Supplemental material for

Fluorimetry compared to spectrophotometry for Uranium evaluation in liquid waste

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To compute the standard uncertainties of the spectrophotometer $u(SP)$ and the calibration standards $u(CS)$, the uncertainty budgets were constructed based on the technical specification provided by the apparatus producer and the passport certificate of the standard reference materials. These budgets are presented in (Table S1).

Table S1. Uncertainty budgets for the spectrophotometer and the calibration standards

ID	Parameter	Limits of variation $\pm v$	Distribution type	Evaluation method [5]	Range, $2v$	Standard uncertainty, $u(X)$	Relative standard uncertainty, $ur(X)=u(X)/X$
Abs1	Photometric reproductibility	$\pm 0.005*Abs$	Rectangular	$(0.5*2v/\sqrt{3})$	$0.01*Abs$	$0.00288675*Abs$	0.00288675
Abs2	Photometric repeatability	$\pm 0.001*Abs$	Rectangular	$(0.5*2v/\sqrt{3})$	$0.002*Abs$	$0.00057735*Abs$	0.00057735
Abs3	Photometric linearity	$\pm 0.002*Abs$	Rectangular	$(0.5*2v/\sqrt{3})$	$0.004*Abs$	$0.0011547*Abs$	0.0011547
Abs4	Noise level	$\pm 0.0001*Abs$	Rectangular	$(0.5*2v/\sqrt{3})$	$0.0002*Abs$	$5.7735E-05*Abs$	5.7735E-05
Abs5	Drift (25 °C; 15 minutes)	$\pm 0.001*Abs$	Rectangular	$(0.5*2v/\sqrt{3})$	$0.002*Abs$	$0.00057735*Abs$	0.00057735
Abs	Photometric uncertainty	$u(Abs) = \sqrt{u(Abs1)^2 + u(Abs2)^2 + u(Abs3)^2 + u(Abs4)^2 + u(Abs5)^2}$				$0.00321507*Abs$	0.00321507
D	Display uncertainty	4 digits	Rectangular	$(0.5*2v/\sqrt{3})$	0.001	0.00028868	
W1	Wavelength accuracy (X set to 665 nm)	± 1 nm	Triangular	$(0.5*2v/\sqrt{6})$	2	0.40824829	0.000613907
W2	Wavelength repeatability (X set to 665 nm)	± 0.2 nm	Rectangular	$(0.5*2v/\sqrt{3})$	0.4	0.11547005	0.000173639
W3	Wavelength resolution (X set to 665 nm)	0.1 nm	Rectangular	$(0.5*2v/\sqrt{3})$	0.1	0.02886751	4.34098E-05
W	Wavelength relative uncertainty	$ur(W) = \sqrt{ur(W1)^2 + ur(W2)^2 + ur(W3)^2}$					0.00063947

<i>SL</i>	Stray light	<0.1 % from transmittance Rectangular (1/ <i>Abs</i>)	(0.5*2v/√3)	0.001	0.00028868/ <i>Abs</i>	0.00028868	
<i>M</i>	Monochromator relative uncertainty	$ur(M) = \sqrt{ur(W)^2 + ur(SL)^2}$				0.00070161	
<i>SP</i>	Spectrophotometer uncertainty	$u(SP) = \sqrt{u(Abs)^2 + u(D)^2 + u(M)^2}$				0.00335229	
<i>CS</i>	Calibration standards (<i>X</i> set to 300 mg L ⁻¹)	1% from <i>X</i>	Normal (0.95)	0.5*2v* <i>X</i>	0.01	1.5	0.005

In (Table S2) are presented the calculated values for uncertainty of the spectrophotometric method, u_{REF} , for each of the concentration standards values. It is observed that the greatest influence in u_{REF} is due to uncertainty of the calibration curve, $u[C(x)]$.

Table S2. Uncertainty of the spectrophotometric method, expressed in [mg L⁻¹]

<i>C</i>	<i>Abs</i>	<i>u</i> [<i>C</i> (<i>x</i>)]	<i>u</i> (<i>Abs</i>)	<i>u</i> (<i>SL</i>)	<i>u</i> (<i>D</i>)	<i>u</i> (<i>M</i>)	<i>u</i> (<i>CS</i>)	<i>u</i> _{REF}
0.25	0.113	0.049655052	0.000363303	0.002554647	0.000288675	0.002633465	0.00125	0.049808266
0.50	0.241	0.046874186	0.000774832	0.001197822	0.000288675	0.001357827	0.00250	0.046982991
1.00	0.532	0.044255852	0.001710417	0.000542622	0.000288675	0.000838663	0.00500	0.044582363
1.50	0.762	0.046017964	0.002449882	0.000378839	0.000288675	0.000743260	0.00750	0.046697797
2.00	0.997	0.051714668	0.003205423	0.000289544	0.000288675	0.000701963	0.01000	0.052776335

The raw data, for the 18 process samples, measured by both methods, **R** (spectrophotometry) and **A** (fluorimetry), are displayed in (Table S3).

