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**Online measurement of phthalate-particulate matter interactions by membrane
introduction mass spectrometry (MIMS)**

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Abstract

To enable further study and assessment of indoor inhalation exposure risk, an online apparatus enabling measurement of semi-volatile compound partitioning on household particulates was developed. An example method for use of the apparatus is described using dimethyl phthalate (DMP). The system employs direct measurement by membrane introduction mass spectrometry (MIMS). The MIMS system was calibrated using known gas phase DMP concentrations produced by gravimetrically calibrated permeation devices. The quantity of DMP sorbed by particles is described first using a model particle type, a reverse-phase liquid chromatography packing material, and then with a household dust sample. In addition, the desorption of semi-volatile compounds from a household dust sample was monitored using the apparatus, and characteristic fragment ion signals for phthalate compounds were observed.

Keywords: Phthalate-particle Interactions, Direct Mass Spectrometry, Membrane Introduction Mass Spectrometry (MIMS), Membrane Inlet Mass Spectrometry, Dimethyl Phthalate (DMP)

Introduction

In 1995, Leech et al. demonstrated that the average Canadian spends 88.6% of their time in the indoor environment.^[1] Indoors, individuals are exposed to contaminant and pollutant gases and suspended particulate matter. Environmental particulates are rarely

comprised of a single chemical species, rather, they are heterogeneous, containing multiple different sorbed compounds, plus soluble and insoluble solids. [2] The insoluble solid-air interface is typically chemically rich, with a high density of sites for sorption of compounds. These interfaces sorb semi-volatile chemical species from various indoor and outdoor sources. [3-5] Phthalate compounds, for which there is an extensive database regarding industrial usage and exposure, are a class of semi-volatile plasticizers used in a variety of household and industrial products. [6, 7] Bis-2-ethylhexyl phthalate (DEHP), for example, is known to leach out of plastics and into the local environments, spanning water, air, and many types of surfaces, including indoor dusts. [8-12] Studies have shown indoor dusts are a large contributor to the summative human exposure to DEHP. [13-16] Improved characterization of phthalate and other classes of semi-volatile compound exposure pathways, and their respective outcomes, are needed to better understand inhalation health risks. [17, 18]

The relative distribution of semi-volatile organic compounds between the gas and sorbed phase can be characterized by a gas/particle partition coefficient $K_d = X_d/C_g$, where X_d and C_g are the concentrations of SVOC in the sorbed and gas phase, respectively. This partitioning behavior is important in determining both the extent and mode of human exposure. [19] In addition to being very sensitive to temperature, the K_d is an intrinsic property of the SVOC and adsorbing material. While a number of empirical approaches have been employed to predict these partition coefficients using linear free energy type relationships involving vapour pressures of the sub-cooled liquid, and/or octanol-water or

octanol-air coefficients, ^[20] there are a limited number of experimentally derived K_d for values for SVOCs in the literature. ^[21]

Methodology described in the literature to characterize indoor phthalate abundance has largely been filter-based, and therefore utilizes the off-line collection of samples.

Following the sampling process, either using passive filters or active filtering of air, the samples are transported to an analytical laboratory for analysis, typically using gas chromatography mass spectrometry. This sampling approach is often summarized simply as ‘trap and release’. ^[13] The assumption with this methodology is that there is no significant physical and chemical change to the sample during transportation to the measurement laboratory. Another off-line approach involves the use of denuding technology. A denuder is designed with interfaces coated with molecules chosen to either sorb or react with species in the air being passed through the device. Denuding has been used to characterize interactions between particulate aerosols and volatile/semi-volatile organic compounds, but these strategies are also offline with respect to separate measurement of gas and particulate phase compositions. ^[22-24]

