



# Determination of Henry's Constant of Polychlorinated Biphenyls Using Epics-Spme-GC Technique

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## ABSTRACT

Polychlorinated Biphenyls(PCBs) are the semi volatile organic pollutants which are lipophilic, hydrophobic and carcinogenic in nature. PCBs are resistant to degradation, due to which, they are persistent in environment and migrate far distances from the origin of their use. Volatilization from water bodies to the atmosphere is a significant environmental pathway for migration of hydrophobic pollutants like PCBs. Knowledge of Henry's law constant (H) is essential in calculating the rate and direction of transfer. Henry's law constant (H) is the ratio of concentration of a compound in air to that of water at equilibrium. A modified equilibration technique was used to determine the Henry's Constants for seven Polychlorinated Biphenyls (PCBs) which are found in the environment. This method involves the combination of Equilibrium Partitioning in Closed systems (EPICS) and Solid Phase Micro Extraction (SPME) sampling technique, in which an aqueous diluted stock solution is prepared and attained equilibrium dynamically in a closed system. Further sampling of headspace and water in the experimental set up is done consequently. SPME is an integrated process in which sampling, extraction and pre concentration is done simultaneously. Analysis was done using Gas Chromatography coupled with Electron Capture Detector. By employing mathematical model, Henry's Constants ranging from 0.0001 to 0.02(non-dimensional) for different individual congeners were observed.

**Keywords :** Poly Chlorinated Biphenyls, Headspace, Equilibrium Partitioning in Closed Systems, Solid Phase Micro Extraction.

## I. INTRODUCTION

Polychlorinated Biphenyls are xenobiotic, aromatic, semi volatile organic chemicals first manufactured commercially about 1930 and which are widely used as transformer coolants, dielectric fluids, solvents, and flame retardants [1]. PCBs are commercially available as mixtures

with a name, Aroclor (e.g. Aroclor1060). They consist of biphenyl structure with two linked benzene rings in which some or all of the hydrogen atoms have been substituted by chlorine atoms. The chemical formula of PCBs is  $C_{12}H_{10-n}Cl_n$ , where  $n$  ranges from 1 to 10. Theoretically, 209 congeners are possible, but only about 130 of these have been identified in

commercial products. All the PCBs are lipophilic and their lipophilicity increases with increasing degree of chlorination. However, they have very low water solubility and low vapor pressure compared to volatile organic compounds. Congeners with a lower degree of chlorination are more volatile than those with higher degree. Pure individual congeners are colorless and often crystalline. Commercial PCB mixtures are clear to light yellow oils or resins and they do not crystallize, even at low temperatures.

PCBs have low degradability, high toxicity and also have the ability to bioaccumulate/biomagnify along food chains [2]. PCBs are practically fire resistant because of their high flash points (170°C – 180°C) [3]. They form vapors which are heavier than air, but are not explosive. They have very low electrical conductivity, high thermal conductivity and high resistance to thermal degradation. Due to these properties they have been used as dielectric isolators in electric equipment. Investigations in many parts of the world have revealed widespread distribution of PCBs in the environment and the universal distribution of PCBs throughout the world, suggests that PCBs are transported through air to very long distances from their point of origin [4-6]. Exposure of Humans to PCBs through air, food and water causes chloracene, hyper pigmentation, liver effects, chronic bronchitis, brain cancer [7], neuro behavioral effects. The occurrence of PCBs have also been reported in remote regions such as Antarctica and the Southern ocean atmosphere [8-14], seawater [8], soils [15,16] and biota [17-22]. The fate, transport and sinks of PCBs in different global regions and environments have received considerable attention during the last two decades [23]. The ability to co-distill, volatilize

from landfills into the atmosphere (adsorption to aerosols with a particle size of <0.05-20 $\mu$ m), and resistance to degradation at low incinerating temperatures, makes atmospheric transport the primary mode of their global distribution.

