

Experimental determination of Henry's Law Constant for some dioxins

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Introduction

In this paper a dynamic method to determine gas-water partition coefficients (K-values), respectively Henry's Law Constants (HLCs), is presented. The K-values, the HLCs and the water solubilities (S) for some lower chlorinated dibenzo-para-dioxins (PCDDs) were measured.

Methods for the experimental HLC determination can be roughly divided into kinetic and static thermodynamic methods. A new dynamic method has been developed to avoid the disadvantages of static methods, like long equilibration time for large gas volumes and the adsorption phenomena. A column operating in concurrent mode was used as published before by Piringer et al. /1/ and Brunner et al. /2/, that produces a guaranteed phase equilibrium. The gas-water contact area is supposed to be as large as possible whereas the adsorption areas are consequently small.

Experimental

In Figure 1 a scheme of the apparatus is shown. An aqueous solution with three lower chlorinated dioxins (2,7-DiCDD, 1,2,4-TriCDD, 1,2,3,4-TetraCDD) is produced by the purging of water through a generator column (B) using a pump (A). Samples can be taken at the two-way tap (C) to determine the water solubility of the substances. Pure gas (nitrogen) flows in concurrent mode with the dioxin-loaded water through the gas-liquid desorption column (D). The phase equilibrium is guaranteed during the gas-water contact. At the bottom of the column, the water is separated from the gas and is collected in a vessel (F). The gas is conducted into an absorption vessel (G), where the dioxins are dissolved in an organic solvent (dichloromethane). The dioxins in the water phase are extracted by liquid-liquid extraction using dichloromethane. The generator column (B) and the gas-liquid desorption column (D) are thermostated. All experiments were carried out at 25°C.

