 'equivalent' to a certain amount of alkali simply because both reacted to saturation by the same quantity of acid.¹³ From this, and the quantitative analyses carried out to determine the quality of commercial potashes, it must have been evident that the composition or ratio of constituents in a compound were constant. It was on this tacit acceptance of equivalence that so much early analysis depended and that molecular formulae and weights, whether represented by symbols or not, played no part.

Dalton's symbols embodied a quantitative and qualitative value, together with a three dimensional aspect and this was a distinctly more embracing new mode of symbolism. It was in 1804 that he realised that relative atomic weights could be shown to explain what we know as the law of constant composition which led him to formulate some empirical atomic and molecular formulae.

From then on, chemists had for the first time a basis and theory for writing balanced chemical equations in terms of the numbers of atoms reacting and the weights of reactants and products. This revelation was not immediate; if Dalton spent ten years in developing his atomic ideas, many more years were taken to usefully apply them in industrial analytical chemistry. Fortunately for analysts it was not necessary to have complete faith in the idea that matter existed in the form of atoms. A written chemical equation was sufficient to lift analysis from that based on simple combining equivalents to that based on a tangible and measured atomic weight unique to every element. However, this idea was only slowly adopted by practising chemists its culmination marked by the explicit recognition given in Turner's *Elements of Chemistry*¹⁴ of 1834.

It was the work of Thomas Thomson (1773-1852) which brought Dalton's ideas to a wider public through his 1807 third edition of *A System of Chemistry*. This was one year ahead of Dalton's own *A New*

¹¹ See the article by Brock, W. H. 'The British Association Committee on Chemical Symbols 1834', *Ambix*, **33** (1986), pp.33-42.

¹² Crosland, M. P. *Historical Studies in the Language of Chemistry* (London, 1962), p. 320.

¹³ Cavendish, H. 'Experiments on Rathbone-Place Water', *Philosophical Transactions*, **57** (1767), pp. 92-108, on p. 102, Expt. V.

¹⁴ Turner, E. *Elements of Chemistry* (London, 1834), p. 235, the four earlier editions had not made the same reference to symbols and formulae.

It was the work of Thomas Thomson (1773-1852) which brought Dalton's ideas to a wider public through his 1807 third edition of *A System of Chemistry*. This was one year ahead of Dalton's own *A New System of Chemical Philosophy* of 1808, but neither gained immediate acceptance of the new atomic theories. Thomson gave the first example of the law of multiple proportions through analysis of the normal and acid salts of oxalic acid, and related his interpretation of the results with Dalton's atomic theory.¹⁵ Furthermore, his ideas on the neutralization of sulphuric acid by potash have since been interpreted by Partington as indicating a belief embodying an atomic theory long before that by Dalton.¹⁶

III. John Dalton's Analyses of Mineral Waters

In 1814 Dalton carried out some analyses of mineral waters. An assessment of his published and unpublished reports on this matter has been made in the hope that these primary sources might reflect some practical or theoretical application of his atomic theory.

His first paper on this subject contains a definitive account of existing methods of water analysis and shows his clear understanding of volumetric analysis.¹⁷ It is not immediately apparent how his atomic theory affected his understanding and methodology in these analyses. Partington has interpreted Dalton's use of the description 'test solutions' as meaning what we now term standard solutions.¹⁸

The use of solutions of known concentration have been shown often as an essential part of simple titrations and other early volumetric methods; in these, the sought component was reacted with a solution of known concentration until the reaction was completed. By means of an indicator, the reaction's completion became apparent. Dalton stated:

The improvements I would propose in the use of tests are, that the exact quantities of the ingredients in each test should be previously ascertained and marked on the label of the bottle.¹⁹

This is followed by a general description of the titrimetric method:

We should then drop in certain known quantities of each from a dropping tube graduated into grains, till the required effect was produced; then from the quantity of the test required, the quantity of saline matter in the water might be determined without the trouble of collecting the precipitate; or if this was done the one method would be a check upon the other.²⁰

This paper contains his directions for determining the alkalinity of water by the use of standardised acid solution:

¹⁵ Partington, J. R. 'Thomas Thomson, 1773-1852', *Annals of Science*, 6 (1949), p. 118.

¹⁶ *Ibid.* p. 119, see also *Supplement to the Encyclopaedia Britannica*, (1824), p. 343.

¹⁷ Dalton, J. 'Remarks, tending to facilitate the Analysis of Spring and Mineral Waters', *Proceedings of the Manchester Literary and Philosophical Society*, 3 (1819, read April 1st 1814) pp. 52-63. Dalton's unpublished paper on the analysis of Buxton waters was read in 1819.

¹⁸ Partington, *op. cit.* (5), p. 822.

¹⁹ Dalton, *op. cit.* (17), p. 59.

²⁰ *Ibid.* p. 60.

Indeed these acids may be considered as sufficient for tests of the quantity of lime in such waters, and nothing more is required than to mark the quantity of acid necessary to neutralize the lime.²¹

This certainly implies that water analysis does not require the use of a chemical balance and is truly dependent upon volumetric measurement alone. Similar reasoning was given in K. H. Farrar's address in 1983:

It is possible that Dalton's paper [read 1814] was intended to help those who needed to find out about the water they were using for manufacturing purposes but who lacked the more expensive equipment like balances, for he explained how the tests might be improved by adding a solution of known strength from a graduated dropping tube. In this way, weighing might be avoided.²²

The charred remains of Dalton's other paper read in 1819, 'Chemical Analysis of the Mineral Waters of Buxton' have been examined and these show close similarities to the earlier (1814) paper.²³ In what remains of this unpublished manuscript the term test nitric acid is used:

3.

The dry powder, 1.2 grains was treated with test nitric acid, it took 5 grains corresponding to 8 grains lime. Most of the powder dissolved with effervescence.. One grain more of acid produced no effect, but left (a) fine particles of earthy powder (sulphate of lime) with a little [illeg] matter from the filter...²⁴

In attempting to determine the amount of carbonic acid in the water, Dalton repeated his earlier comments:

I have in a former essay observed that water containing supercarbonate of lime is alkaline by the colour test. And it further appears from what follows that adding lime water to such supercarbonate does not precipitate the whole, & consequently does not neutralize the liquid by the colour test. In fact the quantity of lime in any supercarbonate of lime in mineral waters is best found by adding the acid to [illeg] till they neutralise the liquid.²⁵

The completed analysis is then given:

Collecting the results it appears that a wine gallon of Buxton water contains as under:²⁶

Carbonate of Lime	8.7 grains
Sulphate of Lime	1.2 "
Muriate of Soda	3.- "
Total of Solid matter	12.9
Free carbonic acid	11.6 "
Azote Gas	1.-
Oxygen	very small

His recommendations to use a volumetric method and solutions of known concentration for the determination of alkalinity mark this work as an important milestone in water analysis. However, there is

²¹ *Ibid.* p. 62.

²² Unpublished paper read to a meeting of the Society for the History of Alchemy and Chemistry at the Science Museum, London, 1983 (personal communication from K. H. Farrar).

²³ Dalton, J. 'Chemical Analysis of the Mineral Waters of Buxton' read 1819, location, John Rylands Library, Manchester Univ. Dalton Papers, 91; without original page numbers, library pagination adopted, pp. 1-13. Described as 'badly charred' in Smyth, A. L. *John Dalton 1766-1844 A Bibliography of Works by and about him* (Manchester Univ. Press, 1966), p. 17.

²⁴ *Ibid.* p. 6, section 3, second paragraph.

²⁵ *Ibid.* p. 7.

²⁶ *Ibid.* p. 10

no discernible reference to or application of his recent great achievements in atomic theory and other laws of chemistry which we now regard as so essential to analytical chemistry. Clearly Dalton found no reason to apply his atomic theory to the subject of water analysis but gave clear directions to use solutions of known concentration in volumetric analysis. These findings to some extent reinforce those found earlier in this research study; these suggest that successful analysis was carried out in the absence of an atomic understanding and the chemical laws which followed Dalton's theory.

IV. The Synoptic Scale of Chemical Equivalents by W. H. Wollaston

In 1813, W. H. Wollaston²⁷ read a paper to the Royal Society concerning a chemical slide rule of equivalents. He claimed that the main advantage of his invention was that it relieved chemists of the calculations necessary in analytical chemistry.

Golinski has described Wollaston's slide rule in the context of practical usefulness which originated from Dalton's discoveries, and having developed from an atomic perspective but not demanding an 'explicit commitment to the atomic theory'.²⁸ But Wollaston had clearly no intention to advance atomic thinking by promoting his slide rule. Indeed he points out that the theoretical combination of certain atoms and the uncertainty over which compounds consist of a single pair of atoms is unnecessary theory to the compilation of a table of equivalents:

I have not been desirous of warping my numbers according to an atomic theory, but have endeavoured to make practical convenience my sole guide.²⁹

His patronising stance to those without understanding of logarithmic scales suggests his misjudgement of the intellectual level of chemists to whom the slide rule was directed. If indeed the slide rule found useful application at artisan level or that of works chemists - a possibility not easy to prove - it is not always obvious to see where the connection with Dalton's atomic theory lies. Thomson regarded the scale 'as an important addition to the atomic theory' and 'of great advantage to the practical chemist',³⁰ but nevertheless it can be seen as nothing more than a refined scale of so called proportionalities found by empirical experience of other chemists.³¹

If Wollaston's slide rule is placed in an atomic context it can only be within the belief that equivalents or ratio proportionalities, which had been used long before Dalton's lifetime, are in fact atoms. Dalton found no difficulty in seeing equivalents, ratios and proportions in this context and criticised those who saw otherwise:

It is not a little remarkable that such men as Berzelius, Davy, and even Wollaston should contemplate a system of chemical equivalents, and not be aware that they were speculating upon the atoms or ultimate combining particles of bodies.³²

²⁷ Wollaston, W. H. 'A Synoptic Scale of Chemical Equivalents', *Philosophical Transactions*, 1 (1814), pp. 1-22.

²⁸ Golinski, J. *Science as a Public Culture* (Cambridge, 1992), pp. 268-9.

²⁹ Wollaston, *op. cit.* (27), p. 7.

³⁰ Thomson, T. *The History of Chemistry*, vol. 2, (London, 1830-1), p. 306.

³¹ Rocke, A. J. *Chemical Atomism in the Nineteenth Century* (Ohio State Univ. Press, 1984), pp. 61-66.