The partitioning of these organic compounds over different environmental compartments is one of the key processes in their environmental behavior. Whereas the partitioning between a solid fraction (sediment or soil) and a fluid (air or water) is a more complex process due to heterogeneity of the solid-phase, air-water partitioning is a better defined process. If air-water partitioning behavior is to be modeled in an environmental system, then in many cases Henry's law coefficients (H) determined in laboratory conditions can be implemented if temperature and salinity data are available. Henry's constant is defined as the ratio of concentration of a compound in gaseous phase to the water phase at equilibrium. Henry's constants play a vital role in explaining the many important industrial, toxicological, and environmental processes which transport chemicals between vapor and aqueous phases [24,25]. From the environmental aspect, Henry's constant (H), is a key parameter essential in modeling the diffusive exchange of semi volatile chemicals such as Poly Chlorinated Biphenyls (PCBs) between surface waters and the atmosphere [26-30]. Accurate knowledge of a pollutant's H and how it behaves with environmental conditions, including temperature and ionic strength, is essential to predict the environmental behavior, transport, and fate. But, the lack of the data available is a major limitation in predicting the environmental distribution and transport of organic pollutants such as PCBs.

Staudinger and Roberts [31] reviewed available and experimental data for Henry's law coefficients and observed the increase of values by 220% as temperature rises from 12°C-25°C. Two main types of experimental techniques are described in the literature. First, dynamic methods are described, such as the batch air stripping technique [32]. Next, static equilibration techniques are used such as the multiple phase equilibration technique [34], Gas purging technique [33] and the EPICS (equilibrium partitioning in closed systems) technique. The EPICS technique was first developed by A.H. Lincoff and J.M. Gossett [35-37] and further applied with modifications. Other static techniques are the vapor phase calibration method [38], and the phase ratio variation method [39]. EPICS is the method, in which dilute aqueous solution is taken in a closed system and allowed to attain equilibrium, then concentrations in headspace and aqueous solution is to be determined whose ratio gives the Henry value of,  $H$ . In this paper, Henry's constants for seven Polychlorinated Biphenyls of environmental concern were determined by the combination of modified EPICS-SPME-GC. SPME (Solid Phase Micro Extraction) is a sampling technique which has wide applications in the field of analytical chemistry and it is a less time consuming technique which can perform an integrated process of sampling, extraction and pre concentration simultaneously.

## II. Materials and Methods

### *Reagents:*

Seven Congeners, PCB 18, PCB 28, PCB 44, PCB 52, PCB 77, PCB 101, PCB118 were dissolved in

Iso-octane to make up a stock solution concentration of 10ng/ul. All the PCB congeners were obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany) with 99.9% purity. These stock solutions were directly used in the preparation of saturated solution without any further purification and dilution. Millipore water used in the experiment is double purified by the Milli-Q Water purification system. High purity Hexane, Methanol and Conc. HNO<sub>3</sub> were used for the cleaning of experimental apparatus.

### *Preparation of PCB Aqueous Solution:*

Aqueous solution of PCB was prepared by combination of generator column technique and ultrasonication. Few glass beads were added to a 100ml isooctane solution containing 5mg of PCB congeners of interest. The solvent was slowly evaporated with a gentle stream of N<sub>2</sub> gas forming a thin layer of PCB on the surface of the glass bead. Then beads are transferred into a conical flask of sufficient capacity and 100ml of water was added. It was ultrasonicated for 20 min to make the saturated solution of PCB. This solution was transferred into the set up with a magnetic bead inside and stirred at regular intervals of time to obtain equilibrium dynamically between headspace and the water.

### *Experimental Procedure:*

#### *a) For determining $H$ , directly:*

A 100ml saturated solution was taken into the vial of volume 300ml inside which a magnetic bead was present. Vial was closed with AOC septa, immediately after the solution was transferred to the experimental setup. Then system was allowed to attain equilibrium dynamically by using

magnetic stirrer. Sampling of headspace and water was done consequently and analysed using GC-ECD.

*b) For determining H, by model:*

To find out the Henry's constant by a model, for each individual PCB congener, two vials of volume 300ml were taken. Vials were cleaned with 1ml of Conc. HNO<sub>3</sub> and heated at 300°C and rinsed with hexane before aqueous solution is transferred to the vials. In the two vials, different volumes i.e., 100ml, 150ml of aqueous solution without differing amount of organic compound was taken followed by immediate closure of vials by AOC septa. Then, this was stirred on a magnetic stirrer at regular intervals of 15 min. At the end of each interval of stirring, air & water sampling was done using SPME for an exposure time of 15min and subsequently analysis was done with Gas Chromatography coupled with Electron Capture Detector. Sampling and stirring was done until the two phases in the system attained equilibrium i.e., responses in headspace and water were constant.

