

# Development of thermal programmed desorption mass spectrometry methods for environmental applications

Sara I. Nicholl, Jeffrey W. Talley \*

*University of Notre Dame, Department of Civil Engineering and Geological Sciences, 156 Fitzpatrick Hall, Notre Dame, IN 46556, United States*

Received 12 April 2005; received in revised form 29 June 2005; accepted 5 July 2005  
Available online 13 October 2005

## 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.

© 2005 Elsevier Ltd. All rights reserved.

*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

\* Corresponding author. Tel.: +1 574 631 5164; fax: +1 574 631 9236.

E-mail address: jtalley1@nd.edu (J.W. Talley).

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  $2\text{--}6 \times 10^{-6}$  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 °C/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

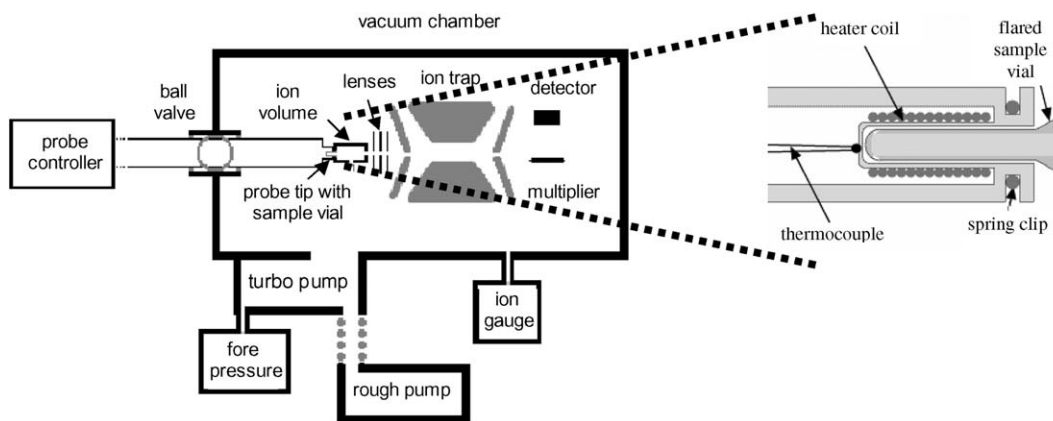


Fig. 1. TPD-MS schematic with direct insertion probe (Talley et al., 2004).

1/8 full, the release of PAHs was independent of the sample volume. This is important because previous work has noted that diffusion resistance and readsorption can cause broadening of the thermogram and a possible shift in the peak temperature (Rudzinski et al., 1999; Joly and Perrard, 2001; Park and Yang, 2005). In addition to limiting sample volume, the high vacuum should further limit readsorption.

The spiked samples (chrysene on glass beads, Ottawa sand and kaolin) were prepared as described by Nicholl et al. (2004). Briefly, dried sorbents were saturated with acetone to make a slurry and the requisite amount of the chrysene solution was added in order to produce a 20 ppm concentration (mg chrysene/kg sorbent). The slurry was shaken (as described by Nicholl et al., 2004) and allowed to evaporate until sorbents were completely dry.

#### 4. TPD-MS thermograms

From a TPD-MS thermogram, the desorbing products can be identified by their mass and mass spectral fragmentation patterns (Hubbard, 1995). Specifically, the ion intensities for selected mass-to-charge ratios ( $m/z$ ) are identified and assigned to desorbing species and the resulting fragmentation patterns are compared with standards. If the fragmentation pattern agrees with a pattern of a known compound, the desorbing species can be identified. Since TPD is performed under ultra-high vacuum and continuous pumping, the instantaneous ion intensity is proportional to the rate of desorption ( $d\theta/dt$ ) (the desorption “speed” at that instant) and the total area under the thermogram curve is proportional to the amount originally sorbed (Hubbard, 1995).

When using TPD-MS, the adsorbate coverage is an important variable that may affect kinetic parameters (Hubbard, 1995). Typically, the adsorbate is bound

more strongly to the substrate than to itself and this is manifested as a difference in peak desorption temperatures (i.e. monolayer desorption will have a higher peak desorption temperature than multilayer desorption) (Hubbard, 1995). For samples of environmental interest (spiked geosorbents and real soils/sediments), it is often difficult to determine coverage using TPD-MS alone, making assumptions concerning the surface coverage dependence necessary.