In this manuscript, an online strategy designed to measure sorption / desorption, and to provide an equilibrium measurement of the sorbed concentration of a semi-volatile compound, is introduced. Silica particles coated with C18 alkyl groups, extensively used as the stationary phase in high performance liquid chromatography (HPLC), were purposely chosen for this study as a well-defined model particulate phase. This material is available world wide, can be used in any laboratory, and as such, represents a potential

methodological reference through which studies in geographically diverse laboratories may be quantitatively compared. This online methodology relies on specific compound detection, afforded by Membrane Introduction Mass Spectrometry (MIMS).^[25-28] MIMS is well suited for real time measurements, and its use in mobile applications has been demonstrated. The membrane interface can handle complex mixtures, from volatile and semi-volatile organic compounds (VOC/SVOC) in gas, liquid or heterogeneous suspensions. These compounds flow over, as well as permeate through a semi-permeable membrane, and are directly measured by electron ionization mass spectrometry (MS). Thus the permeating VOC/SVOCs are not separated, rather they are also presented to the MS as a mixture. Compounds are resolved based upon their ionization characteristics, mass (m/z), and/or fragmentation characteristics (*e.g.* tandem mass spectrometry, MS/MS). Calibration of the mass spectrometer is performed using standardized samples with known concentrations, and the temporal behavior of the compounds permeating through the membrane establishes additional baseline performance criteria regarding the MIMS. This overall system is used to characterize the sorption and desorption interactions between dimethyl phthalate (DMP) and particulate materials, as well as semi-volatile compound desorption from an uncharacterized house dust sample.

Experimental

Reagents and solvents

Solvents used were methanol, hexane and dichloromethane, all HPLC grade (Fisher Scientific, Vancouver, British Columbia, Canada). Dimethyl phthalate, 99% purity (CAS # 131-11-3) was purchased from Sigma Aldrich (Oakville, Ontario, Canada). Deionized water ($> 18 \text{ M}\Omega$) was obtained using a laboratory water purification system (Model MQ Synthesis A10, Millipore Corp., Billerica, MA, USA).

Permeation tube construction and calibration

In the process of constructing re-fillable permeation tubes, all membranes and hardware incorporated into the device were washed three times with HPLC grade hexane, and then dried overnight in a loosely covered beaker at ambient conditions prior to assembly. Each device was constructed in house using a short section of polydimethylsiloxane (PDMS, or Silicone™) capillary hollow fibre membrane (HFM) tubing (Dow Corning, 2.0 cm long, 1.47 mm ID, 1.96 mm OD) that was mounted between a 1/16" OD stainless steel plug and a 1/16" OD stainless steel tube. The end of the tube was sealed with a 1/16" stainless steel union, (Swagelok™) which also provided a means for refilling the permeation tube reservoir with the semi-volatile compound being studied. In this case, dimethyl phthalate was used.

For gravimetric calibration, a permeation device was maintained at 30 °C by placing it in a glass U-tube mounted in a water bath equipped with an immersion heater/recirculator (Model 66590, Precision Scientific, Chicago, IL, USA). A continuous flow of air (1.0 L/min.) was passed through the U-tube during calibration (partially filled with glass

beads to ensure constant temperature) using a small diaphragm pump (Model 300, Rena Air®, Charlotte, NC, USA), with flow control achieved using a rotameter. At timed intervals, the permeation tube assembly was removed from the U-tube and its mass obtained using a four decimal place analytical balance (Model M-220, Denver Instruments, Bohemia, New York, NY, USA).

MIMS system for measurement of phthalate-particulate interactions

The MIMS based apparatus used for these studies was developed in house by modifying a previously described system ^[29], and is detailed in Figure 1. For these experiments, the MIMS flow cell interface used a PDMS HFM (10.0 cm long, 0.94 mm OD, 0.51 mm ID, Silastic® brand, Dow Corning, Midland, MI, USA) mounted in a MIMS flow cell interface. All transfer tubing, unless otherwise noted, was 0.25" OD Teflon tubing with stainless steel connectors (Swagelok™, Burnaby, BC, Canada). A 1 m long coil of 0.25" OD stainless steel tubing filled with 3 mm diameter stainless steel balls was mounted in the oven upstream to the MIMS flow cell interface, acting as a heat exchanger to ensure constant gas temperature (150 °C) prior to entering the MIMS flow cell. Since only gas phase samples were measured in this work, the jet separator was removed from the previously described system. ^[29] For all experiments, the ion trap mass spectrometer was operated with automatic gain control on, in full scan mode (m/z 50-300).