³² Dalton, J. Extract from Series of Essays read to the Manchester Philosophical Society in October 15 1830, quoted by Thackray, A. *John Dalton: Critical Assessments of His Life and Science* (Harvard Univ. Press, 1972), p. 94.

This may seem an unfair criticism of Wollaston³³ who throughout his 1813 paper recognised Dalton's atomic theory but pointed out that it was his own explanation about the nature of neutral and acid salts which gave practical meaning to Dalton's theory.³⁴

The slide rule was, in accordance with the title of Wollaston's paper, based on chemical equivalents founded on the constancy of composition in chemical compounds determined by experiment. This belief, that a compound substance was always of the same composition, was crucial to the accuracy of chemical equivalents. The figures used by Wollaston were not always his own;³⁵ Partington points out that some of the numbers used in Wollaston's table are not equivalents at all and the slide rule merely brought confusion into chemical theory. This resulted in attention passing to Gmelin's (1788-1853) later equivalents and possibly delaying the use of Berzelius's more fundamental atomic weights.³⁶

In 1813, Dalton's theory was still new but the use of equivalents was not. The comprehensive table of equivalents compiled by Wollaston would have proved a valuable aid to analytical chemists but as shown above he took matters further and produced a slide rule showing chemical equivalents for a wide range of reactions. The use of equivalents continued long after Dalton's theory whether or not aided by Wollaston's slide rule. There appears reason to believe that the slide rule was accepted by prominent chemists of the time; Golinski³⁷ names Brande, Prout, Ure and Faraday as endorsing it, but misgivings did exist, some of which are considered next. Whether it found a useful place in ordinary works control situations must be questioned in the absence of supporting primary evidence.

A serious drawback to any slide rule of this period must have been the inaccuracy through dimensional movement of the substrates used in its construction. In Wollaston's model a paper scale was merely pasted onto a mahogany slide rule and the Oxford Museum of History of Science holds three examples of the 'long' model.³⁸ One objective in devising the slide rule was to avoid the necessity of calculations but this is contradicted by Faraday; in his *Chemical Manipulation* (1830) there is no hesitation in demanding proper calculation to avoid the inevitable inaccuracies caused by the mechanical nature of the instrument.³⁹

Ure held no such reservations:

an instrument which has contributed more to facilitate the general study and practice of chemistry than any other invention of man.⁴⁰

³³ Goodman, D. C. 'Wollaston and the Atomic Theory of Dalton', *Historical Studies in the Physical Sciences*, 1 (1969), pp. 37-59.

³⁴ This refers to Wollaston's earlier work in 1808, 'On Superacid and Subacid Salts', *Philosophical Transactions*, 98 (1808), p. 96, in which he showed that the amounts of carbonic acid which combined with equal weights of potash (K_2O) in the carbonate (meaning our modern bicarbonate $KHCO_3$) and sub-carbonate (meaning our normal carbonate K_2CO_3) were in the ratio of 2:1.

³⁵ Wollaston, *op. cit.* (27), p. 13.

³⁶ Partington, *op. cit.* (5), p. 703.

³⁷ Golinski, *op. cit.* (28), p. 268.

³⁸ Cat. no. 292 (W. Cary, 1814). Of three other similar instruments by various makers, one was presented by the Radcliffe Observatory, but there is nothing to indicate these were used other than in a teaching capacity. The scale shown in Wollaston's (1814) paper extends from 10 to 320. Gmelin, L. *Handbook of Chemistry*, vol. 1, (London, 1848), trans. H. Watts, p. 63, reports a range of 10 to 500.

³⁹ Faraday, M. *Chemical Manipulation* (London, 1830), 2nd edit. p. 553.

⁴⁰ Ure, A. *A Dictionary of Chemistry*, (London, 1821), unpaginated, under 'equivalents'.

Brock cites the demonstration by Prout that Wollaston's slide rule could be modified to indicate the empirical formulae of organic substances from gravimetric analytical results, assuming that the law of constant composition applied.⁴¹ No evidence has been found to show that this modification was ever made although Ure reported similarly about modifications to the scale in order to obtain empirical formulae.⁴² William Brande's endorsement appeared in his 1841 textbook by which time the use of a H=1 was adopted.⁴³

Golinski claims, although without supporting evidence, that the slide rule proved very successful in analytical practice, chemical manufacturing and the pharmaceutical trade, and was a universal item of laboratory equipment until the 1850s when greater accuracy was demanded.⁴⁴ There is a lavish expression of its high value to chemists in *The Elements of Chemical Science* (1819) by John Gorham:

This scale is of so much convenience to the practical chemist, that I seize the earliest opportunity to make it known to my readers in general. It gives the composition of any weight whatever of any of the salts contained on the scale, the quantity of any other salt necessary to decompose it, the quantity of new salt that will be formed, and many other similar things, which are perpetually occurring to the practical chemist.⁴⁵

Gorham gives the following example if 100 corresponds to muriate of soda:

It shows, with regard to the different views of the analysis of this salt, that it contains 46.6 dry muriatic acid [hydrochloric acid], and 53.4 of soda, or 39.8 sodium and 13.6 oxygen; or if viewed as chloride of sodium, that it contains 60.2 chlorine, and 39.8 sodium.⁴⁶

The example given above for sodium chloride is surprisingly accurate and works well to illustrate the instrument, but the tables of equivalents used by Wollaston, taken from his 1814 publication on which the slide rule was based, reflect the uncertainties over the composition of soda and potash. Gorham's textbook clearly shows that the slide rule was known in America.⁴⁷

Of course in situations of routine volumetric analysis, once a chemist had established the necessary factors and equivalents associated with a particular determination there was little further reference to a slide rule. Indeed it is difficult to see why a chemist, confined to routine analysis, should need such an instrument when reference to published tables and some elementary arithmetic could achieve the same objective with probably more accuracy.

We conclude that the slide rule aided analytical chemistry only inasmuch as it removed the necessity for calculations. The elementary nature of such calculations and consequently the usefulness of a slide rule appears to have been exaggerated by its inventor and some of the authors mentioned above. To what extent the instrument was used in practising laboratories on a regular basis is now impossible to determine.

⁴¹ Brock, W. H. *From Protyle to Proton*, (Bristol, 1985), p. 15, quotes Prout, W. 'On the Analysis of Organic Substances', *Annals of Philosophy*, 6 (1815), p. 273.

⁴² Ure, *op. cit.* (40).

⁴³ Brande, W. *A Manual of Chemistry*, vol. 1, (London, 1841), p. 237.

⁴⁴ Golinski, *op. cit.* (28), p. 268.

⁴⁵ Gorham, J. *The Elements of Chemical Science*, vol. 1 (Boston, USA, 1819), p. 539, see also pp. 54-57.

⁴⁶ *Ibid.* p. 540.

⁴⁷ See Williams, D. W. 'Some Early Chemical Slide Rules', *Bulletin of History of Chemistry*, 12 (1992), pp. 24-29.

V. The Development and Origins of Normal Solutions: Ure, Griffin and Mohr

Like Dalton, Ure published a paper on mineral water analysis and its consideration here is appropriate for two reasons.⁴⁸ Firstly, it is from the post-Dalton period and could therefore embrace aspects of atomic theory. Secondly, a most important feature of future volumetric analysis became dependent upon normal solutions; in this publication we see their first use, at least in England.⁴⁹

It would be wrong to claim that the development of volumetric analysis depended upon the concept of normal solutions or normality, the term commonly used into the 1950s. The concept is important however because of its usefulness and convenience to industrial analytical chemists. Ure and J. J. Griffin demonstrated normality using a theoretical basis provided by Dalton and Thomson; before examining their work a twentieth-century description of its meaning is worth noting. The account by Mellor, whose pre-war textbook was directed towards the needs of industrial analysts particularly those in the ceramic industry, points to the crucial place of normality in volumetric analysis:

In volumetric analysis a standard solution of known strength is gradually added to a solution of the substance under investigation until the reaction between the two is completed. The volume of the standard solution required for this purpose is proportional to the amount of the substance in the solution under investigation. The two solutions must be of such a kind that the reaction takes place quickly and quantitatively. It must also be possible to recognise the end of the reaction. This is frequently indicated by a change in colour which occurs in the presence of a third substance, the indicator, immediately a small excess of the standard solution has been added. The indicator is usually indifferent to the main reaction. Since a definite amount of the standard solution can react with a definite amount of the substance under examination, given the volume of the standard solution, the amount of the substance under examination can be calculated by simple proportion.

The standard solutions may be of any strength, but it is convenient to make them of such a strength that the weight of the dissolved substance, per litre, bears a simple numerical relation to the molecular weight of the compound. A solution which contains the hydrogen equivalent weight in grams of an element or compound per litre is called a NORMAL SOLUTION, written N-solution; a semi normal solution is one-half the strength of a normal solution - 0.5 N-solution;...

The "equivalent weight" of a substance is the number of grams of the substance which brings into reaction - combination or replacement - the equivalent of 1.008 grms. of hydrogen or 8 grms. of oxygen...

In HCl, NaOH, NaCl for example, the molecular and equivalent weights are the same; in H_2SO_4 , $\text{Ba}(\text{OH})_2$, and CaCO_3 , the equivalent weights are half the molecular weights.⁵⁰

Two important points arise from Mellor's exposition:

1. 'Since a definite amount of the standard solution can react with a definite amount of the substance' - in this statement there can be two interpretations; in one sense it can be seen as a simple comment gained by empirical observation of any acid-alkali titration carried out prior to Dalton's chemical theory. In

⁴⁸ Ure, A. 'On a Mode of Analyzing Soda-Water and other Aerated Waters,' *Pharmaceutical Journal*, 2 (1842-3), pp. 126-127; for biographical details see Farrar, W. V. 'Andrew Ure, F.R.S., and the Philosophy of Manufactures', *Notes and Records of the Royal Society*, 27 (1972-73), pp. 299-324.

⁴⁹ Farrar, W. V. 'The Origin of "Normality"', *Education in Chemistry*, 4 (1967), pp. 277-279.

⁵⁰ Mellor, J. W. and Thompson, H. V. *A Treatise on Quantitative Inorganic Analysis with Special Reference to the Analysis of Clays, Silicates and Related Minerals* (London, 1938), 2nd edit., chap. 3, p. 36.

another sense there is an implication that to know these 'definite amounts' of reacting concentrations, a knowledge of atomic and or molecular weights is essential. Mellor's statement carries the mathematical basis of analysis through both eras of chemistry, and in so doing illustrates the idea that unstated 'laws of chemistry' existed long before Dalton's theories. It also explains why volumetric analysis continued unchanged for so long after Dalton's theories. 'The amount of the substance under examination can be calculated by simple proportion', but this is how early volumetric analysis was performed and calculated.

