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7 **Determination of Octanol-Air-Partition Coefficients (K_{OA}) of Fluorotelomer**
8 **Acrylates, Perfluoroalkyl Sulfonamids, and Perfluoroalkylsulfonamido Ethanols**
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Compound Information on Target Analytes and internal Standards

Table SI1: Information on compounds applied in this study.

Compound name	Abbreviation	Purity /%	Producer
target compounds			
perfluorohexyl ethylacrylate	6:2 FTA	97	Aldrich, Munich, Germany
perfluorooctyl ethylacrylate	8:2 FTA	97	Fluorochem, Old Glossop, UK
perfluorodecyl ethylacrylate	10:2 FTA	97	Fluorochem, Old Glossop, UK
n-methyl perfluorooctane sulfonamide	MeFOSA	-	donated by 3M, Germany
n-ethyl perfluorooctane sulfonamide	EtFOSA	95	ABCR, Karlsruhe, Germany
n-methyl perfluorooctane sulfonamidoethanol	MeFOSE	-	donated by 3M, USA
n-ethyl perfluorooctane sulfonamidoethanol	EtFOSE	-	donated the Mabury group, Toronto University, Canada
compounds used as internal standard			
perfluorobutyl ethanol	4:2 FTOH	97	Aldrich, Munich, Germany
perfluorohexyl ethanol	6:2 FTOH	97	Lancaster Synthesis, Frankfurt, Germany
perfluorooctyl ethanol	8:2 FTOH	97	Lancaster Synthesis, Frankfurt, Germany
n-methyl perfluorobutane sulfonamide	MeFBSA	-	donated by 3M, Germany
n-methyl perfluorobutane sulfonamidoethanol	MeFBSE	-	donated by 3M, USA
compound used as injection standard			
1,3,5-trichlorobenzene D ₃	TCB D ₃	98	Aldrich, Munich, Germany

Experimental Setup

The setup to the device to determine octanol-air partition coefficients is presented in figure SI 1. The two lower glass columns are water-jacket glass columns, the third one is not. The first and the second column were attached to the circulated water bath to assure constant temperatures. The first column contained 2 g of cleaned Amberlite XAD-2 resin (Supelco, Munich, Germany) and glass spheres coated with octanol. The second column contained glass spheres which were coated with a solution of the target analytes in octanol. Compounds partitioned to the gas phase were trapped onto the third column which was filled with XAD-2 and was eluted afterwards.

Figure SI1: experimental setup for the determination of octanol-air partition coefficients.

Recovery Rates

Table SI2: Average recovery rates of internal standards and standard deviations (S.D.) of recovery rates.

compound	average recovery rate	
	/%	S.D. /%
4:2 FTOH	18	7.0
6:2FTOH	43	42.2
8:2FTOH	48	7.0
MeFBSA	115	38.3
MeFBSE	55	11.1

Determination of the Deviation Factor k_{IS} used for the Correction of the measured Analyte concentrations

The recovery rates of compounds used as internal standard in this method (4:2 FTOH, 6:2 FTOH, 8:2 FTOH, MeFBSA, and MeFBSE) differed from those of the target compounds. These differences were taken into account using a deviation factor (k_{IS}) which describes the deviation of the recovery rate of internal standards to the recovery rate of target compounds. The k_{IS} was calculated as $k_{IS} = R_{TC}/R_{IS}$, with R_{TC} being the recovery rates of the target compounds and R_{IS} being the recovery rates of substances used as internal standard. (table SI3). The k_{IS} was determined in two fold repetition for different concentration levels (1.25, 2.5, and 5.0 ng μL^{-1}). The relative standard deviation of the ratios ranged from 3.8 % (8:2 FTOH used for the correction of 10:2 FTA) to 15.8 % (MeFBSA used for the correction of MeFOSA and EtFOSA). Due to this additional correction factor, analyte recoveries were corrected reliably.

Table SI3: Average deviation factors (k_{IS}) and absolute and relative standard deviations (S.D.) of k_{IS} applied in the recovery correction of PFC (n=6).

compound used as IS	for the correction of	k_{IS}	S.D. abs.	S.D. rel.
4:2 FTOH	6:2 FTA	0.98	0.05	5.0
6:2FTOH	8:2 FTA	0.79	0.12	14.6
8:2FTOH	10:2 FTA	1.26	0.05	3.8
MeFBSA	MeFOSA, EtFOSA	0.56	0.09	15.8
MeFBSE	MeFOSE, EtFOSE	0.95	0.09	9.7

Calculation of K_{OA}

Air which was saturated with octanol was utilized to carry out the transfer of the target compounds (TC). The equilibrium, that is being considered is TC (liq soln, c_o) = TC (g soln, c_A).

