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Development of thermal programmed desorption mass spectrometry methods for environmental applications

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Abstract

The physical availability of hydrophobic organic contaminants (HOCs) bound to soils and sediments often controls their environmental toxicity. Currently, complicated and time extensive procedures are necessary to determine physical availability. The development of thermal programmed desorption mass spectrometry (TPD-MS) techniques for environmental samples may make it possible to evaluate the physical availability of HOCs in soils and sediments and also calculate relevant release energy values for bound contaminants. This work focused on developing the analytical protocols and data processing requirements for studying the desorption of HOCs from various simple geosorbents using TPD-MS. The work seeks to document the use of the TPD-MS method as an environmental assessment tool and provide the reader with a working knowledge of the entire process.
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Keywords: Thermal programmed desorption; Physical availability; Release energy; Desorption

1. Introduction

There is widespread contamination of soils and sediments by various hydrophobic organic contaminants (HOCs) and remediation of these compounds often results in residual contamination that exceeds clean-up standards. This has led to an interest in determining whether these residual contaminants are available for uptake by plants and organisms and pose a threat to human health and the environment (Tang et al., 1998; Kraaij et al., 2002). Research has established that HOC concentrations in soils and sediments found by exhaustive extraction methods may not be indicative of the concentrations available to microorganisms (Kelsey et al., 1997; Alexander, 2000) and that contaminant availability tends to decrease with aging and treatment (Hatzinger and Alexander, 1995; Tang et al., 1998). This indicates that an understanding of the relevant sorption and desorption behavior of the solid-bound contaminant is essential for understanding physical availability.

In general, the strength or degree of the total sorption determines the physical availability of HOCs, their associated partitioning into the aqueous phase, and their subsequent uptake by microorganisms. Although bioavailability is defined differently in various disciplines, it is generally agreed that one necessary component of the process is the release of a solid-bound contaminant (Ehlers and Luthy, 2003). This release can be linked to the energy required to release the compound from its

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sorbent matrix, with a higher energy value indicating a more tightly bound compound. In surface science and catalysis literature, this energy is called desorption activation energy and is often found using thermal programmed desorption mass spectrometry (TPD-MS) techniques. These methods have limitations with respect to the assumptions made and many simplify the relevant surface chemistry (Miller et al., 1987; Nieskens et al., 2003; Panczyk and Szabelski, 2003). However, it is possible that one or more of these methods may provide an acceptable estimate of the release energy that can be used in environmental engineering models. For this work, the term release energy is defined as the total energy required to release the compound from its sorbent matrix and it includes the energy required for desorption from and diffusion through the sorbent matrix.

The expansion of TPD methods to evaluate the availability of contaminants in soils and sediments may provide a much needed correlation between release energy, availability and treatability. This work seeks to illustrate the TPD-MS method and its use for the assessment of physical availability of HOCs on various sorbents by documenting both the analytical process details and the data processing requirements.

2. TPD-MS background

TPD is a surface science technique that has been used extensively to study molecular adsorption and desorption and surface reactions. The principles of TPD were first described by Cvetanovic and Amenomiya for first order desorption from homogeneous surfaces (Cvetanovic and Amenomiya, 1972; Rudzinski et al., 2000). In TPD-MS, molecules attached to a surface are thermally activated using controlled heating of the surface, resulting in desorption and/or reactions (Hubbard, 1995). The desorbing products are monitored by a detector and reported as ion signal intensity versus time or temperature (thermogram). The concept behind TPD-MS is relatively simple, desorption products are related to the initially sorbed species and thus the thermograms provide qualitative and quantitative information about the species present and their interactions at the surface (Hubbard, 1995).

TPD methods have been used in the fields of surface science and catalysis for studying the interactions of pure gases on solid surfaces and determining the surface properties of a wide variety of compounds. Specifically, TPD methods have been used to examine the sorption behavior of gases (e.g. ammonia and carbon dioxide) on solid surfaces to determine heats of adsorption and desorption and assess the practicality of using these solid surfaces for adsorbents in industrial settings (Choudhary and Mantri, 2000; Joly and Perrard, 2001; Chang et al., 2003). TPD methods have also been explored for use in detecting and quantifying organic contaminants (e.g. polychlorinated biphenyls (PCBs)) in field soil samples (Robbat et al., 1992). TPD-MS methods have further been applied in conjunction with desorption kinetic studies to study the physical availability of polycyclic aromatic hydrocarbons (PAHs) on geosorbents (Talley et al., 2004) and harbor sediments (Ghosh et al., 2001; Talley et al., 2002). Though TPD methods have been used in many applications, the analysis of TPD data has normally been restricted to semi-quantitative analysis (Rudzinski et al., 2000) with most of the quantitative analysis occurring in the field of catalysis.

TPD-MS techniques use either ovens or thermal probes to heat samples before releasing desorption products into a mass spectrometer. Previous researchers have heated the sample and allowed the desorption products to flow into the mass spectrometer (Ahmed et al., 2000). Other systems have included high vacuum oven chambers that are connected via vacuum lines to a mass spectrometer (Sato et al., 1995; Joly and Perrard, 2001). Though these systems work, using a direct insertion probe (DIP) has the advantage of not requiring transfer lines. In a DIP type system, the probe holding the sample is inserted directly into the ion source and the sample is vaporized into the ion beam. This is useful for the analysis of samples that may be difficult to analyze using traditional chromatography methods (i.e. compounds that are thermally labile or highly active).

3. TPD-MS experimental method

For this work, a TPD-MS equipped with a DIP was used. The instrument setup included a Thermo Finnigan Polaris Q ion trap mass spectrometer and a Thermo Finnigan DIP (Fig. 1). The MS system operates with a typical foreline pressure of 25–30 mTorr and an ion gauge pressure of $2–6 \times 10^{-6}$ Torr. The DIP operates at temperatures ranging from ambient (25–30 °C) to 450 °C and can be heated in 10 °C/min increments up to 100 °C/min. The DIP glass sample vials are cylindrical with an inside diameter of 1.0 mm and a length of 10 mm. The probe holding the vial is inserted into the MS and the temperature is increased at a predetermined linear rate.

For this study, three temperature ramp rates (10 °C/min, 20 °C/min, and 30 °C/min) were used. These temperature ramp rates were chosen based on machine limitations and previous work conducted by Nicholl et al. (2004) and Talley et al. (2004), which found consistent results using a 10°/min temperature ramp rate. For all samples, the sample vials were filled approximately 1/8 full to limit interparticle-diffusion effects (Talley et al., 2004). Work by Talley et al. (2004) found that powdery samples exhibited a volume-dependent TPD response and determined that when sample vials were 1/16 to

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