Gas phase phthalate concentrations, produced using in house constructed permeation tubes, were generated in temperature controlled air flows, using needle valve equipped rotameters (all rotameters used were Model B-436 type, Porter Instruments, Hatfield, PA, USA), and subsequently diluted to desired concentrations by adjusting the dilution flow rate (Fig. 1). For all experiments, room air was scrubbed by drawing it through an activated carbon trap. After suitable dilution(s), the flow of phthalate laden gas is directed to a stainless steel three-way valve (Model SS-43GXS4, Swagelok™), where the flow of gaseous phthalate could be directed over an inline sintered stainless steel frit (5µm pore size, 0.25" ID, No. 4A-F4L-5-SS Parker Hannefin, Hatfield, PA, USA) used to suspend particulate matter, or directly to the MIMS interface for measurement. Downstream of the MIMS interface, the gas flow exits the system through a third rotameter, used to verify the air total flow through the system, through a diaphragm pump (Model DOA-P704-AA, Gast Manufacturing, Michigan, USA) and then to exhaust.

Particulate matter preparation and measurements

The initial characterization of the apparatus to measure sorption and desorption of semi-volatile compounds to/from particles was performed using model particles having well characterized size distribution, composition, morphology and surface chemistry.

Stationary phase particles were removed from a preparatory HPLC column (Vydac #218TP1022, Hichrom, Berkshire, UK) containing 10µm diameter, C18 derivatized, silica stationary phase particles. Their use herein represents sorption behavior for a single type of particle-air interface. The particles were cleaned by sonication in deionized water

(repeated 3X), followed by sonication in methanol, and finally hexane. Prior to use, the particles were dried in air at room temperature in a loosely covered beaker (24 hrs).

House dust samples were collected from a private residence using a high efficiency bag-less vacuum (Model DC40, Dyson Company, Malmesbury, UK). The bulk, large particulate specimen was discarded, and the fine particulate materials adhering to the vacuum canister walls collected in 40 mL glass vials (EPA/VOA Type, Scientific Specialties Inc., Hanover, MD, USA). No further cleaning or preparation steps were used for the house dust sample prior to measurements.

Particulate matter was loaded on a stainless steel frit (inset, Fig. 1) by drawing small portions onto the in-line filter using an airflow provided by a diaphragm pump (Model DOA-P704-AA, Gast Manufacturing). The mass of particles loaded was measured using an analytical balance. Unless otherwise noted, the stainless steel support frit was maintained at ambient temperature (*ca* 25 °C). Particle/phthalate loading measurements were conducted by first flowing gaseous dimethyl phthalate at a known gas-phase concentration directly through the MIMS flow cell interface, bypassing the particulates suspended on the filter, to obtain a calibration response curve from the MIMS. After establishing a steady state signal for the gas phase phthalate, the three-way valve was switched, and the gaseous phthalate flow was directed over the suspended particles. Signal reductions observed for a given phthalate at this point are attributed to adsorption of the phthalate on the surfaces of the suspended particles, the frit assembly itself, and other associated component-air surfaces. The flow of air having known phthalate

concentration was continuously directed through the particles on the frit, until ion signal levels returned to the initial steady state values before the particulate exposure.

To rapidly desorb sorbed phthalates or other semi-volatile species, the flow of gas directed to the frit was switched to scrubbed air, and then the stainless steel frit assembly was heated. Heating was accomplished by a flexible heating rope (Model FGR-030, Omega Engineering, Norwalk, CT, USA) that was wrapped around exterior of the frit housing, and controlled by a ramp/soak power supply (Model CN7500, Omega Engineering). The temperature of the frit assembly was monitored by a thermocouple (Part 5TC-GG-J-30-36, Omega Engineering).

Results and discussion

Phthalate permeation tube calibration

Gravimetric calibration of DMP emission rates for the in house constructed permeation devices was established in advance by monitoring their mass loss until linear emission rates were obtained. The use of in house constructed devices based upon PDMS HFM was necessary because commercially available permeation tubes had phthalate emission rates that were too low to be used effectively in this study. Provided the temperature of a device was held constant in the flow tube, and DMP liquid remained in the reservoir, the mass-loss per unit time was reproducible. Example gravimetric gas-phase emission rate

calibration data for one of the DMP permeation tubes used in these studies is given in Figure 2.