#### 5. TPD-MS and kinetic parameters

TPD-MS thermograms can be used to determine various desorption kinetic parameters including the desorption rate constant ( $k_d$ ), the order of the reaction ( $n$ ), the pre-exponential factor ( $\nu$ ), and the desorption activation energy ( $E$ ). The desorption rate constant describes how fast a species is desorbing from its substrate. The reaction order describes how the rate depends on surface coverage and typically ranges from 0 to 2.0 (Hubbard, 1995). Theoretically,  $n$  indicates the rate-determining step. For example, if  $n = 2$ , two surface species may collide on the surface, react and then desorb (Hubbard, 1995). If  $n = 1$ , a single molecule desorbs and interactions with other molecules do not control the rate of desorption (Hubbard, 1995). The parameters  $E$  and  $\nu$  have model dependent interpretation but can be described as the energy barrier that must be overcome in order for desorption to occur and the vibrational or attempt frequency of the molecule (on average, how many times per second will the adsorbate attempt to desorb), respectively (Hubbard, 1995).

Desorption processes on solid surfaces can be described using a general rate equation that accounts for the dependence of the desorption rate constant on temperature. Specifically, the phenomenological kinetic equation (Eq. (1)) is combined with the Arrhenius

expression (Eq. (2)), resulting in the Polanyi–Wigner equation (Eq. (3)) (Polanyi and Wigner, 1928).

$$\frac{d\theta}{dt} = -k_d(\theta)\theta^n \quad (1)$$

$$k_d(\theta) = v(\theta)e^{-E(\theta)/RT} \quad (2)$$

$$\frac{d\theta}{dt} = -v(\theta)\theta^n e^{-E(\theta)/RT} \quad (3)$$

where  $\theta$  is the surface coverage,  $t$  is time (s),  $v$  is the pre-exponential factor (1/s),  $E$  is the desorption activation energy (J/mol),  $R$  is the universal gas constant (J/mol K), and  $T$  is temperature (K). This set of equations is only applicable if there is no readsorption. If readsorption occurs, an extra term must be added, resulting in Eq. (4) (Joly and Perrard, 2001).

$$\frac{d\theta}{dt} = k_a(\theta)p(1 - \theta)^n e^{-E_a(\theta)/RT} - v_d(\theta)\theta^n e^{-E_d(\theta)/RT} \quad (4)$$

where subscripts a and d indicate adsorption and desorption, respectively,  $k_a$  is the pre-exponential factor expressed in reciprocal pressure units, and  $p$  is the pressure in the gas phase.

When readsorption is negligible,  $E$  and  $v$  are assumed to be coverage independent, the rate of temperature increase of the system is constant ( $\beta$  in K/s), the reaction order is one, and coverage is assumed to correspond directly to concentration ( $C$ ), the Polanyi–Wigner equation simplifies to Eq. (5).

$$\frac{dC}{dT} = -\frac{v}{\beta} C e^{-E/RT} \quad (5)$$

Though the equations described above (known as the absolute rate theory (ART) approach) have been used almost exclusively to describe and interpret adsorption and desorption kinetic data (Rudzinski and Panczyk, 2002), a new theoretical approach has been developed and initially tested for use with TPD data. This approach is called statistical rate theory (SRT) and it relates the kinetics of adsorption and desorption to the chemical potentials of adsorbed and bulk phase molecules (Rudzinski and Panczyk, 2002). SRT has been found to predict TPD spectra for several metal-gas systems and appears to explicitly include all the necessary coverage and temperature dependence of the desorption parameters (Elliot and Ward, 1997). Though the SRT method shows promise, it requires detailed knowledge of the adsorbed molecules and their interactions with the surface of interest and may be difficult to apply to real geosorbent systems, necessitating further study regarding application of SRT to real world sorbents.

## 6. TPD-MS data validation

TPD-MS requires a data validation technique to ensure that the data are valid and not artifacts of con-

tamination, user error, etc. For this work, the instrument was tuned at the start of each operational day and an internal standard (40 ppm indeno(1,2,3-*c,d*)pyrene on glass beads) was run following successful tuning and after the final sample for that day. The tuning procedure ensures that the TPD-MS is functioning properly (electronics, carrier gas, seals, etc.) and that there are no large sources of contamination present. The internal standard allows the user to identify further sources of contamination and determine if, at that time, the instrument can be used for sample analysis. The internal standard used must be a compound that is stable in the experimental temperature range and whose thermogram is easily identifiable. The compound should be different than the compound (s) expected to be present in the sample but similar enough that the same temperature protocol can be used for both the standard and the samples.

## 7. Thermogram initial data processing

In order to utilize TPD-MS thermograms to determine kinetic parameters, individual compound thermograms have to be identified and verified and smoothed. These steps are especially important when TPD-MS is used to analyze samples (spiked sorbents and contaminated soils/sediments) whose surfaces are heterogeneous. For all samples, the raw thermogram must be separated into thermograms for individual compounds by selecting the specific mass to charge ( $m/z$ ) value (s) for the ion (s) of interest. The mass spectrum of the selected ion (s) can then be verified using a spectral database. Fig. 2 illustrates the raw thermogram for chrysene spiked on glass beads and the individual thermogram for chrysene ( $m/z$  228). In this case, the raw thermogram is similar to the individual thermogram, which is expected because the sample contains one compound on a sorbent whose composition does not change in the experimental temperature range. For contaminated soil/sediment samples, the raw thermograms may be broader (due to diffusional effects), may have many peaks (due to the presence of many compounds) and may not resemble the individual compound thermograms.