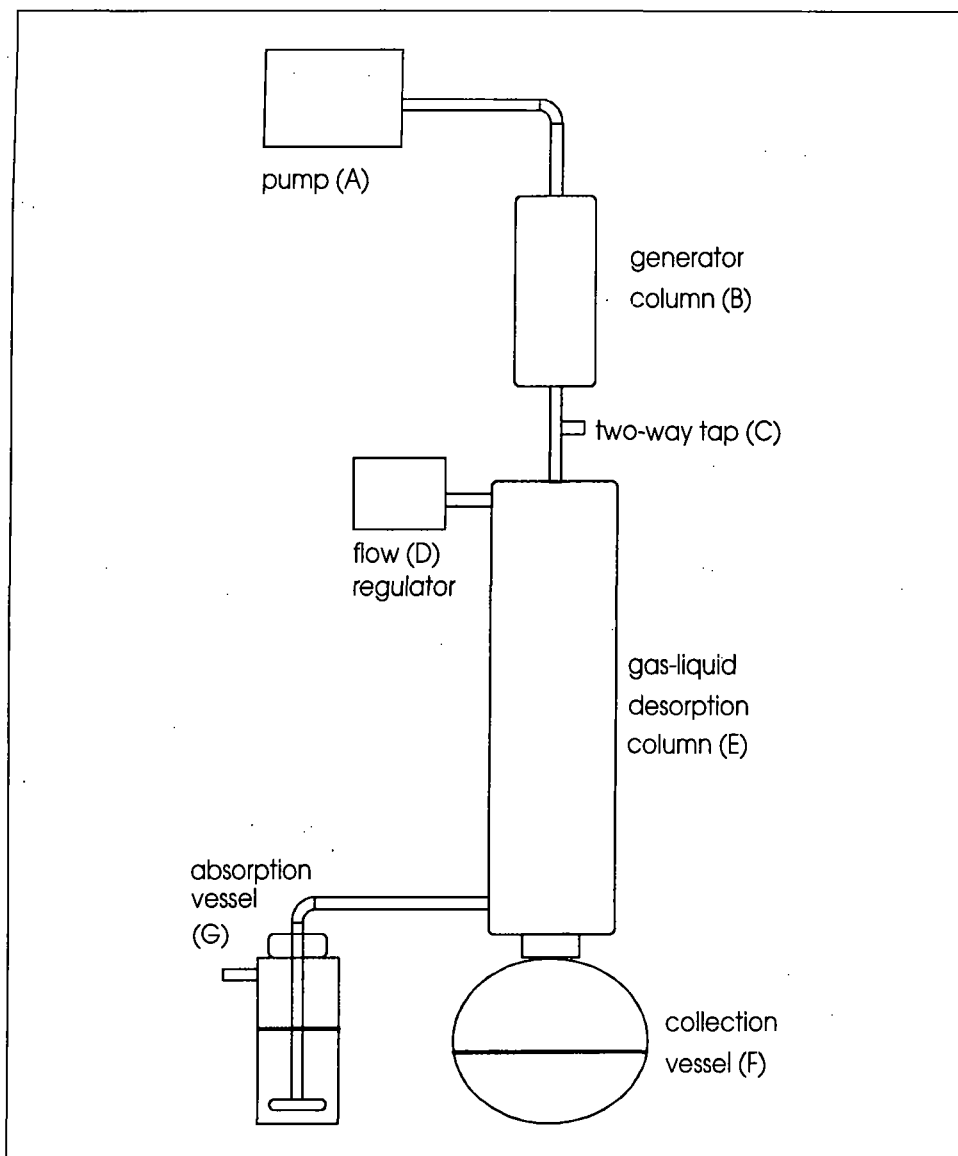


Figure 1: Scheme of the apparatus for the determination of gas-water partition coefficients

All samples were evaporated to dryness and dissolved in 2.0 ml hexane and spiked with an internal standard ($^{13}\text{C}_{12}$ labeled DiCDD and TCDD) for quantification. The analyses were carried out by GC/HRMS using a DB-5 capillary column.

With this method the air and water concentrations of the dioxins can be determined and the gas-water partition coefficients, respectively Henry's Law Constants, are calculated as their ratio. For the control of mass balance, samples from the initial aqueous dioxin solution were taken at the two-way tap (C) before and after each experiment and were compared with the

solutions in the vessels from the water (F) and the gas phase (G). This is important to evaluate uncontrolled losses of dioxins, for example by adsorption.

Results and Discussion

In Table 1 the dimensionless K-values and the corresponding HLC values (in Pa m³/mol) and the values of the water solubility (in µg/l) are shown. The mean values of seven experimental runs for DiCDD and TriCDD, respectively five runs for TetraCDD, are given together with the corresponding standard deviations (SD). For each run also the mass balance has been determined as mentioned before in order to prove the reliability of the results.

Table 1: Experimental determined K-values, HLCs and water solubilities of some dioxins

Substance		2,7-DiCDD	1,2,4-TriCDD	1,2,3,4-TCDD
No. of runs		7	7	5
Solubility (µg/l)	mean	2,33	6,95	0,404
	SD	0,41	0,83	0,053
K-value (dimensionless)	mean	2,40 E-3	1,47 E-3	8,16 E-4
	SD	0,31 E-3	0,27 E-3	1,23 E-4
HLC (Pa m ³ /mol)	mean	5,96	3,64	2,02
	SD	0,77	0,67	0,31
mass balance (%)	mean	101	106	94

The measured values of the water solubility were slightly lower than those reported by Doucette et al. /3/ and Shiu et al. /4/, whereas the standard deviations were a little bit higher. This depends on the higher variations of the temperature control unit of the apparatus ($\pm 0,4^{\circ}\text{C}$).

The values of the gas-water partition coefficients ranged between 8,16 E-4 for 1,2,3,4-TetraCDD up to 2,40 E-3 for 2,7-DiCDD, the Henry's Law Constants from 2,02 Pa m³/mol to 5,96 Pa m³/mol respectively. These experimental determined datas have the same order of magnitude as the values which were calculated by Shui et al. /4/. The guaranteed equilibrium and the verification of the mass balance, as shown in Table 1, confirm the high reliability of our values despite of the large standard deviation range. Unfortunately it is not possible to compare our results with other experimental data, because until yet only Webster et al. (cited in /4/) have presented one experimental determined HLC of 1,3,6,8-TCDD.

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References

- /1/ Piringer O, Sköries H. In: *Analysis of Volatiles*, Schreier P (Ed.), Walter de Gruyter, Berlin, 1984, pp 49-60
- /2/ Brunner S, Hornung E, Santl H, Wolff E, Piringer O, Altschuh J, Brüggemann R. *Environ Sci Technol* 1990, Vol.24, No.11, pp 1751-1754
- /3/ Doucette W, Andren A. *Chemosphere* 1988, Vol.17, pp 243-252
- /4/ Shiu WY, Doucette W, Gobas F, Andren A, Mackay D. *Environ Sci Technol* 1988, Vol.22, No.6, pp 651-658