A single permeation device was used for all presented experiments, and it still contained DMP in its reservoir after more than four months use. The permeation tube used throughout provided 109 ppb_v DMP at 30 °C with a 1.0 L/min. air flow. To investigate phthalate-particle interactions for different phthalates or other semi-volatile compounds, similar devices can be fabricated by first optimizing the permeation tube membrane composition and thickness for the physical and chemical properties of the desired compound, followed by gravimetric calibration.

MIMS system calibration

Alkyl phthalates typically produce the $[C_8H_5O_3]^+$ cyclic oxonium ion at m/z 149 as a major fragment ion (usually the base peak) in electron ionization (EI) mass spectrometry, formed by a McLafferty rearrangement, followed by the loss of an alkoxy radical.^[30] DMP is somewhat unique in that methoxy elimination is not dominant in EI, producing $[C_9H_7O_3]^+$ ions as a base peak at m/z 163.^[31] MIMS calibration curves for DMP were obtained in the ppb_v range by monitoring the ion signal at m/z 163 (Fig. 3). For these experiments, the three-way valve (Fig. 1) was positioned so that the gaseous phthalate standard flow bypassed the particulate filter frit. The calibration response curve was generated by using the average of 100 steady state, background subtracted measurements at several gas phase concentrations. The measured detection limit for DMP (S/N = 3) was

7 ppb_v. The membrane interface assembly was maintained at 150 °C throughout these measurements, and the t_{10-90%} signal response time for DMP measurement was *ca* 100 seconds.

Phthalate-particle adsorption studies

The process of characterizing phthalate-particle interactions was initiated with a study to determine the extent of adsorption of phthalate on model particulate matter, C18 derivatized silica particles (10 μM HPLC stationary phase). Two different masses of model particles, 1.67 and 3.77 mg were loaded onto a clean stainless steel frit (inset, Fig. 1). Blank measurements involved no particles loaded on the frit. The three-way valve (Fig. 1) was positioned so that gas phase DMP standard was directed to the MIMS interface, and the tubing and stainless steel frit were not initially exposed. Steady state MIMS signals for DMP, using a gas phase concentration of 54 ppb_v in a stream of air at 2.0 L/min. (*i.e.* 7.1 ng/s of DMP) were first demonstrated. The valve was then switched to direct the DMP gas standard to pass over the stainless steel frit. DMP sorbed to the frit, the walls of the tubing, and any loaded particles. As the DMP in the air flow achieved equilibrium with the sorbed DMP, the MIMS signal level returned to the previously attained steady state levels. The flow of DMP from the permeation tube was then stopped, and 2.0 L/min. of scrubbed air was directed through the frit and loaded particles. This overall experimental sequence and example data for the particulate-DMP interactions are presented in Figure 4. To determine the total mass of phthalate sorbed, the mass of phthalate not detected during adsorption (*i.e.* exposure period) is subtracted

from the total quantity of DMP flowed through the system during the defined exposure period. This is described by Equation 1, where t_{Tot} is the total particulate exposure time,

$\frac{Signal_i}{Signal_{max}}$ is the ratio of the observed signal during a sorption event to the maximum

steady state signal in the absence of sorption, and t_i the time for a given signal

measurement, represented graphically in Figure 4 by the shaded area.

$$Sorbed\ Mass = \left(t_{Tot} \times \frac{7.1\ ng}{sec} \right) - \sum_{i=1}^n \frac{Signal_i}{Signal_{max}} \times \frac{7.1\ ng}{sec} \times (t_{i+1} - t_i) \quad (1)$$

A plot of the data from these trials for adsorbed DMP (μg) versus mass of particulate matter loaded onto the frit, 0, 1.67, 3.77 mg, yielded least squares linear regression coefficients of $y = 0.906x + 1.35$, $r^2 = 0.9689$ ($n=3$ for each experimental data point). Using this data, the equilibrium adsorption for DMP on the model particles, was $0.9\ \mu\text{g}$ per mg particles used. Using the gas phase concentration of $428\ \mu\text{g}/\text{m}^3$ ($54\ \text{ppb}_v$), we calculate a gas/particle partition coefficient of $2.1 \times 10^{-6}\ \text{m}^3\ \mu\text{g}^{-1}$ for DMP on $10\ \mu\text{m}$ sized C18 coated silica. This is greater than the recently reported median predicted value for DMP of $6.5 \times 10^{-7}\ \text{m}^3\ \mu\text{g}^{-1}$, [20] but not unexpected given that the C18 surface modification of these particles yields a near perfect hydrophobic interface.