2. 'A solution which contains the hydrogen equivalent weight in grams of an element or compound per litre is called a NORMAL SOLUTION'. It is only in this statement that Dalton's relative atomic weights become relevant and necessary. Analysts could have coped quite well without Dalton, indeed this present study has shown this to be, and again offers an explanation for the apparent absence of any noticeable 'revolution' in volumetric analysis in the post Dalton era. Mellor's definition of normal solution is not a chemical necessity for good analysis but a mere recipe for a fairly rapid and convenient means of analysis.

This study has shown that the idea of some kind of standard solution in volumetric analysis has existed from such early analysts as Lewis, Joseph Black and others. Their solutions functioned in a comparative way only and bore little resemblance to present day standard solutions. It has been suggested that Andrew Ure first used, in English, the words 'normal test liquors' in 1842 but without expressing the present day meaning.⁵¹ This was fourteen years after Gay-Lussac's use of the term 'acide normal' for a solution containing 100g of pure sulphuric acid per litre, recorded in his description of what was a classical titration.⁵²

Clearly both Gay-Lussac and Ure were describing solutions of known concentration against which a comparison of an unknown or sought component could be made. Their descriptions of course did not satisfy the requirements made by Mellor's modern definition, or bring into consideration any aspects of Dalton's theories by using stoichiometrically significant measures.

An aspect of industrial volumetric analysis has always been that of convenience to the operator; it is noteworthy that Ure, Gay-Lussac and Dalton referred to their test solutions as of convenient strength. Also, Mellor suggested 'any convenient concentration so long as the weight per litre bears a simple numerical relation to the molecular weight of the compound'.

Referring now to Ure's (1842-3) publication on the analysis of soda water and other aerated waters;⁵³ he points out appropriately, that a soda water should contain soda in sufficient amount to offer 'antacid and renal' properties. In his method of determining this constituent he refers to 'the normal test liquor'. His standard test nitric acid solution, for use with his alkalimeter, is made to a particular specific gravity by using a floating glass bead.⁵⁴ There is no indication of how this bead had been calibrated or the actual strength of the nitric acid:

⁵¹ Farrar, *op. cit.* (49), pp. 277-9.

⁵² Gay-Lussac, J. L. 'Essai des potasses du commerce', *Annales de Chimie et de Physique*, **39** (1828), pp. 337-368, on p. 347.

⁵³ Ure, *op. cit.* (48), pp. 126-127.

⁵⁴ Sometimes called hydrostatic or philosophical beads; see the collection in Museum of History of Science, Oxford, cat. nos. 19 and 20.

This mode of preparing the normal test liquor is both much more ready and precise than that by one of the ordinary instruments for taking specific gravity.⁵⁵

There is no description of the alkalimeter in this paper but it is clear that the acid solution could be carefully and accurately delivered to give a 'continuous stream of any tenuity, or in fractions of a drop, at pleasure'.⁵⁶ He then pointed out that by using 'rightly tinted litmus paper' the determination of potash, soda or ammonia could be made without calculation by reading off the result given by the graduated glass. There is nothing in this paper which suggests that Ure had any concept of normality in a modern sense although his term normal test liquor approaches this closely.

Two years later, in another paper, Ure added a quantitative aspect to his test solutions and also referred to Dalton's theories.⁵⁷ In order to illustrate the simplicity of his alkalimeter he cited an extract from the *Belfast News Letter* of 9 July 1816; this described the observations made and confirmed by four prominent members and physicians, when a porter of the Linen Hall in Belfast was requested to carry out the determination of alkali in a prepared sample.⁵⁸ Referring to Descroizilles's earlier alkalimeter (see chap. 3, sec. VIII) Ure commented 'that the alkalimeter so made and graduated denoted comparative, but not absolute, quantities of alkalies present in the commercial samples.'⁵⁹

Then follows Ure's important reference to Dalton:

In constructing this instrument [Ure is referring to his own], I availed myself of the lights recently shed on chemical proportions by Dr. Dalton's atomic theory, and I thus made it to represent, not relative, but absolute measures of the amount of real alkali existing in any commercial sample.⁶⁰

Ure then describes the determination of the 'absolute' content of soda as 'oxide of soda' using red cabbage or litmus as an indicator in the titration. Mention of an atomic aspect comes in his description of the preparation of ammonia solution for use in his acidimeter and this is very probably the first known reference of this kind:

Pure water of ammonia is made of such a standard strength by an adjusted glass bead, as that 1000 grain measures of it neutralize exactly a quantity of any one real acid, denoted by its atomic weight, upon either the hydrogen or oxygen scale or radix; as for example, 40 grains of sulphuric acid.⁶¹

This closely resembles the definition stated by Mellor. From this time onwards Ure saw his acidimeter as of universal significance and application.

After the neutralization of 10 or 100 grains of any acid, as denoted by the well defined colour of the litmus-tinted ammonia, the test-tube [as a burette] measures of ammonia

⁵⁵ Ure, *op. cit.* (48), p. 126.

⁵⁶ *Ibid.*

⁵⁷ Ure, A. 'A Lecture on Alkalimetry, Acidimetry, & Chlorimetry', *Pharmaceutical Journal*, 3 (1843-4), pp. 430-447, on p. 433.

⁵⁸ The same account appears in his *Dictionary of Chemistry* (London, 1821), xii. Ure mentions his engagement by the Belfast Academical Institution to analyse barillas and potashes (xi), see Appendix II.

⁵⁹ Ure, *op. cit.*, (57), p. 433.

⁶⁰ *Ibid.* pp. 433-4.

⁶¹ *Ibid.* p. 434; Ure, A. *A Dictionary of Chemistry* (London, 1821), states dry sulphuric acid as 'three atoms of oxygen, united to one of sulphur'. The value is obviously not based on Dalton's atomic weights but probably whole numbers of Thomson, O = 8, and S = 16.

expended being multiplied by the atomic weight of the acid, the product denotes the quantity of it present in 10 or 100 grains.⁶²

He then approaches modern practice in suggesting that the standard potash solution should be prepared by direct weighing:

so that 1000 grain measures contain one atom of the salt counted in grains, ..., for if the centigrade measures expended in effecting neutralization, are multiplied by the atomic weight of the given acid, the product is the quantity in grains of acid present.⁶³

Much of the remainder of this lengthy publication describes ingenious pieces of apparatus for the determination of carbonates by liberation of carbon dioxide 'by their solution in acids upon the data of the atomic theory.' Such methods are not based on any titrimetric method and are not discussed here.

On the subject of chlorometry, Ure described a method of determining chlorine liberated from muriatic acid using manganese (dioxide) as a means of assessing the latter. This is a much improved method than that by Dalton in connection with bleaching powder (see chap. 5, sec.III). Ure based his quantitative method on the oxidation of ferrous sulphate solution by chlorine, detecting the completion of the reaction by spot testing the ferrous sulphate onto red iron prussiate which formed a blue stain whilst any ferrous iron remained.

His calculations, though based on Dalton's atomic weights, appear complicated, also, in preparing the standard solution of ferrous sulphate the choice of concentration 'was determined more by arbitrary convenience than by strict definition'.⁶⁴ Ure adopted a 1000 grain measure of volume for one atom of solute but gave other dilution suggestions depending on the anticipated manganese dioxide quality. In preparing the standard ferrous sulphate solution he realised that two grain atoms of copperas (278) would be 'equivalent to 36 of chlorine, 8 of oxygen, and to 44 of peroxide of manganese'.⁶⁵ From his own earlier experiments, he claimed that copperas contained seven atoms of water and not six as Berzelius had reported. Ure's atomic weight for green ferrous sulphate was 139, and for the standard solution 'take a solution of copperas, containing 278 grains in 1000 water-grain measures.' This amount is not soluble at the concentration suggested and there is nothing to suggest that Ure was using elevated temperatures (solubility of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ is 15.65 g/100ml cold water).

Ure was the first to use the term normal solution; he used weights of substances corresponding to Dalton's atomic weights dissolved in a stated volume or weight of liquid. In the two papers considered above, his arbitrary choices of concentration and use of older uniting combinations or equivalents, suggest however, that he had not entirely applied a modern concept. It is perhaps surprising that Ure made little reference to written chemical equations which so conveniently illustrate the inter relationship between reactants and products with atomic weights. At the time of Ure's publication (1844) equations were in use in textbooks and teaching, after their introduction by Graham and Turner in the 1830s.⁶⁶

⁶² Ure, *op. cit.* (57), p. 434.

⁶³ *Ibid.*

⁶⁴ Farrar, *op. cit.* (49), p. 277.

⁶⁵ Ure, *op. cit.* (57), p. 446.

⁶⁶ See Brock, *op. cit.* (9), p. 155; also 'The British Association Committee on Symbols 1834: Edward Turner's Letter to British Chemists and a reply by William Prout', *Ambix*, 33 (1986), pp. 33-42; Turner, *op. cit.* (14), (1833), 4th edit., used Berzelius's

J. J. Griffin (1802-77) took the idea of normality somewhat further than Ure; this is seen in his work in connection with what happens to the weight and bulk of substances when dissolved.⁶⁷ These investigations employed the concept of 'normality' and his published results represent an extensive piece of research, some of which is outside the interests of this study.

Under the heading 'Chemical Standards' Griffin set out his basis of solution standardisation. Using the atomic weights determined by Berzelius who chose 100 as the atomic weight of oxygen, Griffin defined his term, test atom as signifying the atomic weight of a substance expressed in English grains. His term degree then meant a hundredth part of a test atom and as an example he stated:

5.01165 grs. is 1° of SO₃
501.165 " is 1 test atom, or 100° of SO₃ I prepare normal test liquors of 100° of strength, in all cases, by dissolving 1 test atom of the substance in so much water as produces 1 decigallon [0.1 of an Imperial gallon] of solution at 62°F.⁶⁸

Griffin's unit of volume, by which the idea was fully defined, was one decigallon (454ml.). Why he chose this volume and not one within the metric system - such as the litre - is not clear; the latter was certainly known to him for he points out that 'one litre contains 2200 septems', a name he proposed to describe 7000 grains of pure water at 62°F. From this apparently arbitrary choice can be seen the relationship between the decigallon (454ml), his standard volume, and the septem, his smallest practical operational measurable volume, as the same as that of the litre to the cubic centimetre or c.c. It almost seems that Griffin is straddling two unit systems or perhaps anticipating adoption of full metric use. It may be relevant that a tenth of a gallon (a decigallon) weighs 7000 grains and that this is the same weight as one pound.