Table S3. Raw data for the uranium concentration measurements by the two methods, expressed in [mg L⁻¹]

Level	R	A									
1	0.770	0.766	0.765	0.767	0.769	0.767	0.775	0.775	0.773	0.776	0.771
2	0.580	0.550	0.552	0.559	0.600	0.557	0.559	0.558	0.559	0.600	0.600
3	0.090	0.080	0.082	0.086	0.088	0.090	0.091	0.090	0.089	0.088	0.086
4	0.308	0.294	0.296	0.300	0.299	0.300	0.300	0.302	0.302	0.302	0.303
5	0.136	0.130	0.132	0.135	0.138	0.139	0.138	0.140	0.139	0.140	0.140
6	0.372	0.369	0.370	0.369	0.370	0.371	0.372	0.373	0.374	0.374	0.375
7	0.250	0.245	0.246	0.245	0.248	0.249	0.250	0.251	0.252	0.252	0.252
8	0.264	0.260	0.260	0.261	0.259	0.265	0.266	0.264	0.265	0.266	0.264
9	0.060	0.050	0.055	0.055	0.059	0.060	0.065	0.062	0.060	0.059	0.062
10	0.140	0.130	0.136	0.137	0.140	0.142	0.143	0.145	0.147	0.145	0.146
11	0.114	0.113	0.112	0.113	0.115	0.114	0.116	0.115	0.117	0.115	0.115
12	0.980	0.990	0.992	0.993	0.994	0.994	0.995	0.996	0.996	0.997	0.998
13	0.542	0.535	0.538	0.540	0.540	0.543	0.544	0.545	0.548	0.549	0.549
14	0.436	0.429	0.430	0.431	0.431	0.430	0.431	0.431	0.432	0.432	0.432
15	0.894	0.895	0.896	0.899	0.900	0.901	0.900	0.902	0.901	0.902	0.901
16	0.640	0.646	0.650	0.651	0.652	0.654	0.660	0.658	0.662	0.661	0.662
17	0.900	0.916	0.912	0.918	0.919	0.921	0.927	0.929	0.929	0.931	0.932
18	0.614	0.615	0.616	0.619	0.618	0.620	0.622	0.621	0.620	0.622	0.621

Each measurement value of raw data for the fluorimetric method was scrutinized for one outlying observation, applying the Grubbs test and comparing the test value with the critical value of 2.29 (10 measurements for a 5 % significance level) for each level. The results of the Grubbs test are shown in (Table S4).

Table S4. Grubbs test for the fluorimetric method

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1.06	0.91	1.95	2.03	1.99	1.22	1.39	1.11	2.01	2.06	0.99	1.86	1.68	1.91	1.95	1.67	1.05	1.82
1.30	0.82	1.39	1.33	1.43	0.77	1.05	1.11	0.86	0.95	1.66	1.04	1.06	0.91	1.54	0.98	1.62	1.41
0.82	0.49	0.28	0.07	0.59	1.22	1.39	0.74	0.86	0.76	0.99	0.62	0.64	0.10	0.29	0.80	0.77	0.17
0.34	1.43	0.28	0.28	0.25	0.77	0.35	1.48	0.07	0.20	0.33	0.21	0.64	0.10	0.12	0.63	0.62	0.58
0.82	0.58	0.84	0.07	0.53	0.32	0.00	0.74	0.30	0.17	0.33	0.21	0.02	0.91	0.54	0.28	0.34	0.25
1.11	0.49	1.11	0.07	0.25	0.14	0.35	1.11	1.46	0.35	0.99	0.21	0.19	0.10	0.12	0.77	0.51	1.08
1.11	0.53	0.84	0.77	0.81	0.59	0.70	0.37	0.76	0.72	0.33	0.62	0.39	0.10	0.96	0.42	0.80	0.66
0.63	0.49	0.56	0.77	0.53	1.04	1.05	0.74	0.30	1.10	1.66	0.62	1.02	1.11	0.54	1.12	0.80	0.25
1.35	1.43	0.28	0.77	0.81	1.04	1.05	1.11	0.07	0.72	0.33	1.04	1.22	1.11	0.96	0.94	1.08	1.08
0.14	1.43	0.28	1.12	0.81	1.49	1.05	0.37	0.76	0.91	0.33	1.45	1.22	1.11	0.54	1.12	1.22	0.66

Figure S1. Calibration curve for the spectrophotometric method

In (Figure S1) is displayed the calibration curve achieved with the standard values, the curve equation and the R -squared value (coefficient of determination that expresses the statistical level of agreement between the approximated regression line and the real data, where value of 1 means a perfect fit).

Figure S2. Cause and effect diagram for uncertainty sources of the spectrophotometric method

In (Figure S2) is presented the cause and effect diagram for the uncertainty sources of the spectrophotometric method.

Figure S3. Relation between uncertainty and concentration for the spectrophotometric method

A polynomial relation of grade 2 was detected, plotting the associated uncertainty values versus the concentration values (C ; u_{REF}) for the spectrophotometric method.