K_{OA} was calculated as

$$K_{OA} = \frac{c_o}{c_A} = \frac{c_o * T_1}{m_A * V * T_2} = \frac{c_o}{\frac{(A - a)/b * (A_{IS} - a_{IS})/b_{IS} * k_{IS}}{(V * T_2)/T_1}}$$

with

c_o = concentration of the target compound in octanol [$\text{ng } \mu\text{L}^{-1}$]

A = peak area of the target ion [area]

a = intercept of the target ion calibration curve

b = slope of the target ion calibration curve

A_{IS} = peak area of the injection standard [area]

A_{IS} = peak area of the internal standard [area]

a_{IS} = intercept of the internal standard calibration curve

b_{IS} = slope of the internal standard calibration curve

k_{IS} = deviation factor

V = volume of synthetic air at the column head [μL]

T_1 = temperature of the synthetic air column head [K]

T_2 = temperature of the column [K].

The concentrations of target compounds in octanol are assumed to remain constant. However, a decrease of c_o over experimental time is expected due to the slow partition into the air phase (Harner and Mackay, 1995). Experimental conditions (flow and volume of synthetic air passing the system) were chosen that less than 10 % masses were lost due to partitioning to the gas phase.

Average K_{OA} Values determined at different Temperatures

Table SI4: Average (n=3) log K_{OA} values, absolute and relative standard deviations (S.D.) of 6:2 FTA, 8:2 FTA, and 10:2 FTA at temperatures from 278 to 313 K. ^a: n=2. ^b: n=1.

T /°K	6:2 FTA			8:2 FTA			10:2 FTA		
	K_{OA}	S.D.abs.	S.D.rel /%	K_{OA}	S.D.abs.	S.D.rel /%	K_{OA}	S.D.abs.	S.D.rel /%
278	5.02	0.09	1.79	5.90	0.06	0.99	6.54	0.02	0.27
283	4.81	0.04	0.91	5.65	0.05	0.93	6.32	0.05	0.73
288 ^a	4.71	0.00	0.06	5.52	0.01	0.14	6.19	0.03	0.53
293 ^a	4.72	0.02	0.43	5.43	0.04	0.72	5.78	0.05	0.87
298	4.67	0.06	1.30	5.34	0.01	0.15	5.68	0.01	0.17
303 ^a	4.62	0.02	0.48	5.40	0.04	0.69	5.68	0.05	0.82
308	4.04	0.03	0.73	4.80	0.05	0.97	5.29	0.08	1.56
313 ^b	3.99	-	-	4.61	-	-	5.08	-	-

Table SI5: Average (n=3) log K_{OA} values, absolute and relative standard deviations (S.D.) of MeFOSA, EtFOSA, MeFOSE, and EtFOSE at temperatures from 278 to 308 K. ^a: n=2. n.a.: not analysed.

T /K	MeFOSA			MeFOSE			EtFOSA			EtFOSE		
	K_{OA}	S.D.abs.	S.D.rel /%	K_{OA}	S.D.abs.	S.D.rel /%	K_{OA}	S.D.abs.	S.D.rel /%	K_{OA}	S.D.abs.	S.D.rel /%
278	6.68	0.01	0.21	6.69	0.01	0.14	6.88	0.02	0.29	6.95	0.01	0.11
283	6.62	0.03	0.50	6.69	0.01	0.19	6.89	0.02	0.34	6.94	0.01	0.13
288	6.53	0.06	0.86	6.64	0.03	0.46	6.76	0.06	0.84	6.87	0.06	0.88
293	6.44	0.04	0.62	6.52	0.02	0.27	6.72	0.03	0.46	6.75	0.02	0.25
298	6.32	0.01	0.17	6.48	0.02	0.32	6.65	0.04	0.58	6.71	0.02	0.37
303	6.24	0.03	0.42	6.36	0.01	0.17	6.54	0.02	0.23	6.59	0.01	0.15
308	6.14 ^a	0.04	0.67	6.26	0.03	0.45	6.40	0.02	0.25	6.52	0.03	0.49

Determination of the Volume of synthetic Air necessary for establishing Equilibrium Conditions

The measurement of a chemical's concentration in air over experimental time results in a curve that reaches a plateau after a certain time. At this plateau, the concentration in the air and in the octanol are supposed to be at equilibrium and the K_{OA} can be calculated as ratio of c_O/c_A (Harner and Mackay, 1995). Thus, the volume used for the determination of K_{OA} values had to be chosen that equilibrium conditions at the plateau are established.

300 μL of the standard solution I (6:2 FTA, 8:2 FTA, 10:2 FTA) or II (MeFOSA, EtFOSA, MeFOSE, EtFOSE) in octanol, 200 $\text{ng } \mu\text{L}^{-1}$ each, were spiked to the generator columns. The column was shaken for 1 min to ensure good dispersion. To determine the plateau regions several volumes of air were blown over the generator column at a flow rate of 0.05 L min^{-1} and temperatures of 278, 298, and 313 K. After a fixed volume of synthetic air 200 μL of the internal standard solution ($c = 5 \text{ ng } \mu\text{L}^{-1}$) was added to the top of the third column. The column was eluted with 50 mL of acetone in the direction opposite to the gas flow. After the solvent volume was reduced to 200 μL , 50 μL of the injection standard trichlorobenzene ($5 \text{ ng } \mu\text{L}^{-1}$) were added. The samples were measured by GC-MS using positive chemical ionization.