As mentioned above, Griffin's system of standardised solutions appears to have developed during his researches on aqueous solutions published in 1845.⁶⁹ This work was lengthy and laborious and the convenience given by standard solutions must have proved invaluable.

The capacity of his alkalimeter was one centigallon, graduated into 100 septems; the instrument held therefore one tenth of a 'test atom', or 10°. The smaller graduations allowed a delivery of a 1000th part of the 'test atom' reagent solution and this was the same as an extreme dilution of 10,000th part of an imperial gallon. On this basis of 'centigrade testing' and by his alkalimeter Griffin claimed, 'it is easy to find the relation between the chemical strength and the physical mass of a given solution.'⁷⁰

Ure's suggested standard volume was 1000 grain measures (65ml.) but Griffin chose a larger amount, that of one decigallon, being 454 ml. Both agreed on one atom weight of material to be used (provided

symbols; Partington, J. R. *A History of Chemistry*, vol. 4, (London, 1964), p. 160; Brock, W. H. and Gee, B. 'The Case of John Joseph Griffin', *Ambix*, 38 (1991), p. 49, refers to Graham's notebook (1832-1834) which contains symbolic notation. MS location Strathclyde Univ. Library.

⁶⁷ Griffin, J. J. 'On the Constitution of Aqueous Solutions of Acids and Alkalies', *Chemical Society Memoirs*, 3 (1845-8), pp. 155-199.

⁶⁸ *Ibid.* p. 159.

⁶⁹ *Ibid.* p. 197.

⁷⁰ *Ibid.* p.160.

this was demanded by the reaction) and made up to the chosen volume. Here, Griffin stipulated English grains and the temperature at which the final volume was to be measured.

Atomic weights are without units of themselves, and present-day chemists, whether considering 'one atom weight' or one mole, or molecular weight, think in terms of grams, and litres. These standards were not generally accepted then and the confusion about units of weight and volume may have presented problems not immediately obvious in our present time.

Brock suggests that volumetric analysis only gained widespread use in the 1860s⁷¹ after Mohr's *Lehrbuch* was published.⁷² This seems a reasonable conjecture in view of the confusion existing at the time of Griffin's first statement (1846). Standard solutions of some kind existed before the definitions of Ure and Griffin; the solutions of Gay-Lussac and Descroizilles have been considered but these were not based on atomic weights; their solutions could only be used for specific titrations or fixed amounts of sample material, but those based on atomic weights gave immediate universal application so long as units of weight and volume were agreed. Volumetric analysis using standard solutions did not rule out the necessity for weighing procedures although it reduced the number of weighings; any unknown sample had to be weighed initially of course. Chemists in this country had difficulties because of the system of Imperial measure then in use; this was seen in Griffin's report. Other problems arose when attempts were made to define standard solutions whereby their consumption, in a titration, gave a direct reading of the unknown component. Adoption of a metric system relieved this problem if only because weight and volume are more easily interchangeable. While confusion continued it seems probable that acid/alkali balancing, in industrial laboratories, remained in common use long after the work by Ure and Griffin on standard solutions. As the concept of normality was put into practice the necessity for pure primary standard compounds arose. The use of normal solutions allowed information about standards, methods and results to be compared between different laboratories. Eventually these solutions became a commercial commodity through the enterprise of Griffin⁷³ (which became Griffin & George Co.), and were available to works chemists.

Farrar's paper on 'normality' concludes by referring to the achievements of Karl Friedrich Mohr (see chap. 5, sec.VIII) who,⁷⁴ after the work by Ure and Griffin, stimulated greater use of volumetric analysis through his *Lehrbuch* (1855-6).⁷⁵ This text adopted the use of normal solutions as accepted practice and emphasised the necessity of the litre as a standard volume.

VI. Some Concluding Comments Regarding Normality

The concept of normality and the use of standard solutions played an important part in providing volumetric analysis with a wider and more universal basis of theory and practice. Its value was more practical than theoretical in its early application if only because it reduced the number of other reference

⁷¹ Brock, W. H. 'An Attempt to Establish the First Principles of the History of Chemistry', *History of Science*, 6 (1967) pp. 156-69, on pp. 163-4; see also Brock, *op. cit.* (9), p. 183.

⁷² Mohr, K. F. *Lehrbuch der chemisch-analytischen Titrimethode* 2 parts, (Braunschweig, 1855-6).

⁷³ Brock and Gee, *op. cit.* (66), p.56.

⁷⁴ Farrar, *op. cit.* (49).

⁷⁵ Mohr, *op. cit.* (72).

solutions needed in a laboratory. It also gave greater 'universality' to volumetric methods so that chemists of different laboratories had similar standards of reference.

The origin of the idea of standard solution appears to have arisen from Gay-Lussac but there are earlier instances where tacit dependence on reference solutions existed. The more specific developments through Ure and Griffin have been shown, followed by Mohr's further elaboration and its establishment through his *Lehrbuch*. It was not until the seventh edition in 1896 that Griffin's part was fully acknowledged by its editor, A. Classen:

So far as is known, this scheme was first introduced by John Joseph Griffin of London about 1860 [1846 more probably], in an effort to bring about a uniformity in the employment of standard solutions, . . .⁷⁶

Griffin's work on standard solutions and the concept of normality may have been influenced by his commercial interests insofar as an accepted scale of concentrations, understood by all industrial chemists, would facilitate sales.

The concept of normality in a modern sense depends upon atomic and molecular weights. For early analytical chemists this was an entirely new basis of conducting volumetric analysis. No longer was it necessary to refer to tables of equivalents or to use Wollaston's slide rule; these referrals could be swept aside by the use of standard normal solutions. The need for chemical purity, if only in one or two primary substances, remained however, as it has done to this day. Kolthoff and Stenger noted in 1928:⁷⁷

The accuracy of all volumetric methods depends primarily upon the accuracy with which the solutions are standardised - and this in turn necessarily depends upon the purity of the primary standards....in most works of reference on volumetric analysis they are only touched upon briefly. In many cases there are not available exhaustive processes for testing the primary standard.

Atomic weights and molecular formulae on which the concept of normality depended were not the certain data that they are today. It has been shown how earlier chemists expressed solution strength in terms of experimentally determined equivalent weights, but there is no evidence to suggest that this practice retarded the development of solution normality. Whilst standard solutions found useful, practical application in industrial laboratories, there is little reason to assume that the concept was pivotal to the future development of volumetric analysis. The credit accorded to Ure, Griffin, and Mohr in this field may therefore be overstated.

As a supplier of chemical apparatus, Griffin received a Prize Medal at the 1851 Great Exhibition. His exhibits included graduated glassware used in the analysis of sodium carbonate, potash and a range of other chemicals by volumetric means. Part of the entry in the Reports of the Juries,⁷⁸ states:

⁷⁶ Classen, A. (editor) *Friedrich Mohr's Lehrbuch der Chemisch Analytischen Titrimethode* (Braunschweig, 1896), 7th edit., p. 56, quoted by Lee, J. 'Normality - An Unnecessary Concept', *Education in Chemistry* 2 (1965), pp. 229-235, on p. 229, taken from Fales, H. A. *Inorganic Quantitative Analysis* (London, 1928), p. 153.. See biographical note on Classen in Szabadváry, F. *History of Analytical Chemistry* (Oxford, 1966), p. 315.

⁷⁷ Kolthoff, I. M. and Stenger, V. A. *Volumetric Analysis*, vol. 2, *Titration Methods* (New York, 1947), page x.

⁷⁸ *Exhibition of the Works of Industry of All Nations 1851. Reports of the Juries* (London, 1852), p. 295.

GRIFFIN (cat. no. 457.) ...the graduation of these instruments is executed on the principle of assigning a fixed volume to the atomic weights of each chemical compound when in solution, and so producing a series of equivalent test liquors. The standard is made on the consideration that 100 grains of oxygen, in a deci-gallon of solution [being in the proportion of 1,000 grains in a gallon], at the temperature of 62° Fahr., produce a solution of 100° which represents a quantity of any chemical substance equivalent to 100 grains of oxygen, or its atomic weight expressed in grains, contained in a deci-gallon of the solution.

Thus -

503.38 grains of hydrate of soda,

667.34 " anhydrous carbonate of soda,

1792.13 " crystalline carbonate of soda,

dissolved respectively in water, so as to make a deci-gallon of solution at 62° Fahr., are of the same chemical strength.

In like manner;

643.19 grains of anhydrous acetic acid,

455.13 " " muriatic acid,

501.165 " " sulphuric acid,

2028.64 " nitrate of silver

brought into aqueous solution of the above bulk at 62° Fahr., are all solutions of 100° of chemical strength.

The writer of this entry was almost certainly Thomas Graham who obviously understood the advantages of the system adopted by Griffin:

The extreme convenience of this system carried out in a laboratory in respect to the saving of time, thought, and calculation, and in power of securing uniformity of manipulation, must be obvious to every chemist.⁷⁹

It was in Friedrich Mohr's *Lehrbuch* that solution normality first appeared as an analytical *fait accompli*; but, as already mentioned, there were shortcomings because some atomic and molecular weights were uncertain. Furthermore it is possible that substances of a bivalent character posed queries. By 1871 no such doubts were held by Sutton:⁸⁰

In the case of reagents of a bivalent character, such as crystallised oxalic acid, for instance, the formula of which is $C^2O^4H^2$, $H^2O = 126$, half its atomic weight = 63gm., is dissolved in water so as to make up exactly a litre at 16°C. This constitutes the normal solution of oxalic acid used in alkalimetry.

The definition of normality has changed with time;⁸¹ the varying valency in some compounds resulted in the original expression 'one gram equivalent' (the amount of substance made up to one litre) being changed to 'one gram atom of replaceable hydrogen' which took into account acids such as sulphuric and phosphoric having two and three replaceable hydrogens respectively. When phenolphthalein and methyl orange were synthesized and found to be useful indicators,⁸² further failings in the definition of normality arose when titrating sodium carbonate with hydrochloric acid. In this, the reaction proceeds to different stages related to intermediate products depending on which indicator is used. Lee concludes that:

⁷⁹ *Ibid.* Thomas Graham is named as a contributor.