*Analytical Technique:*

Measurements were carried out using a Gas Chromatography (GC-2010 Plus) SHIMADZU coupled with Electron Capture Detector (ECD). The analytical column was Rxi®-5Sil MS of 30m length and 0.25 internal diameter capillary column. The mobile phase used was Helium and make up gas for ECD was nitrogen. The injector and detector temperatures were 250°C and 310°C respectively. The GC oven temperature was programmed as follows: initial temperature of 45°C for 0.5 min, then increasing to 230°C at the rate of 35°C per min and hold it for 7 min, then increasing to 280°C at the rate of 5°C and holding it for 13 min, then increasing to 310°C at the rate

of 15°C per min and holding for 10 min. The whole data was managed by GC solution software.

*Calculations:*

It is evident that the amount of a gas that will dissolve in water is directly proportional to its pressure. The constant of proportionality between equilibrium gas partial pressure and liquid concentration is now known as "Henry's constant". "Henry's law" is expressed a number of ways. Two that are commonly used in the environmental studies are:

$$H = P_i / C_l \dots \dots \dots (1)$$

Where H is the Henry's constant of the solute (m<sup>3</sup>-atm/mol), P<sub>i</sub> is the partial pressure of the solute (atm), and C<sub>l</sub> is the liquid phase solute concentration (mol/m<sup>3</sup>) [40].

$$H_c = C_g / C_l \dots \dots \dots (2)$$

Where H<sub>c</sub> is Henry's constant in dimensionless units and C<sub>g</sub> is the gas phase solute concentration (mol/m<sup>3</sup>). The dimensionless Henry's constant (H<sub>c</sub>) is used to simplify the derivation of the EPICS technique.

EPICS is based on a comparison of mass balances. When a volatile chemical is added to a closed system and a gas phase, a simple mass balance shows:

$$M = C_l V_l + C_g V_g \dots \dots \dots (3)$$

Where M is the mass added (mol), C<sub>l</sub> is the concentration in the liquid (mol/m<sup>3</sup>), V<sub>l</sub> is the total liquid volume (m<sup>3</sup>), C<sub>g</sub> is the concentration in the gas (mol/m<sup>3</sup>) and V<sub>g</sub> is the gas volume (m<sup>3</sup>). At equilibrium, the ratio of gas to liquid phase concentrations can be expressed as Henry's constant (Eq. 2), and the mass balance can be rewritten to include Henry's constant:

$$M = C_g V_l / H_c + C_g V_g \dots \dots \dots (4)$$

If the same mass of organic is added to two identical bottles (1 and 2) at the same temperature, but with different liquid volumes, Eq. 4 can be written for both and solved for Henry's constant.

$$Hc = \frac{\left(\frac{C_{g1}}{C_{g2}}\right)v_{l1}-v_{l2}}{v_{g2}-\left(\frac{C_{g1}}{C_{g2}}\right)v_{g1}} \dots\dots\dots(5)$$

Eq.5 [35] expresses Henry's constant as a function of the ratio of concentrations in only one phase. Plots of Henry's constant versus gas phase concentration ratio ( $C_{g1}/C_{g2}$ ) for various liquid volumes show that the technique has maximum sensitivity when one system has a low liquid volume and the other has a high liquid volume [40]. The total system volume was 300 ml and the two liquid volumes were 100 and 150 ml. It can be seen that the technique loses utility when the dimensionless Henry's constant ( $H_e$ ) is greater than two or three since the curve flattens out and the gas phase concentration ratio becomes nearly constant with respect to Henry's constant.

### III. Results and Discussion:

#### Selection of Fiber

A series of experiments was carried out for determining the maximum extraction efficiency for each PCB congener using three SPME fibers i.e., PA 85, PDMS 100, PDMS-DVB 65. The fibers were exposed to a constant concentration of standard. As shown in fig-1., PDMS-DVB fiber showed maximum response i.e. extraction efficiency for all the studied congeners. The response obtained by PDMS-DVB were about 2-10 time higher than other two fibers. Hence PDMS-DVB was used for all the further experimental analyses.