Figure SI 2 shows $\log K_{OA}$ values of FASA and FASE at different volumes exemplarily for a temperature of 298 K. The volumes used for final determination of the K_{OA} of FTA, FASA and FASE over a temperature range from 278 to 313 K are shown in table SI6.

Figure SI2: Log K_{OA} values of MeFOSA, MeFOSE, EtFOSA, and EtFOSE determined at 298 K for air volumes of 0.1 to 10 L. □, EtFOSA; ▲, MeFOSA; ○, MeFOSE; ▼, EtFOSE. Note that the K_{oa} values are based on single measurements and that the method uncertainty may have influenced the deviations in the plateau region.

Table SI6: Final volumes used for the determination of K_{OA} values over a temperature range from 278 to 313 K.

Temperature		V FTA	V FASA/FASE
/K	/°C	/L	/L
278	5	9	10
283	10	8	10
288	15	7.5	9
293	20	7	9
298	25	6.5	8
303	30	5.5	6
308	35	4	4
313	40	2	1.2

Calculations of the combined Uncertainty of the Method

The combined uncertainty is an estimated standard deviation equal to the positive square root of the total variance obtained by combining all the uncertainty components, using the law of propagation of uncertainty. The combined uncertainty of the entire method was calculated as follows:

$$K_{OA} = \frac{c_O}{c_A}$$

$$\text{with } c_O = \frac{m_O}{V_O} \quad c_A = \frac{m_A}{V_A} \quad V_A = \frac{V * T_2}{T_1}$$

$$m_A = \frac{A/A_{Inj} - a}{b} * \frac{A_{IS}/A_{Inj} - a_{IS}}{b_{IS}} * k_{IS}$$

$$K_{OA} = \frac{\frac{m_O/V_O}{(A - a)/b * (A_{IS} - a_{IS})/b_{IS} * k_{IS}} * P}{(V * T_2)/T_1}$$

with

m_O = mass of the target compound in octanol [ng]

V_O = volume of octanol [μ l]

P = purity of the target compound standard [%].

For the remaining parameters see section *calculation of K_{OA}* .

The standard uncertainty of each instrument used and of each sample treatment were added as described in guide for the expression of uncertainties in measurements (GUM) and EURACEM/SITAC^{1, 2}. If the standard uncertainty was not determined directly, a rectangular distribution of the manufacturer information was used. The deviations of the GC-MS were determined by multiple measurements (n=10) of a calibration standard (c= 0.5 ng μ L⁻¹). Values used for the calculation of the combined uncertainty of the K_{OA} of the target compounds are shown in table SI7. The combined uncertainty and the expanded uncertainty of the K_{OA} determination of each target compound are shown in table SI8.

Table SI7: Standard uncertainties at 298 K used for the calculation of the combined uncertainty of 6:2 FTA, 8:2 FTA, 10:2 FTA, MeFOSA, MeFOSE, EtFOSA, and EtFOSE.

	6:2 FTA	8:2 FTA	10:2 FTA	MeFOSA	MeFOSE	EtFOSA	EtFOSE
u(m)	2.31	2.31	2.31	2.31	2.31	2.31	2.31
u(Vo)	0.16	0.16	0.16	0.16	0.16	0.16	0.16
u(A)	6168	41243	20186	202	88	1691	82
u(a)	0.04	0.03	0.03	0.01	0.06	0.07	0.03
u(b)	0.03	0.02	0.02	0.01	0.05	0.08	0.03
u(AIS)	436	1013	1240	3106	1868	3520	2117
u(aIS)	0.02	0.03	0.03	0.13	0.07	0.13	0.07
u(bIS)	0.02	0.02	0.02	0.15	0.07	0.15	0.07
u(kIS)	0.06	0.13	0.04	0.19	0.08	0.17	0.11
u(V1)	0.00	0.00	0.00	0.00	0.00	0.00	0.00
u(T2)	0.01	0.01	0.01	0.01	0.01	0.01	0.01
u(T1)	0.08	0.08	0.08	0.08	0.08	0.08	0.08
u(P)	0.02	0.02	0.02	0.02	0.02	0.02	0.02

Table SI8: Relative combined uncertainty and relative expanded uncertainty of the determined K_{OA} values of 6:2 FTA, 8:2 FTA, 10:2 FTA, MeFOSA, MeFOSE, EtFOSA, and EtFOSE (%) at 298 K.

	combined uncertainty / %	expanded uncertainty / %
6:2 FTA	5.1	11.6
8:2 FTA	10.0	22.6
10:2 FTA	7.8	17.7
MeFOSA	17.6	39.8
MeFOSE	14.9	33.8
EtFOSA	14.8	33.5
EtFOSE	13.1	29.6

References

- (1) ISO, *Guide to the Expression of Uncertainty in Measurement*. 1995, Geneva, Switzerland: International Organization for Standardization.
- (2) Ellison, S.L.R.R., M.; Williams, A., *Quantifying Uncertainty in Analytical Measurement*. EURACHEM/CITAC Guide. 2004.