⁸⁰ Sutton, F. *A Systematic Handbook of Volumetric Analysis* (London, 1871), 2nd edit., pp. 20-21.

⁸¹ Lee, *op. cit.* (76), pp. 229-235.

⁸² Szabadváry, *op. cit.* (76), pp. 260 and 365.

there might be a case for avoidance not only of the term 'normality' but also of the associated 'equivalent weight' idea, except in considerations of the historical and philosophical aspects of chemistry, surely two of its more difficult branches.⁸³

It is to the historical considerations that this chapter has been addressed; the 'normality' of the trio of originators named above provided a fundamental basis for future volumetric analysis, one based upon an atomic theory. Industrial chemists may have continued to develop their earlier methods of analysis without this new concept - this we cannot now ascertain.

⁸³ Lee, *op. cit.* (76), p. 235.

CHAPTER EIGHT

CONCLUDING DISCUSSION

This thesis began by considering the simple analytical efforts of Francis Home in connection with the use of chemical materials in the early Scottish bleaching industry; the period corresponded approximately with the beginnings of the Industrial Revolution in Britain. Home, together with Joseph Black, established the value of analysis and chemical understanding to this growing industry. This is not to suggest that analysis originated in the bleaching industry although it can be argued, from the evidence in this thesis, that it was this industry where quantitative analysis, of the kind instituted by Home, was first used. Of course other analytical influences arose from non-industrial settings such as those from the period of iatrochemistry, mineral water interests and assay offices.

Within the time period of this study 1750-1860s, great changes occurred in the understanding of chemistry especially after the rejection of phlogistic beliefs by Lavoisier an event which is usually described by historians as the chemical revolution. Before Dalton, analysis was not an exact science although it has been shown that early analysts were proficient in determining the quality of raw material chemicals by empirically devised methods of comparison. No general quantitative laws emerged however and early analysts could therefore not predict or calculate the amounts of substances used or formed in chemical reactions as a means of analysis. The contextual setting for the development of analytical chemistry was one of considerable theoretical change not always reflected in industrial analytical methodology. It seems a reasonable expectation that Dalton's ideas should have changed analytical practice fairly quickly; this was not so in the branch of analysis considered here, i.e. volumetric. The development of standard solutions was a slow and frequently confused process, and the older established methods, based on equivalent or combining proportions, retained popularity long after Dalton's introduction of atomic weights. The advances made in analytical methods during the period considered seem to have arisen more from intuitive empirical observation than anything based on what we might now term fundamental new chemistry. Of course, the turning point in the basis of quantitative analysis did originate from Dalton's theory, if only slowly, and then through others such as Ure and Griffin. Although Dalton used the terms standard solution and test measures these did not fit our modern definition or that of Ure or Griffin. There is a danger for historians when looking at the atomic work of Dalton and recognising its value and potential use in analysis. We wrongly assume that all previous similar analysis was inferior. This study has not supported this view. His theories, of course, depended upon analytical results for confirmation and yet he took little initiative to apply his knowledge to analytical chemistry at a practical or commercial level.

Much of the primary source material examined relates to industrial or commercial enterprises and originated from the 'managerial entrepreneurs' as company owners, or from externally appointed consultants. Indeed although 'works chemist' and 'laboratory' are terms which have been used, these only gained credibility from the demands of the Alkali Acts (1863).¹ Surprisingly, methods of commercial

¹ For the early role of chemists in the British alkali industry see Donnelly, James. 'Consultants, Managers, Testing Slaves: Changing Roles for Chemists in the British Alkali Industry, 1850-1920', *Technology and Culture*, 35 (1994), pp. 100-128, on p. 101

analysis have been shown to develop with little regard or apparent need of chemical laws. The supposition that nineteenth-century industrial chemical analysis usually follows in the wake of commercial chemical interests, while not true for twentieth-century industry, is confirmed by this thesis. The exception is early chlorine bleaching; here commercial pursuit, analytical control, and understanding developed together.

Although analysis provided the essential practical data for chemical laws to come into being, industrial chemists were content to pursue and develop methods directly related to their commercial interests without seeking a theoretical understanding of their results. For example, alkali was reported as alkali and this description satisfied their needs - whether it existed as caustic soda or sodium carbonate was not of immediate concern.

There is little evidence that the practical understanding and techniques of analysis gained by early industry were passed on to academic chemists for theoretical explanation. Dissemination of knowledge in the reverse direction was similarly rare. The best example is Descroizilles's development of the 'indigo blue test', which originated from Berthollet, and became a commonly used method throughout the industry. The test was used as a means of controlling bleaching strength as a safeguard against over bleaching and more importantly as a measure of performance of bleaching liquors; it clearly assisted the continued expansion of the textile industry. Of course, we have no way of proving that industrial progress and analysis would have been accelerated if two way dissemination of such knowledge had been better than it was.

One constant difficulty throughout this research has been to establish the methods used by early analysts. Both original archives, where these have been found, and the few historians of this subject, have reported analytical figures but with only little reference to the methods used. The scarcity of useful archives has been a regular characteristic of this research and my conclusion is that chemists' notebooks and other analytical records have not been deemed worthy of preservation.² This has caused a greater dependence upon published papers which, although primary sources, do perhaps lack the spontaneity of hand written laboratory notes.

It was intended to end this research at a time when Dalton's theories came into being, but it was found necessary to extend this to a time when his atomic theories found actual practical application in industrial settings. So far as analytical chemistry was concerned, there is no better example than the practical quantification established by Ure and Griffin. By using standard solutions based on known weights of substances related to their molecular weights instead of 'equivalents' obtained by empirical measurement through acid/alkali balancing or some other method, Ure and Griffin changed existing volumetric analysis into a convenient and more quantitative system. No longer was it necessary to refer to Wollaston's slide rule or the early combining ratios of Ernst Fischer or earlier still, those of Homberg, or even the teaspoon measure of Francis Home.

² See comments by Brock, W. H. 'An Attempt to Establish the First Principles of the History of Chemistry', *History of Science*, 6 (1967), pp. 156-169, on p. 163, which suggests an oral tradition, 'some of the material will not be found recorded on paper'.

From Dalton, and through Berzelius and Thomson who showed how accurate atomic weights could be determined, a new breed of analytical chemists had the necessary foundation on which to build a system of analysis quite different from that using simple modes of saturation, acid/alkali balancing and calculations made against 'equivalents' determined from compounds presumed to be pure. Such a quantification in analysis, which Dalton's theories allowed, came in time to provide a firmer quantitative basis for control in the Alkali Acts. Yet there must be something of an anachronistic *non sequitur* about such a statement. The innovative chemists considered in this thesis have shown abilities that would no doubt have continued to give an acceptable basis for analytical reliability with or without an atomic theory. This thesis has shown that reliable analysis connected with commercial interests was practised for almost a century before Dalton's theories found practical application. From the many facets of industrial analysis during the period examined, a clear thesis has emerged that industrial analysis was never dependent upon an atomic theory. An answer to a secondary question, of whether the introduction of chemical symbols and equations aided chemical analysis, is not so clear. The value we now give to these cannot be indicative of a hypothetical earlier usefulness in the absence of an atomic theory. It may well be argued that symbols and equations have little value without an atomic theory; but the premise that analysis itself was not valid in the absence of an atomic theory has turned out to be incorrect. The fallacy of this assumption has been made abundantly clear by the many examples of reliable analysis by early industrial chemists, albeit they were often measurements of performance rather than actual composition.

Atomic weights, molecular weights, and some ideas on compound structure made visible by symbols and equations confirmed earlier empirically derived combining proportions. Also, they allowed reactions to be predicted although this was not a requirement of the early chemical or bleaching industry. Methods by which quality and strength of raw material purchases could be judged were important requisites of early industrial chemists. Physical observations of raw materials became insufficient evidence of their quality; but chemical tests, however simple, made by comparison with other substances of known standard, provided a reliable quantitative assessment. These results could only be expressed in comparable terms - not absolute units of content - but nevertheless they served the needs of the early chemical industry. Dalton provided an explanation of homogeneity through homogeneous atoms; this concept had not been available before and gave a better understanding of purity. But more importantly, it gave the means of determining absolute content through his atomic theory.

This study has shown that early chemical analysts tacitly assumed that individual chemical substances were of approximately constant composition. On this assumption their work remained valid even in the light of such questionable aspects as water of crystallization and their inability to see clearly the real differences between caustic alkali and mild alkali and the even greater problems of mixtures. The law of constant composition, as a universal statement of truth about chemical compounds, did not come about until 1799 but throughout this thesis it has been apparent that the lack of such a law did not hold back analysis.

Practical analysis undoubtedly played an important role in the control of processes more than in their understanding, for example, in bleaching solutions and in the early Leblanc process. In these instances

analytical chemistry did not stand still awaiting the atomic theory, but developed and found improved methods. What followed Dalton's theory in the period 1800-1860 changed more the prediction of chemical reactions. The knowledge that re-arrangement of atoms occurred in reactions remained a theoretical point - but its practical usefulness became apparent with the slow realisation that chemical formulae and equations, supported by atomic and molecular weights, could be written down and shown to work in analytical practice. Dalton provided the basis for this new concept though not immediately apparent to him and not applied in his mineral water analyses. Early industrial chemists saw little value in this and made no attempt to predict the course of chemical reactions. Perhaps we should not be surprised given that James Keir came very close to this realisation a generation before Dalton.

The use of combining proportions as a basis of practical analysis must surely have indicated the existence of a definite numerical relationship between reactants and products. It has been constantly noted that early analysts accepted that so much alkali reacted with so much acid if both were of 'proper standard'. However, this was only interpreted in terms of useful analysis and did not apparently bring forward chemical laws. Such fundamental aspects remained tacit if simply because early chemists set out to measure one particular constituent in terms of its likely performance and did not concern themselves about unaccountable percentages in their analyses.