It is worth noting that there are several small desorption features in the raw thermogram (at approximately 11, 18, 29, and 38 min) that represent phthalates, rhenium oxides, and diffusion pump oil breakdown products. These features are typical contamination symptoms for this system, however, as they are not present in the individual thermogram, they do not impact further analysis. Though chemical noise is always present in any mass spectrometer, the high sensitivity of the ion trap may make it easy to confuse background noise with actual contamination symptoms. In general, if samples have been prepared carefully, the main

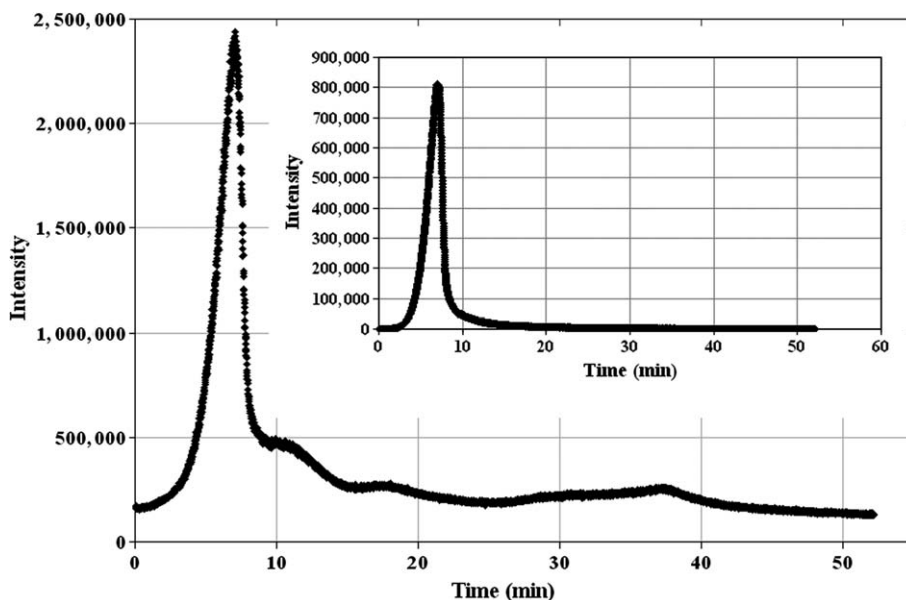


Fig. 2. Raw thermogram for chrysene spiked on glass beads (10 °C/min) with individual thermogram for chrysene shown in inset.

contamination sources include hydrocarbon contamination from the carrier gas, diffusion pump oil, or instrument cleaning solvents. Table 1 lists typical ions found due to these types of contamination.

Once the individual thermogram has been identified, its corresponding mass spectrum must be compared with a standard spectrum (e.g. the NIST Mass Spectral database). Fig. 3 shows the mass spectrum for the individual chrysene thermogram and the NIST mass spectrum for chrysene. From the comparison of the two spectra, it can be seen that the individual chrysene thermogram does represent the release of chrysene.

## 8. Thermogram smoothing procedures

Once an individual thermogram has been identified, it is important to smooth the thermogram and identify any background and or noise in the signal. Data

smoothing is simply a process by which data points are averaged with nearby points in the series using a specifically shaped function to calculate the average of the neighboring points (e.g. Gaussian and Boxcar). Smoothing results in evenly spaced data points and, for TPD thermograms, does not alter the important characteristics of the desorption curve. Identifying and subtracting background and noise in the thermogram ensures that the data are representative of only the compound of interest. Fig. 4 illustrates the effect of Gaussian smoothing on the individual chrysene thermogram.

From Fig. 4, it can be seen that smoothing the thermogram makes the peak more defined and makes the entire curve more uniform without changing the curve itself. This is especially important for models that require any type of curve fitting. Though the glass bead thermogram does not illustrate much background noise or tailing effects, thermograms for more complex

Table 1

TPD-MS typical contamination symptoms

Type of contamination	Typical ions ( $m/z$ )
Phthalate background (sample handling, solvent contamination, packaging materials)	Fragments of bis(2-ethylhexyl)phthalate (149, 167, 279)
Excessive hydrocarbon contamination (carrier gas contamination)	Breakdown of aliphatic hydrocarbons (43, 57, 71, 85, 99)
Rhenium oxide contamination (filament wire)	Re (185/187), ReO (201/203), ReO <sub>2</sub> (217/219), ReO <sub>3</sub> (233/235), ReO <sub>4</sub> (250/252)
Solvent contamination (cleaning procedure residue)	Methanol (31), acetone (43, 58, 59), methylene chloride (83/84), hexane (41, 43, 56, 57, 58, 85, 86), toluene (91, 92)
Diffusion pump oil contamination	Synthetic aliphatic hydrocarbon (CH <sub>2</sub> ) <sub>n</sub> ( $n$ ranges from 20 to 40) (446)