In an analogous experiment, 0, 1.86, and 5.33 mg samples of fine house dust were loaded individually on the stainless steel frit. The determined relationship between the amount of adsorbed DMP (μg) and mass of particles was $y = 0.155x + 1.23$, $r^2 = 0.9996$. This corresponds to a DMP adsorption of $0.16\ \mu\text{g}$ per mg house dust, indicating this house dust sample has a lower sorption capacity than the model C18 silica particles used. This

corresponds to a gas/particle partition coefficient of $3.7 \times 10^{-7} \text{ m}^3 \mu\text{g}^{-1}$, which is in good agreement with the median predicted value for DMP.^[20] Collectively, the data indicates the potential to quantitatively study the adsorption and desorption characteristics of semi-volatile compounds with the variety of solid particulate material types found in indoor environments.

As a final illustrative study, a separate 3.92 mg house dust sample was loaded on a clean stainless steel frit, initially set at 25 °C. With scrubbed air flowing over the house dust sample at 2 L/min., stable baseline ion signals were initially observed (Fig. 5). The frit housing was then rapidly heated to a final temperature of 240°C in *ca* 1 minute.

Compounds desorbed from the dust sample during this time were swept to the MIMS by the flow of scrubbed air, and full scan mass spectra recorded. The extracted ion signal trace for *m/z* 163 (proposed assignment as DMP) reaches a maximum earlier in time as compared to that for *m/z* 149 (proposed assignment as higher molecular weight alkyl phthalate(s)). Although the MIMS experiment operated in full scan mode cannot confirm the postulated identities, the observed *m/z* signals are consistent with the expected desorption behaviors of DMP and higher molecular weight phthalates: because DMP is more volatile than other phthalates, it would be expected to desorb at a lower temperature.

Comparing of the total ion current signal (Fig. 5A) versus the extracted ion signals at *m/z* 149 and 163 (Fig. 5B) suggests that a significant fraction of the desorbed compounds are not phthalates. The full scan mass spectra (not shown) are dominated by fragment ions

differing by m/z 14, suggesting molecules with aliphatic hydrocarbon structures. No further attempts were made in this study to identify these desorbed compounds. Although beyond the scope of the presented work, the future use of alternative ionization sources, tandem mass spectrometry, and/or high resolution mass analyzers will enable improved confidence of making measurements for different classes of analytes, as well as identification of unknown compounds.

Conclusion

An apparatus and example methodology to study interactions between gas phase phthalates and particulate matter is described. The apparatus utilizes Membrane Introduction Mass Spectrometry as a direct analytical approach to selectively detect and quantify gas phase semi-volatile compounds in real time. The online monitoring of the adsorption and desorption behavior of dimethyl phthalate with C18 derivatized silica particles and fine house dust, as well as gas/particle partition coefficients, are presented. An example of how the apparatus can be used is also demonstrated by monitoring the thermal desorption of compounds from a house dust sample.

Future development of this general approach to minimize sorption interactions with transfer line surfaces and improve particulate handling strategies, as well as solving technical details regarding mobilization of the apparatus, are currently under way. The use of this infrastructure and methodology to characterize temperature dependent

partitioning constants and the kinetics of sorption/desorption processes are ongoing, and relevant to understanding inhalation exposure risk in indoor air environments.

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FIGURE CAPTIONS

Figure 1. Schematic diagram of the experimental apparatus. Not to scale.

Figure 2. Gravimetric calibration data for a permeation device filled with DMP. With an air flow rate of 1.0 L/min at 30 °C, a gas phase DMP concentration of 109 ppb_v is achieved. The structure of DMP is given in the inset.

Figure 3. Calibration data obtained for the measurement of online gas phase DMP by MIMS. The inset illustrates the raw data from which the calibration plot was generated.

Figure 4. Phthalate-particle adsorption monitoring experiment for 1.67 mg of 10 μm diameter C18 silica particles loaded onto the stainless steel frit. The shaded area was quantified using Equation 1 to determine the phthalate-particle adsorption.