It is impossible to recreate the exact circumstances of the early analytical work examined in this thesis through modern day experimental testing such as Rancke Madsen's; we cannot therefore judge the accuracy obtained. What must be accepted is that in the period to the time of Dalton's theory, which led to the work of Ure and Griffin in creating standardised solutions, early analysts chose a most reliable route of analysis, that of comparison of the unknown product with one of known performance. The practice of acid-alkali balancing, which this thesis has shown to have been a common method, sufficed for the early acid and alkali industries, for what better method could there be for measuring one against the other where one product was of known standard or strength? Its failings have been commented upon insofar as the uncertain understanding of purity is concerned and because it could never be conclusively shown that the unknown substance was intrinsically the same as the comparative substance. Such early analysts were measuring performance and this perhaps explains the apparent lack of emphasis to establish the full composition of unknown materials. The early bleaching industry demanded analysis in terms of bleaching capacity or strength. This is exactly what the 'blue test' provided and to this day it reminds industrial analysts of their dependence upon a colour change at the centre of volumetric analysis. If we attribute the development of another branch of analysis, colorimetry, to Walter Crum, there can be little doubt that his work sprang from an intimate knowledge of the 'blue test' used in the bleaching industry. •

APPENDIX I

The invention of blue sugar paper is attributed to Charles Hilderyard of England in 1665, in Desmond, Kevin. *The Harwen Chronology of Inventions, Innovations, and Discoveries* (Constable, 1987). There was a patent application by one Hilderyerde in 1665 (later corrected to 1666) on 16th February, entitled Making Blue Paper, and reported in Bennet Woodcroft's *Alphabetical Index of Patentees and Inventions* (1969 reprint of first edition, 1854). This has not been researched and it would be unlikely that the patent would name the specific colouring material used. Whatever natural colorant (lichen) was used it remains possible that the coloured paper might have been seen as a useful means of indicating the quality of the sugar.

APPENDIX II

The Comments of Andrew Ure about his alkalimeter and acidimeter from *A Dictionary of Chemistry* (London, 1821), page xi (Introduction):

In prosecution of this plan of simplifying analysis, I contrived, about five years ago, an alkalimeter and acidimeter. Being then connected by a biennial engagement with the Belfast Academical Institution, I was occasionally called upon to examine the barillas and potashes so extensively employed in the linen manufacture, the staple trade of Ireland. I was sorry to observe, that while these materials of bleaching differed excessively in their qualities, no means was possessed by those who imported or who used them, of ascertaining their value; and that a generous people, with whom every stranger becomes a friend, frequently paid an exorbitant price for adulterated articles. The method which I devised for analyzing alkaline and acid matter, was laid before the Honourable Linen Board in Dublin, and by them referred to a competent chemical tribunal. The most decisive testimonies of its accuracy and importance were given by that tribunal; and it was finally submitted, by desire of the Board, to a public meeting of bleachers assembled at Belfast. Unexceptionable documents of its practicability and value were thence returned to Dublin, accompanied by an official request, that measures might be immediately be taken to introduce the method into general use. Descroizilles had several years before described, in the *Annales de Chimie*, an alkalimeter, but so clumsy, operose, and indirect, as to be not at all adapted to the purposes of the linen manufacture. My instrument, indeed, was founded, as well as his, on the old principle of neutralizing alkali with acid; but in every other respect it was different. Of the two hundred and ten thousand pounds expended that year (1815-1816) on imported alkalis, a very large proportion might have been saved by the application of my alkalimeter; and what is perhaps of more consequence, the alkaline leys used in bleaching, would, by its means, have been rendered of a regulated strength, suited to the stage of the process, and fabric of the cloth.

Ure then reprinted a copy of a letter dated June 12. 1816. Dublin:

That the quantity of alkali, present in any portion of potash or barilla, is directly proportional to the quantity of acid requisite to produce saturation, is a fact which has been known for upwards of a century to every chemist, and forms a fundamental law of science.

The novelty which I lay claim to in my contrivance, is this, that it enables a person versant neither in chemical researches nor in arithmetical computation, to determine by inspection of a scale, as simple as that of a thermometer, the purity or value to one part in the hundred, of the alkalis, oil of vitriol, and oxymuriate of lime, so extensively, and often so injudiciously employed by the linen-bleacher.

It seems that Ure made known 'his invention' of the alkalimeter to Dr. Henry who passed this knowledge to John Dalton, and then bemoaned the fact that in Henry's *Elements* no credit was given to Ure but only to Descroizilles.

for the smallest leakage will occasion a considerable loss of the Gas or 2^d Or air, which is extremely frustrating the Glasses stand as in the sketch below



The retort a, being placed at a proper height in one of the rings belonging to its stand so that its bottom may be about 9 inches distant from the flame of the Lamp at g, one of the glass tubes, with a single turn as at d e, is to be fixed into the receiver f so that the lower end may reach near to the bottom of the receiver & is to be made tight to the receiver & by putting up the new middle of the mouth of the receiver with the 2^d half of a spirit cock, & secured out to fill the tube & forced in along with it into the mouth of the Receiver 2^d by covering all the rest &

Fig. 'A' courtesy of Birmingham City Archives.

at in one of the rings may be about 9 inches high, one of the glass tubes, into the receiver & the bottom of the receiver being up the new middle half of a spirit cock in along with it into covering all the rest & length put up, which then must be made to adhere but none of it must go of a bladder must be inches long, which must

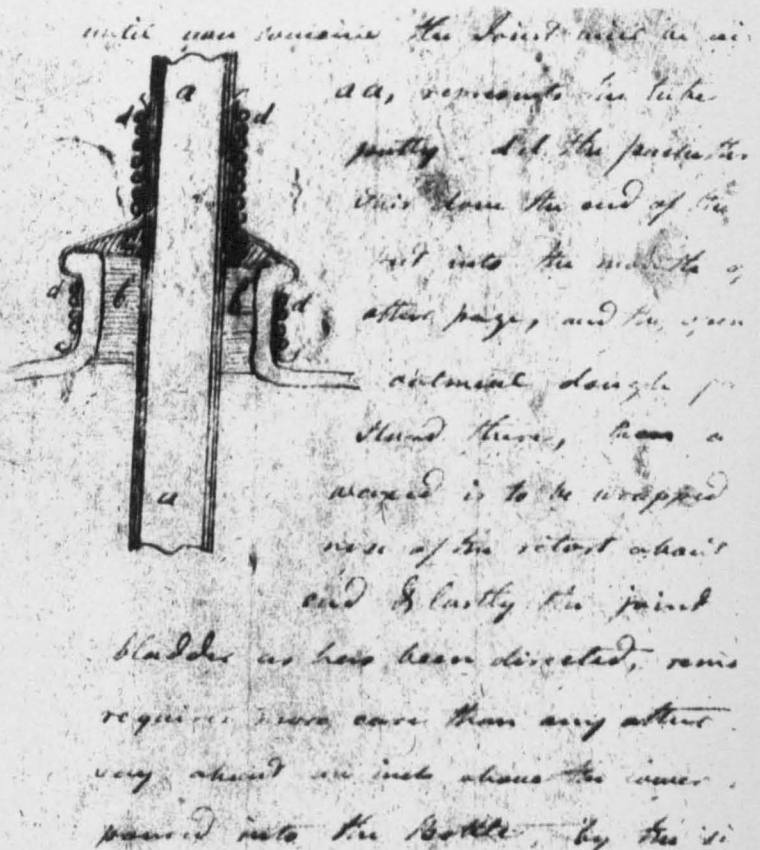


Fig. 'B' courtesy of Birmingham City Archives.

Under the entry for Bleaching, Ure expressed uncertainties about test liquors based on dissolved indigo in sulphuric acid:

But they are all more or less uncertain, from the changeableness of these colouring matters. I have met with indigo of apparently excellent quality, of which four parts were required to saturate the same weight of oxymuriate of lime, as was saturated by three parts of another indigo. Such coloured liquors, however, though they give no absolute measure of chlorine, afford useful means of comparison to the bleacher.

APPENDIX III

James Watt to McGrigor, 27 April 1787. Loc. BCA. JWP. LB/1 p. 202.

Refers to Berthollet:

In relation to the inventor he is a man of science and a member of the Royal Academy at Paris and a Physician, not very rich, a very modest and worthy man and an excellent chemist - my sole motives in meddling with it were to procure such reward as I could to a man of merit who had made an extremely useful discovery in the arts and secondly I had an immediate view to your (McGrigor) interest. as to myself I had no lucrative views whatsoever it being a thing out of my way which both my business and my health prevented me pursuing further than it might serve for amusement when unfit for more serious business. Lately by a letter from the inventor he informs me that he gives up all intentions of pursuing it with lucrative views as he says he will not compromise his quiet and happiness by engaging in business, in which perhaps he is right, but if the discovery has real merit as I apprehend, he is certainly entitled to a generous reward which I would wish for the honour of Britain to procure for him, but I much fear in the way you state it that nothing could be got worth his acceptance. I would myself venture provisionally to give him a sum for the invention and secure myself by the patent the best way I could which I think not impossible, but unfortunately for that scheme a friend of his and mine had without my knowledge very imprudently formed a connection for the inventor with two people in London who would now drop it and assist the inventor but I should not like either to make them partners with me nor endeavour to take a patent without them. I however know more of it than either they or I believe the inventor does (as to making it cheap and portable) and even if the matter shd be published by the inventor it may certainly be made very beneficial to you as I can put you in the way of going directly to work and even of supplying ? others ? if you chose it. I have not wrote the inventor in answer until I see how it answers as to money and am not sure what I shall write him yet but shall ask his leave for you to pursue it, which I dare say he will have no objection to.

APPENDIX IV

Watt to McGrigor. Loc. BCA. JWP. LB/1, p. 212.

Presumably these are instructions to McGrigor: (see fig. A.)