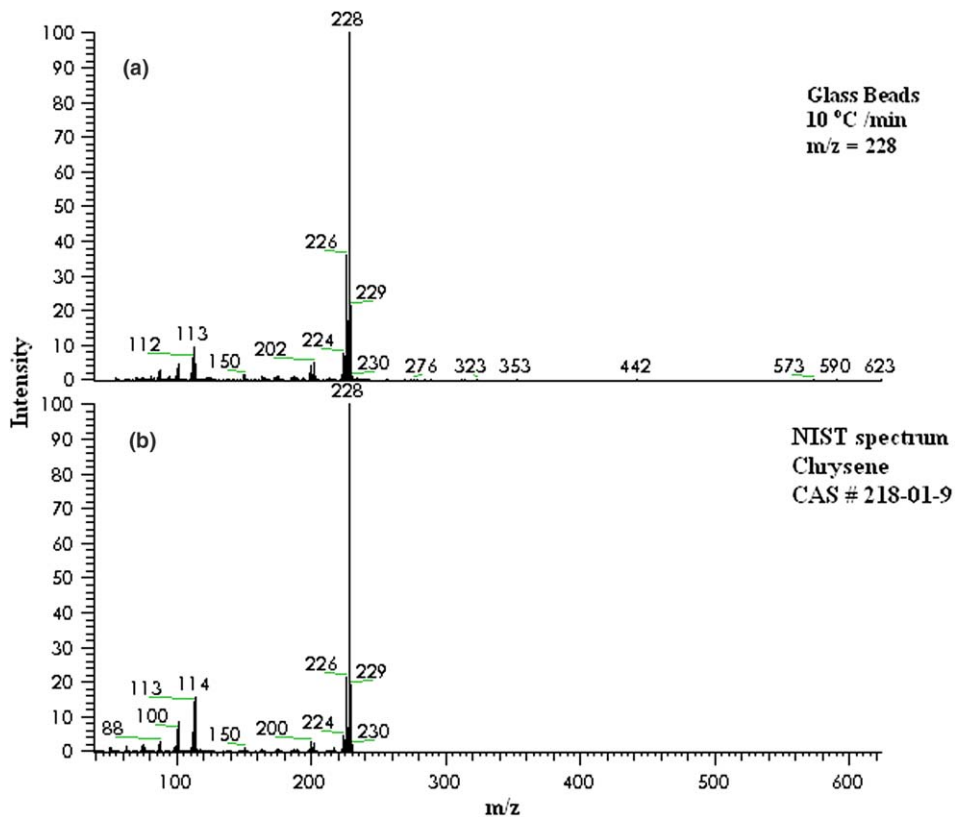


Fig. 3. Comparison of mass spectrum for (a) the individual chrysene thermogram and (b) the NIST standard mass spectrum for chrysene.

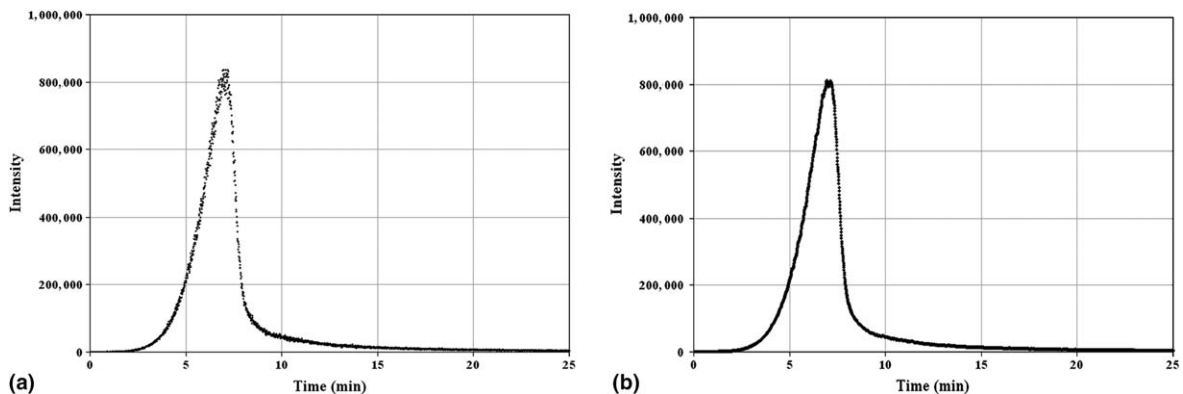


Fig. 4. Comparison of (a) the initial individual chrysene thermogram and (b) the individual chrysene thermogram smoothed using the Gaussian smoothing function (10 °C/min).

sorbents (e.g. sand and kaolin) and real soils/sediments often exhibit a low signal to noise ratio and tailing on both ends of the thermogram. If this is the case, the user must determine if the data are usable and, if so, which portions of the thermogram should be used for input into desorption kinetics models.

