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Determination of ambient gas-particle partitioning constants of non-polar and polar organic compounds using inverse gas chromatography

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Abstract

Gas-particle equilibrium partition coefficients for organic compounds, K_{ip}, are traditionally determined using sample-and-extract methods, in which particles and the surrounding air are simultaneously sampled and concentrations are determined from extracts. Though these techniques are necessary for determining actual ambient concentrations, they have several shortcomings when they are used to gain insight on the sorption properties of ambient particles. Some examples are that (i) the role of relative humidity and temperature are difficult to account for due to fluctuating conditions, (ii) only compounds that are present in ambient air can be studied, and (iii) extracts themselves do not directly indicate if particle-bound compounds are in equilibrium with the air phase or not. An alternative approach that could overcome these shortcomings is inverse gas chromatography (IGC). In this work, we developed an IGC method that uses particle-loaded fiber filters as a stationary phase. The measured retention of analytes injected into the IGC system is a direct measure of the collected particle's sorption behavior. A validation study that used particles with known sorption properties indicates that this approach gives reliable K_{ip} values for a wide variety of compounds. Further, ambient particles from a suburban and urban location were found to be stable over time and to exhibit equilibrium sorption in the IGC, showing that this method is suitable for studying ambient particles. The IGC method presented here is a promising new tool for gaining deeper insights into the gas-particle partitioning behavior of polar and non-polar organic compounds.

Keywords: Ambient; Gas-particle partitioning; Fiber filters; IGC

1. Introduction

Sorption to airborne particulate matter is widely considered the dominating process for the long-range transport of various semi-volatile organic compounds (SVOCs), such as pesticides, PAHs, and PCBs. To better understand this important sorption process, in the last two decades, much effort has been put into measuring and modeling equilibrium gas-particle partition coefficients, K_{ip} (e.g. Pankow,

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1987; Harner and Bidleman, 1998; Mader and Pankow, 2002; Gotz et al., 2007). Most of the experimental K_{ip} values in the literature are determined from methods that can be categorized as "sample-and-extract" setups. In these setups, particles are sampled using a filter while gaseous organics are simultaneously collected using upstream denuders and/or downstream sorbents. Following sampling, extractions are carried out, and gas and particle bound concentrations of specific chemicals are determined. Though sample-and-extract methods are widely used, they are known to suffer from various artifacts, such as filter sorption artifacts (Arp et al., 2007; Volckens and Leith, 2003a, b) and radicals reacting with the sorbed organic compounds (Schauer et al., 2003). Further, extracts are not able to differentiate between chemicals in aerosol components that are available for equilibrium partitioning and those that are not, an example of a compound class where this issue has been raised is PAHs (Dachs and Eisenreich, 2000; Pankow and Bidleman, 1991; Lohmann and Lammel, 2004).

In the earlier work, we introduced an alternative to sample-and-extract methods that could overcome these artifacts (Roth et al., 2005a, b). This method involved packing collected particles into a column, mounting the column into a commercially available gas chromatograph, and determining the K_{ip} values using traditional inverse gas chromatography (IGC) techniques. IGC uses the same equipment and principles as gas chromatography; the main difference is that IGC involves dynamic sorption experiments to characterize the sorption behavior of the stationary phase (i.e. the column packing material itself is what is being studied). IGC methods have successfully been used for sorption studies of absorbing polymers and adsorbing surfaces before (e.g. Arp et al., 2006a; Charmas and Leboda, 2000; Gray, 1977) and should therefore also be appropriate for studying aerosol sorption. In addition to overcoming the above-mentioned artifacts, there are other advantages for using this method for determining K_{ip} values. For instance, IGC methods allow for the determination the K_{ip} values of compounds not already present on the particles and facilitate measurements at controlled relative humidities (RH) and temperatures. However, with the method we introduced previously, an inherent shortcoming is that it requires several mg of loose particulate matter (i.e. as a fine powder). Besides the practical disadvantage of obtaining such a quantity of collected particles, such samples may not be representative of *in situ* ambient particles depending on the sampling procedure. In addition, the chemicals that could be measured were considerably more volatile than typical SVOCs of environmental concern.

This paper presents substantial improvements to this IGC method, in which fewer particles are needed, where sorption to freshly collected particles can be measured without being removed from the collection filter, and in which compounds with a lower volatility can be measured. This method is validated here using the same particles that were used in our earlier study, as well as other particles with known sorption properties. In addition, the suitability of using this method for ambient particles is shown for freshly sampled urban and suburban particles, and accordingly, several K_{ip} values (Eq. (1)) are presented:

$$K_{ip}\,(\mathrm{m^3\,g^{-1}}) = \frac{c_{i\,\mathrm{particle}}}{c_{i\,\mathrm{air}}}, \tag{1}$$

where $c_{i\,\mathrm{particle}}$ is the equilibrium concentration of compound "*i*" sorbed to the particulate phase ($\mathrm{mol\,g^{-1}}$) and $c_{i\,\mathrm{air}}$ is the equilibrium concentration of *i* in the air phase ($\mathrm{mol\,m^{-3}}$). If sorption occurs by adsorption to the surface of the particle, such as in the case of mineral particles, it is more appropriate to use an adsorption coefficient normalized to the surface area:

$$K_{i\,\mathrm{surf/air}}\,(\mathrm{m^3 m^{-2}}) = \frac{c_{i\,\mathrm{surf}}}{c_{i\,\mathrm{air}}}, \tag{2}$$

where $c_{i\,\mathrm{surf}}$ is the equilibrium concentration of compound *i* sorbed to the particle surface ($\mathrm{mol\,m^{-2}}$).

2. Materials and methods

2.1. Chemicals

All chemicals investigated were ordered from Fluka (Buchs, Switzerland) except for Fluorotelomer compounds from Clarient (Sulzbach, Germany) and Fluorochem (Derbyshire, U.K.) and are listed in Part 1 of the Supporting information (SI).

2.2. Particle standards

Standard urban aerosol particles purchased from NIST (Standard Reference Material 1649a) are the same as used previously (Roth et al., 2005b).