The retort a, being placed at a proper height in one of the rings belonging to its stand so that its bottom may be about 9 inches distant from the flame of the lamp at g, one of the glass tubes, with a single bend as at dc, is to be fixed into the receiver A so that the lower end may reach near to the bottom of the receiver and is to be made tight to the receiver 1st by filling up the [illegible] width of the mouth of the receiver with the two halves of a split cork hollowed out to fit the tube and forced in along with it into the mouth of the receiver. 2ndly by covering all the cork and rim of the mouth of the bottle with the tough putty (which the receipt for making follows) the putty must be made to adhere firmly to the tube and to the rim of the bottle but none of it must go below the edge of the rim then a stripe of an ox bladder must be cut about 2½ inches wide and 8 or 9 inches long which must be soaked in cold water until it be quite pliable and soft. In that state it is to be wrapped about the neck of the bottle and the tube so as quite to cover the putty and to go about an inch above it on the tube & care is to be taken that there be no putty on the part of the tube or neck of the bottle where the bladder is to fasten as that would hinder it from taking hold

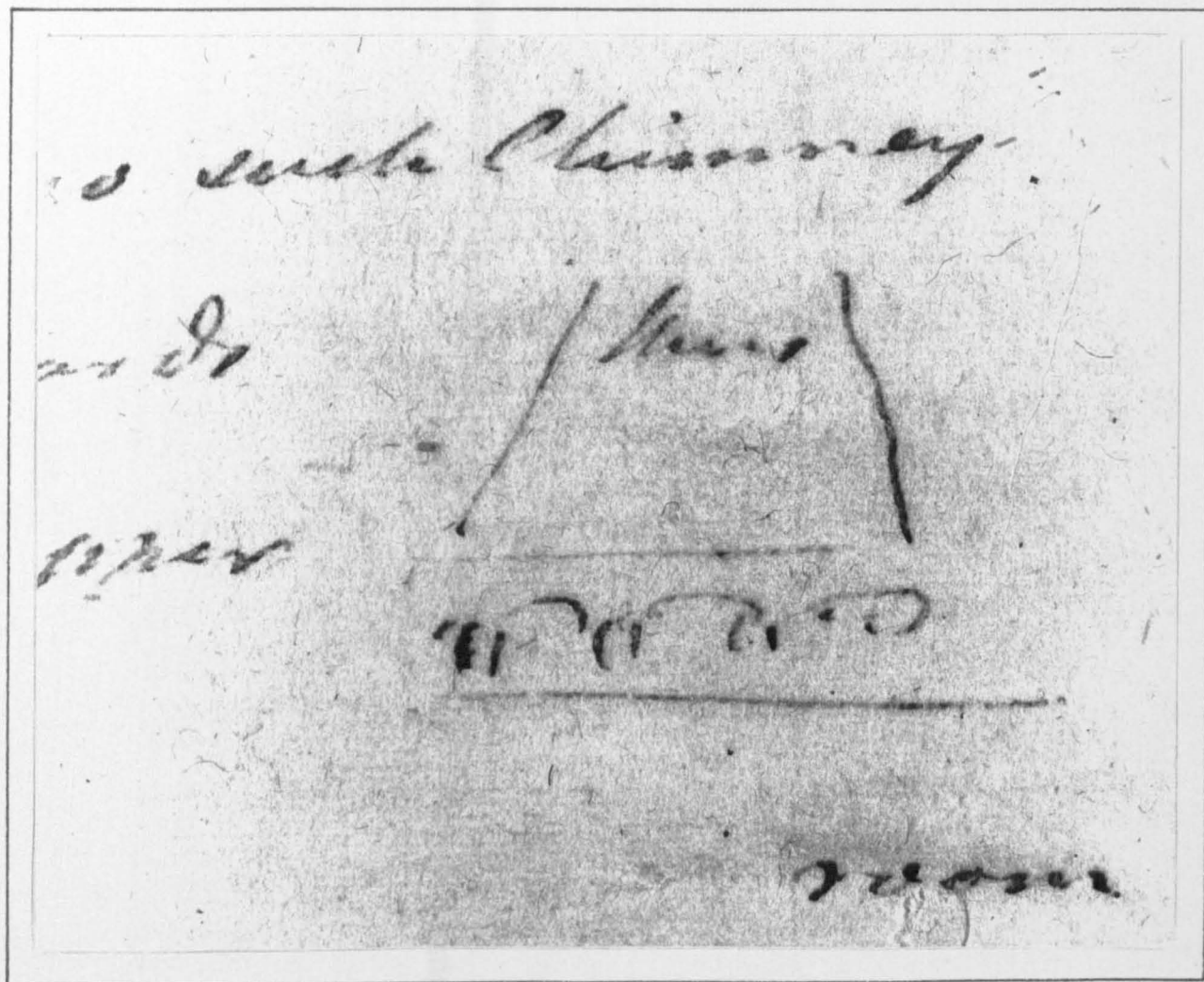


Fig. 'C' courtesy of Birmingham City Archives.

A piece of small (illeg) twine (illeg) is then to be wrapped round the bladder first upon the neck of the bottle and then about the bladder on the tube until you surmise the joint will be air tight [see fig. B.]. aa represents the tube, bb the cork, cc the putty, dd the (illeg) thread tying on the bladder. This done the end of the treated? tube is to be put into the retort at d on ye other page and the opening is to be (illeg) filled up with oatmeal dough for the putty will not stand there, then a taylor's thread well waxed is to be wrapped 3 or 4 times round the nose of the retort about $\frac{1}{2}$ an inch from the end and lastly the joint is to be well secured with bladder as has been directed remarking that this joint requires more care than any other - Then a little water say about an inch above the lower end of the tube is to be poured into the bottle by the side opening.

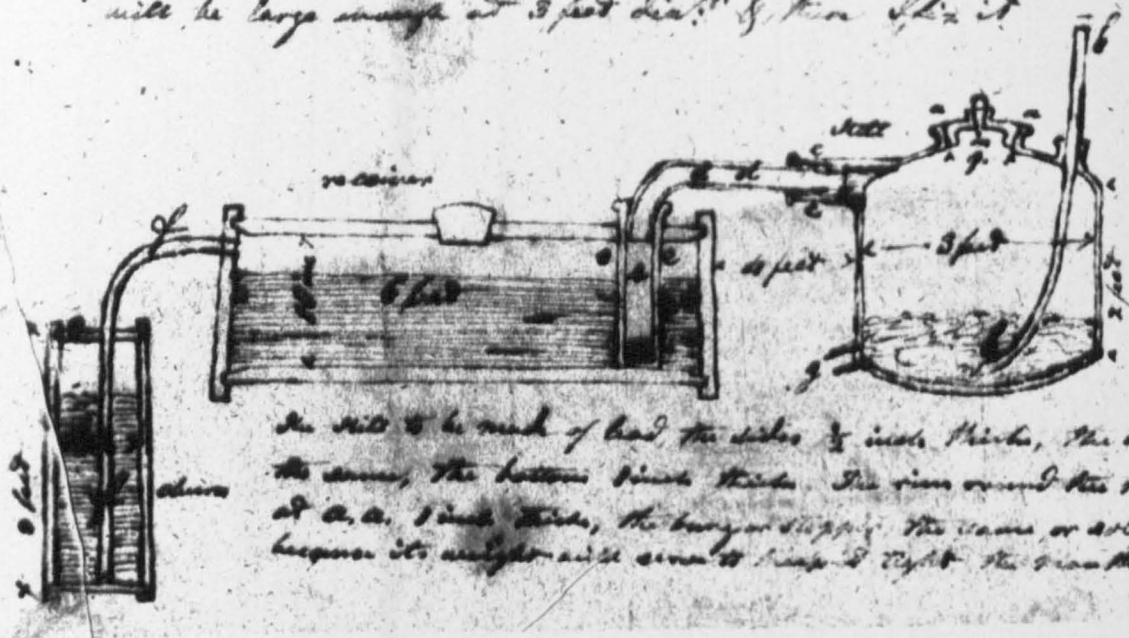
Next the receiver C is to be placed in an earthen vessel BB about $2\frac{1}{2}$ inches all round wider than the receiver say about 10 inches diam. and as deep as the receiver is high or nearly so. One of the tubes with a double bend as cf is to be adapted so that the straight end may reach to the bottom of the receiver while the short bended end at e fits into the side opening of A about an inch from the rim of the nipple (measuring from outside) at the same time the bend at f should be about 2 inches above the rim of the receiver C If the tube proves too long either end may be cut off by a new 3 square file to the proper length. The straight leg of the tube is then to be fastened into the mouth of the bottle C by means of a split cork, putty and bladder as have been described then the end at e is to be fastened into the nipple in the same manner only as it will not admit of a cork you may wrap paper round it till it fits cutting the paper off level with the mouth of the nipple the putty and bladder it as has been directed in the like manner you are to proceed with the receivers D E and F with their tubes. The tube of F goes into the bottle G which is left open in the mouth. To avoid embarrassment in the first trial you may use only the receivers A C D and E with the open bottle G.

As you proceed the bottles except A must be respectively filled with cold water nearly to the inner opening of the nipple or to the short end of the tube as represented in the drawing but no water is to be put into the earthen vessels until all the joints are made. It will be proper to make the joining of the straight legs of the tubes out of the earthen vessels for more convenience but the joints of the nipples must be made in their places as the receivers cannot be moved afterwards - The bottle G is not to be filled with water but with weak Alkali very caustic about 6 inches deep. Each bottle will hold about three pints so that the four receivers will hold about four quarts of water and much depends upon it being extremely cold - You are now to pour very cold water into the earthen vessels until it stand a little higher than the surface of the water in the receivers the use of which is to keep them cold and if ice can be got a quantity should be put into each of the earthen vessels.

Take [symbol for manganese] pounded and sifted through a coarse hair (search?) 1 oz avoirdupois, Common [symbol for salt] salt dried and rubbed fine 2 oz mix them well together by rubbing them on a board or stone then turning out the stopper of the opening of the retort at c pour them in by means of a paper funnel taking care that no part of them fall upon the part of the retort at x Then weigh 3 oz of strong oil of vitriol OV and mark the bottle you weigh it in that you may measure it afterwards in other operations. This done and ready - weigh or measure 2 oz of [symbol for water] and pour the [symbol for water] by means of a glass funnel into the retort so that it may fall upon the [symbol for common salt] and [symbol for manganese] and wet them all over. Lett your funnel not be wide in the bore - Then having the stopper at hand, pour in your OV Gently keeping out of the fumes which will instantly arise. When all the OV is gone in, pour a few drops of water through the funnel withdraw it and instantly put in the stopper turning it a little to make it tight. If it does not prove perfectly so or does not (illeg) quite fast tye a double bladder over it, both to keep it tight and to prevent it springing out during the operation.