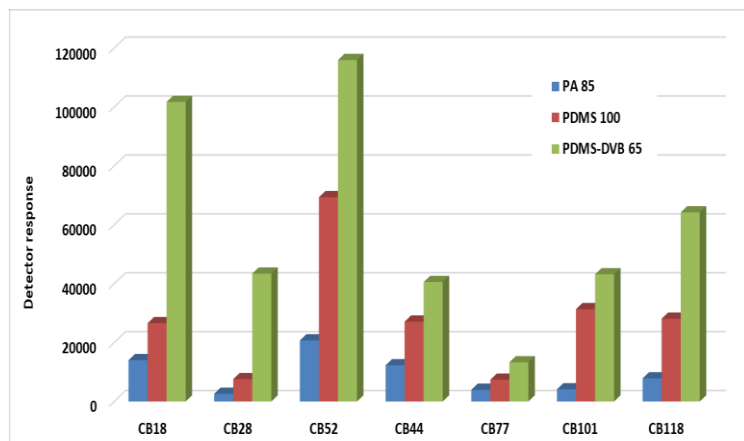


Fig-1: Detector Responses by different fibers.

#### Reproducibility

It is necessary for trace level analyses by SPME to check the reproducibility or repeatability response of the fiber. This was done by exposing the fiber to the known and constant concentration of the congeners for multiple times. As shown in fig.2, PDMS-DVB showed linear response to all the congeners. The minute variations in consecutive extractions were well within the expected statistical variations.

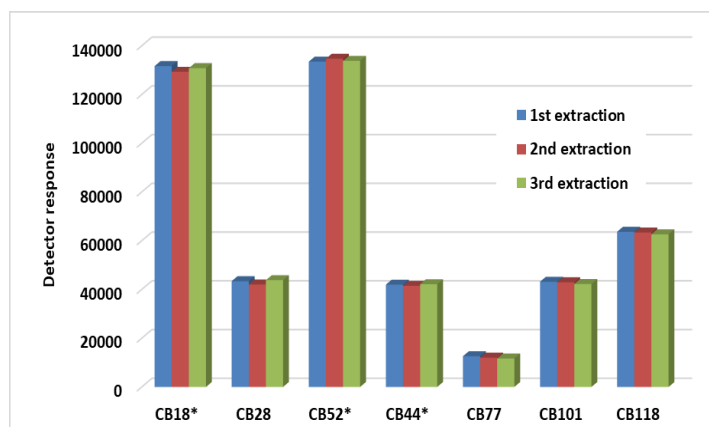


Fig-2: Linearity of response by PDMS-DVB fiber.

#### Experimental and mathematical determination of H values:

Two approaches were followed to determine Henry's constants (H) for seven polychlorinated Biphenyls with two experimental setups. In first experiment, EPICS was performed on a single

sample and the ratio of equilibrium concentrations of headspace and liquid phase was taken as H. In second approach a mathematical model was applied. For this the analysis were done for same mass of the analyte but different

volume in two different setups. Table 1 shows the results of both approaches alongwith their comparison with the literature values.

**Table-1: Comparison of H values by experiment, model and literature**

Compound	By Experiment	Literature values [41-46]	By Model
PCB 18	0.004±0.0002	0.102,0.023,0.010,0.0155,0.0129	0.05
PCB 28	0.008 ± 0.00056	0.015,0.0091,0.00129,0.0081	0.12
PCB 44	0.011 ± 0.00088	0.011,0.0098,0.0132	0.37
PCB 52	0.018 ± 0.00135	0.0125,0.0089,0.021,0.013	0.76
PCB 77	0.015 ± 0.0015	0.006,0.0017,0.0038,0.0041	0.49
PCB 101	0.019 ± 0.00076	0.016,0.013,0.0102,0.01005,0.0036	0.48
PCB 118	0.021 ± 0.00189	0.014,0.005,0.0037	0.33

PCB18 had the lowest H values while PCB 118 had the highest value. All the results showed an increasing trend in the H value with the degree of chlorination. However, PCB 77 showed slightly lower H value than expected, which could be due to planarity of its structure and also due to its aqueous solubility. Lower value of H indicates that the rate of transfer of the low chlorinated congeners from atmosphere to water is comparatively more and vice versa. The experimental H values were in good agreement with the literature values. However, the model values showed variation of the order of about 2 orders of magnitude. H values are dependent on a number of factors. Since there was only one system involved in the experimental determination, the variation in H wasn't

significant. On the other hand, the model approach uses two systems thus the number of variables in each system affects the value of the other system. Thus large variation in the H value was observed in this case.

#### IV. Conclusions

Henry's constants obtained by EPICS- SPME approach were in good agreement with the literature values, however literature values are scarce for PCBs. The values obtained for seven PCBs were following an increasing trend with increasing degree of chlorination except PCB-77. The values obtained by the mathematical model setup were higher than the experimental values. The results show that the air to water partitioning

of PCBs is mainly favored towards the water phase.

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