## 9. Thermogram data for use in desorption kinetics models

Once TPD-MS data have been validated and initially processed, they require further processing before input into desorption kinetics models. The process for

integrating the TPD-MS data into the kinetics models involves four steps.

1. The variation between multiple TPD-MS analyses on the sample replicates must be addressed.
2. A method for averaging the TPD-MS data must be chosen.
3. A method for normalizing the curves to eliminate the effects of differences in intensity must be chosen.
4. The kinetic model parameters must be extracted from the fully processed thermogram or the thermogram must be fit with desorption rate equations.

## 10. Variation in TPD-MS analysis

Variation between replicate analyses can and does occur when using TPD-MS. Potential variations include changes in peak intensity and temperature and, rarely, changes in thermogram shape. These variations are typically caused by heterogeneity associated with the small sample size (0.5–5 mg), chemical noise related to the presence of other compounds in the sample and machine contamination. The small sample size required for TPD-MS analysis may be problematic because the composition of both spiked geosorbent and real soil/sediment materials may vary, resulting in TPD-MS replicate samples that are not identical. Fig. 5 illustrates the variation between triplicate runs used to generate the average individual chrysene thermogram for glass beads and the triplicate runs used to generate an average individual chrysene thermogram for chrysene spiked on kaolin.

From Fig. 5, it can be seen that, for both glass beads and kaolin, the intensity varies while peak temperatures remain relatively constant. The figure also shows a greater variation between kaolin replicate runs (peak

temperature =  $657.2 \text{ K} \pm 12.5$ ) than glass beads replicate runs (peak temperature =  $273.1 \text{ K} \pm 2.5$ ). This is most likely due to the fact that kaolin is a more complex sorbent (i.e. it is a layered material that has several types of surface sites available for adsorption), thus, there is the potential for greater variation between the samples used for TPD-MS analysis. The possible lack of homogeneity in sample materials can be addressed by careful mixing of the material before TPD-MS samples are collected, however, the operator must always be aware that variations in thermograms will occur. However, if the peak temperatures and the thermogram shapes remain fairly constant, the data can be used for input into desorption kinetics models.

## 11. Normalizing and averaging TPD-MS results

When utilizing TPD-MS data for use in desorption kinetics models, the smoothed data must be averaged and normalized to limit the effects of the thermogram variations. For data averaging, two methods can be used. The data can be averaged before model entry resulting in a single model output or each of the replicate TPD-MS runs can be input into the model and the model results subsequently averaged. For the first method, an average thermogram is created by averaging the intensity values of the replicate runs at each time increment (times at which the TPD-MS reports an intensity value). This average thermogram is then used for all model calculations and curve fitting. For the second method, the data (either bulk peak characteristics or the full thermogram) from individual TPD-MS runs are input into the model and the model results from each of the replicates are averaged.

These two averaging approaches were tested on glass beads data for the three ramp rates and the results for

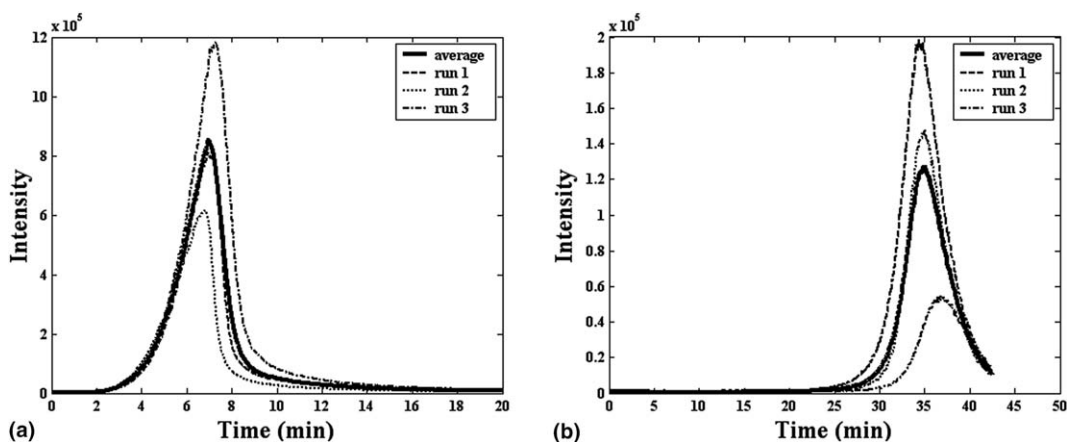


Fig. 5. Variation in TPD-MS triplicate runs for (a) chrysene spiked on glass beads and (b) chrysene spiked on kaolin (both at  $10 \text{ }^\circ\text{C}/\text{min}$ ).