The best way to avoid the fumes is to place the whole apparatus under a wide chimney and to open a door or window at your back which may determine them to go up the chimney. If you have no such chimney convenient one may be made with boards going through the ceiling into an upper room or into a common chimney and coming down within 18 inches of the retort [see fig. C.]. As soon as you stop the retort the Gas will begin to proceed through the tubes and Receivers, in the form of air and what is not condensable will issue at the open mouth of G the retort and first receiver will be filled with yellow fumes and the water in A will soon assume the same colour - The lamp is now to be lighted and with a very short flame, when you perceive the gas or air comes slowly

or we have 74 nearly which shows that the still must have 74 times the surface of the 5 inch vessel, which will give 43 inches for the dia. of the vessel or still, for $5 \times 5 = 25$ & $74 = 1850$ the sq. root of which is 43 inches. But as the ingredients may be allowed to be somewhat deeper in the still than they are in the vessel, I think it will be large enough at 3 feet dia. & I think it



the still to be made of lead, the sides 1/2 inch thick, the top the same, the bottom 1/2 inch thick. The rim round the mouth of the still 1/2 inch thick, the bung or stopper the same or solid because its weight will serve to keep it tight. The mouth

Fig. 'D' courtesy of Birmingham City Archives.

the lamp is to be sett under the retort and the flame raised gradually so as to keep the air coming slowly and regularly and so that little of it escapes at G, if much comes there give less heat. When you have encreased the flame to the utmost it admits of without smokeing and yet the air comes slowly the lamp must be raised b putting pieces of boards under it about an inch at a time until the Glass of the lamp comes within about $\frac{1}{2}$ an inch of the bottom of the retort. when in that state and with a full flame you perceive the air coming very slowly and the neck of the retort very hot with watery vapours even to the point it is a mark that the operation is over. another mark is that the black [symbol for manganese] in the retort will become of a light buff colour when all these signs occur the bladder must instantly be cut off the stopper and the stopper taken out, avoiding the fumes, and the lamp soon after withdrawn from under or extinguished then to stop more fumes from rising an ounce or two of [symbol for water] may be poured into the retort. Then the joint at d and all the joints at the nipples may be untied and the bladders put in water to serve again, but the joints of the tubes with the mouths of the bottles need npt be undone as they will serve many times, the nipples may be immediately corked to keep in the Gas or you may immediately pour out the contents of all the bottles except A and G into some large Glass bottles to be kept for use C and D will be the strongest but the whole may be mixd and is then the Whitening liquor to which as much mild [symbol for alkali] may be added as will just take away the Colour.

Then follows a paragraph regarding the preparation of putty.

APPENDIX V

James Watt to McGrigor, 14 November 1787. Loc., BCA. JWP. LB/1, p. 229:

The next principle vessel reached is some kind of a distilling vessel of lead for which I send you drawing below as also the manner of connecting it with the receiver. To find the size of the still I proceed thus. The receiver being filled with water one foot deep will contain 883 quarts and as a retort of 5 inches diam is sufficient to contain the ingredients for impregnating 12 quarts of liquor divide 883 by 12 we have 74 nearly which shows that the still must have 70 times the surfacr of the 5 inch retort which will give 43 inches for the diam of the vessel or still, for $5 \times 5 = 25 \times 70 = 1850$ the square root of which is 43 inches. But as the ingredients may be allowed to be somewhat deeper in the still than they were in the retort I think it will be large enough at 3 feet diam. and there I fix [see fig. D.] The still to be made of lead the sides $\frac{1}{2}$ inch thick, the top the same the bottom 1 inch thick. The rim around the mouth at aa 1 inch thick the bung or stopper the same or solid because its weight will serve to keep it tight the mouth to be made very round and the bung turned to fit it well. The pipe bb of lead has also $\frac{1}{2}$ inch or $\frac{3}{4}$ inch diam. The large pipe cc 4 inches diam. the crooked pipe dd to have its outside to fit the inside of the other and to be $\frac{1}{4}$ inch thick, also of lead. The pipe ee to be of wood 4 inches inside diam and 1 inch thick The ff of lead 1 inch diam. The churn and receiver you have had directions for. All is drawn nearly to dimensions except the distance from the receiver to the still. g is a short pipe 2 inches diam to empty the still by. The still must not be soldered but what the plumbers call burnt together by means of red hot lead, and every care should be taken to make the lead solid and all the joints perfectly tight. The pipe ee is to be shut at bottom and to have a hole on one side the air going out at which will keep the water in motion and cause it to impregnate faster. The receiver is to be filled with water 1 foot deep and the churn 2 feet deep with weak caustic alkali the weight of the pillar of which will cause the air to press upon the water in the receiver and receive its full impregnation. My paper and time both being nearly out I must resume the subject in another letter.

APPENDIX VI

Marshall Papers, MS 200, item 55, pp. 57 and 58.

Loc., Brotherton Library Special Collections, University of Leeds:

Dec. 1800. Continued to use 90 lb cask material for a making, but only 20 lb lime in the receiver which now holds 350 galls

The liquor is stronger & bleaches more yarn when less lime is used, & 20 lb takes off the smell as much as is necessary.

A making bleaches 70 bundles the Suffol Col. If the yarn be laid out 6 or 8 days after boiling then taken up & chymicked, it uses less liquor & is whiter but not so yellow.

Tried a cask of bleaching powder from Tennant Knox & Co - 42 lb. cost as much as making of our own & only bleaches 10 bundles therefore was 7 times dearer. Though it appeared as strong by the Hydrometer and the Blue test, it had much less effect on the yarn than ours, which we cannot account for but by supposing that the acid is so far neutralised by the chalk as to make it act weakly on the linen yarn. It could then (illeg.) that this is not the case with respect to cottons, for the bleachers near Glasgow buy the powder speak of it as being as cheap as the liquor they made themselves.

March 1802. Used for 350 Galls water with 20 lb lime -----126 lb Salt 84 Manganese or 112 lb unconcentrated acid 90 vitriol 90 water a greater proportion of salt costs little & the liquor is stronger, and makes the yarn a fine pale yellow.

Dec 1802. Found that using a larger proportion of salt made the yarn too white for Suffk. Col. that is too pale and yellow. ...therefore reduce the quantity to 112 lb for the colour, but kept to 126 lb for full colour.

APPENDIX VII

Analyses of kelp samples.

Taken from Hendrick, J. 'The Value of Seaweeds as Raw Material for Chemical Industry', *Journal of the Society of Chemical Industry* **35** (1916), p. 569.

1914.

Potash ...	24.05	20.69	21.96	15.10	5.17	8.51%
Soda.....	10.44	8.90	16.85	13.68	2.55	10.05 %

1915

Potash....	19.34	8.89	10.32	8.97	10.84 %
Soda.....	9.45	15.93	15.02	9.37	10.90 %

Places of origin; Heisker Island, S. Uist, N. Uist, Benbecula.

APPENDIX VIII

The Chemical Constituents of Kelp.

%	1.	2.	3.	4.	5.	6.	7.
Na ₂ CO ₃	3.9	3.4	5.8	4.4	2.5	5	5-6
NaCl	14.0	6.8	9.9	10.2			
KCl	17.8	18.1	27.2	21.0			
K ₂ SO ₄	14.0	12.7	11.1	12.6			

%	8.	9.	10.	11.	12.	13.	14.	15.
Na ₂ CO ₃	2.8	4.4	4.0	4.9	3.5	5.0	4.0	3.2
NaCl	24.4							
KCl	3.3							
K ₂ SO ₄								

Sources.

- Imperial Institute Monograph on Potash (1922)
1. Scottish Weed burnt to a slag.
2. " " " a loose ash.
3. Irish Weed
4. Average of 1, 2 & 3 above.
5. Kirwan. Alkali in Scottish Kelp. Quoted by Clow, p.80.
- B.P.P. 1818 V. Salt Duties Enquiry.
6. Evidence, Alexander MacDonald.
7. Evidence, Benjamin Hawes Jr.
- Trans. Highland Society.
8. Vol. I Robert Jameson. Average of four samples.
9. " " " " " five good samples.
10. " 5 Andrew Fyfe " " thirty five samples.
11. " " " " " nine samples Driftwood
12. " 5 Parkes. Isle of Lewis kelp, Kelp.
13. " " " " Skye kelp.
14. " " Galway kelp.
15. " 5 (1820) Andrew Fyfe. Average of eight samples.

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APPENDIX IX

Copy of part of a letter by John Collison to George Goldie, 7th February 1782. Edin Univ Lib, Gen 875/11/42,43.

We received yours, of the 26 Ult and are sorry to find that you make so little progress in the Sale of our Marine Acid, it gains ground here and no one who has tried it will use any thing else as they find it so much more superior to oil of Vitriol, we have no doubt but your Bleachers and Callicoe printers will soon be of the same opinion. Finding by our partner Joseph Fry that the Bleachers and Callicoe printers in North Britain complain that the adulteration of Pot & Pearl Ashes is now become so universal as to render a genuine article exceedingly scarce & almost impossible to be procured we have now entered into the Manufacture of such Alkaline Salts from a conviction that we can make them of a quality much better than any that ever were imported..

28

Dear Sir

I have examined the sample of ^{ash} ~~the~~

~~is~~ prepared by Collison & Co & find it to be very strong & powerfull, ^{It contains more alkali than the} ~~compared with the~~

Best Alcant Barilla ^{about} ~~it is one half from~~ ^{in the proportion of 68 to 44} ~~the proportion of 68 to 10~~ ^{& more than the best} ~~in the quantity of~~

~~alkali which it contains~~ and the alkali which it contains is in a more active state than that of Barilla ^{it would be dangerous to use more} ~~inasmuch that~~ ^{one}

hundred w^t of this ash ^{will go further} ~~in place~~ of two or ^{some what} ~~more~~ of the ^{best} Barilla — It is an excellent ash for the soap boilers — It will ^{take} ~~only~~

a quantity of ^{Tallow} ~~oil~~ ^{proportional to the} ~~alkali which it contains~~ that is one half more than the best Barilla — and there is ~~not the~~ no need to use lime in drawing the lye from it

as it is already in a Caustic State — I made my Essay on the black or grey ash the bits of white ash appears ^{much} ~~weaker~~, but too little of it for an Essay



APPENDIX X

Draft reply of Black to George Goldie of the Edinburgh Linen Hall, n.d. (soon after 19 March 1782)
Location: Edin Univ Library Gen 873/II/47. Copy of original document reproduced opposite by permission of EUL.

Dear Sir

I have examined the ash prepared by Collison & Co. & find it to be very strong and powerfull [sic], It contains more alkali than the best Alicant Barilla in the proportion of 68 to 44 & more than the best Kelp in the proportion of 68 to 10 and the alkali which it contains is in a more active state than that of Barilla insomuch that I reckon [it would be dangerous in bleaching to use more] one hundred wt of this ash in place of two or somewhat more of the best Barilla It is an excellent Ash for the Soap boilers It will take a quantity of Tallow &c proportional to the alkali which it contains that is one half more than the best Barilla and there is no need to use lime in drawing the leys from it as it is already in a Caustic State

I made my Essays on the black or grey Ash the bits of white ask appeared much weaker, but too little of it for an Essay

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