three desorption kinetics models compared. It was found that for the low ramp rate (10 °C/min), the release energy values were very similar for both types of averaging. As the ramp rate was increased (20 °C/min and 30 °C/min), the variation between thermograms increased and, accordingly, the two averaging methods produced slightly different release energy values (values remained within an order of magnitude). For the desorption model that used all three ramp rates, the two averaging methods produced nearly identical release energy values. Thus, if the experimental ramp rate is low or the model uses multiple ramp rates, using either type of thermogram averaging produces acceptable results. It is worth noting that, as the ramp rate is increased, the thermogram peak intensity and temperature increase (Fig. 6) while the area under the thermogram remains relatively constant, making it possible to use models that relate peak temperature and ramp rate. Though the reasons for this shift are not entirely known, this effect has been noted in other research (Rudzinski et al., 1999; Joly and Perrard, 2001; Long and Yang, 2001; Park and Yang, 2005).

Following averaging, TPD-MS thermograms can be normalized using either the maximum intensity or the total area under the thermogram. If the maximum intensity is used, each intensity value is divided by the maximum intensity and the resulting thermogram has a peak intensity of one. This normalization method is best for models that require bulk peak characteristics such as peak height, width, etc. For the second normalization method, the area of the thermogram present at each time increment is divided by the total area of the thermogram, resulting in a thermogram with a total area of one. This normalization method is best for models that utilize curve fitting techniques because it allows the ini-

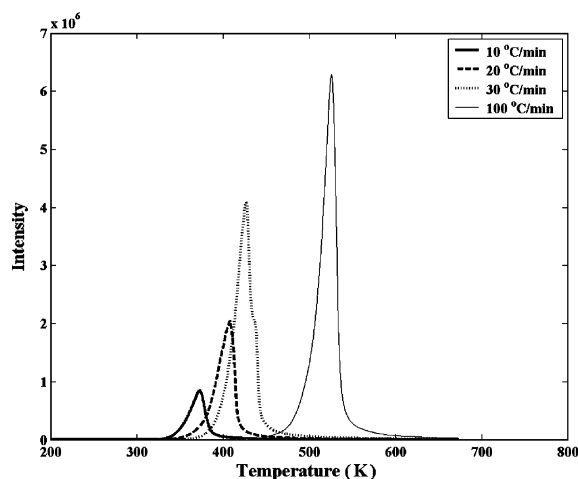


Fig. 6. Variation in peak intensity and peak temperature with changing ramp rate for chrysene spiked on glass beads.

tial concentration to be set to one, simplifying further calculations.

## 12. Parameter extraction and curve fitting

After averaging and normalization of TPD-MS thermograms, the extraction of applicable model parameters and/or curve fitting is completed. The straightforward extraction of bulk peak characteristics (peak temperature and intensity, rate of desorption, etc.) can be done utilizing the TPD-MS software, additional mathematical software, by hand from a thermogram, or any combination of these methods.

Table 2  
TPD-MS analysis methods summary

TPD-MS analysis method	Energy parameter determined	Equations
Non-linear Fit Method (Talley et al., 2004; Nicholl et al., 2004)	$E$ (release energy)	<ul style="list-style-type: none"> <li><math>dC/dT = -(v/\beta)Ce^{-E/RT}</math></li> <li><math>C = C_0 \exp[k_1(T_0 e^{-k_2/T_0} - T e^{-k_2/T}) + k_1 k_2 (\text{Ei}(k_2/T) - \text{Ei}(k_2/T_0))]</math> (<math>C_0</math>, <math>T_0</math> refer to initial conditions)</li> </ul>
Arrhenius Plot Method (Hubbard, 1995)	$E$ (activation energy of desorption)	<ul style="list-style-type: none"> <li><math>d\theta/dt = -v(\theta)\theta^n e^{-E(\theta)/RT}</math></li> <li><math>\ln(d\theta/dt) - n \ln \theta = \ln v(\theta) - (E(\theta)/RT)</math></li> </ul>
Long and Yang Method (Long and Yang, 2001)	$E$ (activation energy of desorption)	<ul style="list-style-type: none"> <li><math>k_d(\theta) = v(\theta)e^{-E(\theta)/RT}</math></li> <li><math>2 \ln T_m - \ln b = E/(RT_m) + \ln ZA</math> (subscript m refers to value at peak intensity)</li> </ul>
Minglegrin Method (Hayes and Minglegrin, 1991)	$\Delta H$ (enthalpy of desorption)	<ul style="list-style-type: none"> <li><math>dS/dt = -kC(t)e^{-\Delta H/RT}</math></li> <li><math>\Delta H = \frac{2RT_m^2}{W}</math></li> </ul>
Readsorption (Park and Yang, 2005)	$E$ (activation energy of desorption)	<ul style="list-style-type: none"> <li><math>E/RT_m + \ln K = 2 \ln T_m - \ln \beta - 2 \ln(1 - \theta_m)</math> (subscript m refers to value at peak intensity)</li> </ul>

Note:  $C$  = concentration;  $S$  = amount of sorbent adsorbed;  $\theta$  = surface coverage;  $v$  =  $A$  = pre-exponential factor;  $\beta$  =  $b$  = ramp rate;  $n$  = reaction order;  $k_d$  = desorption rate constant;  $k_1 = v/\beta$ ;  $k_2 = E/R$ ;  $Z$  = constant;  $R$  = gas constant;  $\text{Ei}$  = exponential integral;  $t$  = time;  $T$  = temperature;  $W$  = peak width at half height;  $K = k_d/k_a$  (adsorption rate constant).

For curve fitting analysis methods, a specific desorption equation or set of equations (e.g. Polanyi–Wigner equation) must be chosen and then applied to the TPD-MS thermogram to determine which combination of model parameters result in the best fit (as defined by the absolute error or fit residuals present between the data and the model). If necessary, a least-squares optimization method (e.g. Gauss–Newton method) may also be used for nonlinear parameter estimation. When utilizing curve fitting methods, it is important to ensure the uniqueness of the solution that produces the “best fit”. The nonlinear fitting of multiple parameters often results in several solution sets that produce similar absolute error or fit residual, making it difficult to ascertain the correct solution set (Nicholl et al., 2004). If this problem is addressed, release energy values can be calculated. Table 2 provides a summary of possible TPD-MS analysis methods.

### 13. Conclusions

This work demonstrates the analytical protocol and data processing requirements for utilizing TPD-MS for the initial assessment of the physical availability of HOCs on geosorbents. It documents the details of the entire process and provides an operational guide for utilizing TPD-MS for environmental applications. Since TPD-MS results are directly related to both the adsorbed species and their respective desorption rates, a good deal of qualitative information can be gathered from a single thermogram. The expansion of TPD-MS techniques from surface science and catalysis research to geosorbent systems can provide a much simpler method for assessing the physical availability of HOCs. Although TPD-MS does not give a direct description of the behavior of the adsorbate as it desorbs, it does provide a meso-scale view of the desorption process (Hubbard, 1995). Thus, a thermogram can provide information on the relative complexity of the sorption behavior and the relative degree of physical availability. Specifically, thermograms illustrate differences in ramp rates, sorbent types and sorbate types. These differences can be seen in both spiked geosorbents and real contaminated sediment samples, indicating that the TPD-MS analytical technique can be used to qualitatively and semi-quantitatively assess the physical availability of HOCs on geosorbents and possibly identify the geosorbent systems where the compounds are more tightly bound.

### Acknowledgments

We would like to thank the Department of Defense (DOD) Strategic Environmental Research Development

Program (SERDP) and the United States Army Engineer Research Center (ERDC), Waterways Experiment Station (WES) for their support of this work.

### References

- Ahmed, S.I., Perry, S.S., El-Bjeirami, O., 2000. Desorption and reaction of water on MgO(100) studied as a function of surface preparation. *J. Phys. Chem. B* 104, 3343–3348.
- Alexander, M., 2000. Aging, bioavailability, and overestimation of risk from environmental pollutants. *Environ. Sci. Technol.* 34, 4259–4265.
- Chang, A.C.C., Chuang, S.S.C., Gray, M., Soong, Y., 2003. In situ infrared study of CO<sub>2</sub> adsorption on SBA-15 grafted with  $\gamma$ -(Aminopropyl)triethoxysilane. *Energ. Fuel.* 17, 468–473.
- Choudhary, V.R., Mantri, K., 2000. Temperature programmed desorption of toluene, *p*-xylene, mesitylene and naphthalene on mesoporous high silica MCM-41 for characterizing its surface properties and measuring heats of adsorption. *Micropor. Mesopor. Mater.* 40, 127–133.
- Cvetanovic, R.J., Amenomiya, Y., 1972. A temperature programmed desorption technique for investigation of practical catalysts. *Catal. Rev.* 6, 21–85.
- Elliot, J.A., Ward, C.A., 1997. Temperature programmed desorption: a statistical rate theory approach. *J. Chem. Phys.* 106, 5677–5684.
- Ehlers, L.J., Luthy, R.G., 2003. Contaminant bioavailability in soil and sediment. *Environ. Sci. Technol. A* 37, 295A–302A.
- Ghosh, U., Talley, J.W., Luthy, R.G., 2001. Particle-scale investigation of PAH desorption kinetics and thermodynamics from sediment. *Environ. Sci. Technol.* 35, 3468–3475.
- Hatzinger, P.B., Alexander, M., 1995. Effect of aging of chemicals in soil on their biodegradability and extractability. *Environ. Sci. Technol.* 29, 537–545.
- Hayes, M.H.B., Mingelgrin, U., 1991. Interactions between small organic chemicals and soil colloidal constituents. In: Bolt, G.H., Deboodt, M.F., Hayes, M.H.B., McBride, M.B. (Eds.), *Interactions at the Soil Colloid–Soil Solution Interface*. Kluwer Academic Publishers, Boston, MA, pp. 323–407.
- Hubbard, A., 1995. *Surface Imaging and Visualization*. CRC Press, New York.
- Joly, J., Perrard, A., 2001. Determination of the heat of adsorption of ammonia on zeolites from temperature-programmed desorption experiments. *Langmuir* 17, 1538–1542.
- Kelsey, J.W., Kottler, B.D., Alexander, M., 1997. Selective chemical extractants to predict bioavailability of soil-aged organic chemicals. *Environ. Sci. Technol.* 31, 214–217.
- Kraaij, R., Seinen, W., Tolls, J., Cornelissen, G., Belfroid, A.C., 2002. Direct evidence of sequestration in sediments affecting the bioavailability of hydrophobic organic chemicals to benthic deposit-feeders. *Environ. Sci. Technol.* 36, 3525–3529.
- Long, R.Q., Yang, R.T., 2001. Carbon nanotubes as superior sorbent for dioxin removal. *J. Am. Chem. Soc.* 123, 2058–2059.

- Miller, J.B., Siddiqui, H.R., Gates, S.M., Russell, J.N., Yates, J.T., 1987. Extraction of kinetic parameters in temperature programmed desorption: a comparison of methods. *J. Chem. Phys.* 87, 6725–6732.
- Nicholl, S.I., Talley, J.W., Silliman, S., 2004. Model verification of thermal programmed desorption-mass spectrometry for estimation of release energy values for polycyclic aromatic hydrocarbons on mineral sorbents. *Environ. Toxicol. Chem.* 23, 2545–2550.
- Nieskens, D.L.S., van Bavel, A.P., Niemantsverdriet, 2003. The analysis of temperature programmed desorption experiments of systems with lateral interactions; Implications of the compensation effect. *Surf. Sci.* 546, 159–169.
- Panczyk, T., Szabelski, P., 2003. The influence of lateral interactions between adsorbed molecules on adsorption kinetics. A statistical rate theory approach. *J. Phys. Chem. B* 107, 5586–5597.
- Park, J., Yang, R.T., 2005. Predicting adsorption isotherms of low-volatile compounds by temperature programmed desorption: iodine on carbon. *Langmuir* 21, 5055–5060.
- Polanyi, M., Wigner, E., 1928. *Z. Phys. Chem.* 139, 439.
- Robbat Jr., A., Liu, T., Abraham, B.M., 1992. Evaluation of a thermal desorption gas chromatograph/mass spectrometer: on-site detection of poly chlorinated biphenyls at a hazardous waste site. *Anal. Chem.* 64, 358–364.
- Rudzinski, W., Borowiecki, Dominko, A., Panczyk, T., 1999. A new interpretation of temperature programmed desorption spectra from heterogeneous solid surfaces, based on statistical rate theory of interfacial transport: the effects of simultaneous readsorption. *Langmuir* 15, 6386–6394.
- Rudzinski, W., Borowiecki, T., Panczyk, T., Dominko, A., 2000. A quantitative approach to calculating the energetic heterogeneity of solid surfaces from an analysis of TPD peaks: comparison of the results obtained using the absolute rate theory and the statistical rate theory of interfacial transport. *J. Phys. Chem. B* 104, 1984–1997.
- Rudzinski, W., Panczyk, T., 2002. Remarks on the current state of adsorption kinetic theories for heterogeneous solid surfaces: a comparison of the ART and the SRT approaches. *Langmuir* 18, 439–449.
- Sato, S., Minoura, S., Urisu, T., Takasu, Y., 1995. IRAS and TDS study on the photolytic decarbonylation of iron pentacarbonyl adsorbed on a SiO<sub>2</sub> film with a buried metal layer. *Appl. Surf. Sci.* 90, 29–37.
- Talley, J.W., Ghosh, U., Tucker, S.G., Furey, J.S., Luthy, R.G., 2002. Particle-scale understanding of the bioavailability of PAHs in sediments. *Environ. Sci. Technol.* 36, 477–483.
- Talley, J.W., Ghosh, U., Tucker, S., Furey, J., Luthy, R.G., 2004. Thermal programmed desorption of PAHs from mineral and organic surfaces. *Environ. Eng. Sci.* 21, 647–660.
- Tang, J., Carroquino, M.J., Robertson, B.K., Alexander, M., 1998. Combined effect of sequestration and bioremediation in reducing the bioavailability of polycyclic aromatic hydrocarbons in soil. *Environ. Sci. Technol.* 32, 3586–3590.