Figure 5. Extracted ion signals obtained for the online monitoring of compounds desorbed from a house dust sample. (A) total ion current (TIC); (B) ion signals at m/z 149 and 163, with two phthalate fragment ion structures indicated as proposed identification of the respective ion signals.

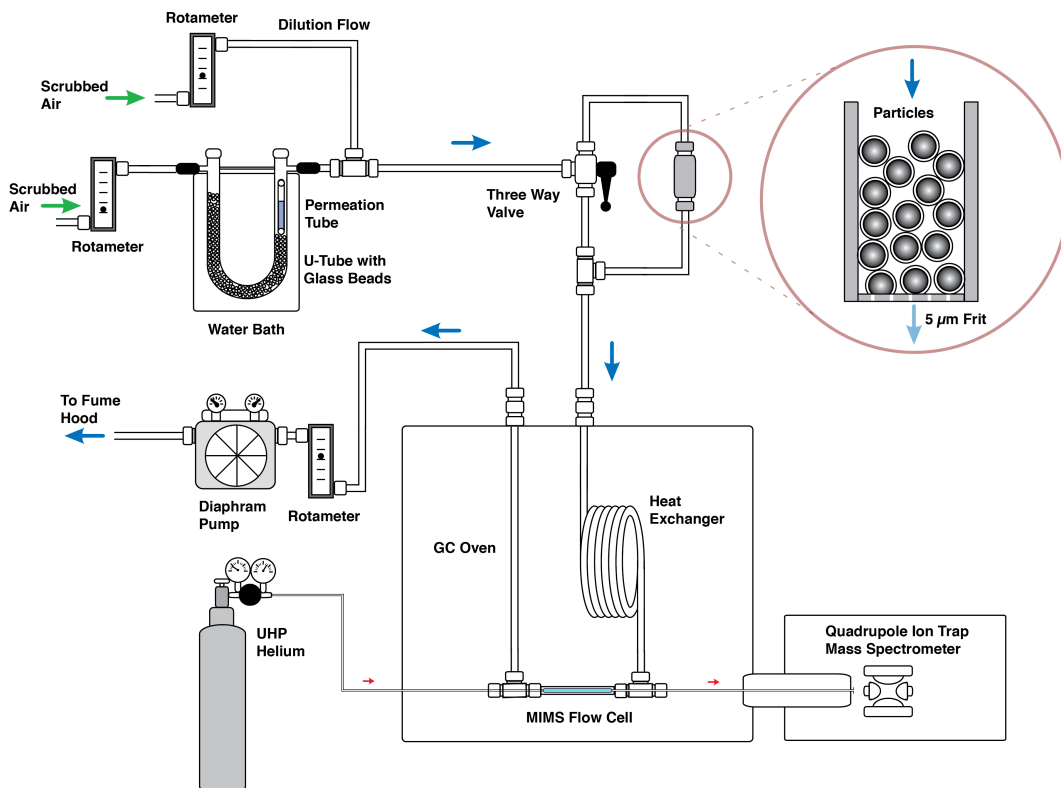


Fig. 1

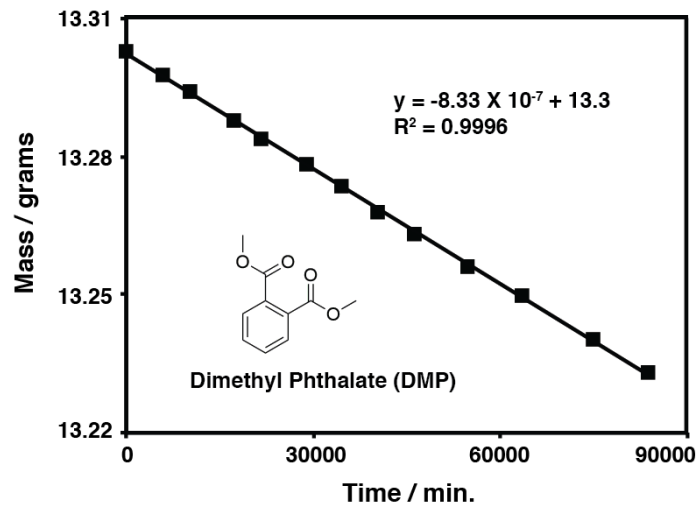


Fig. 2

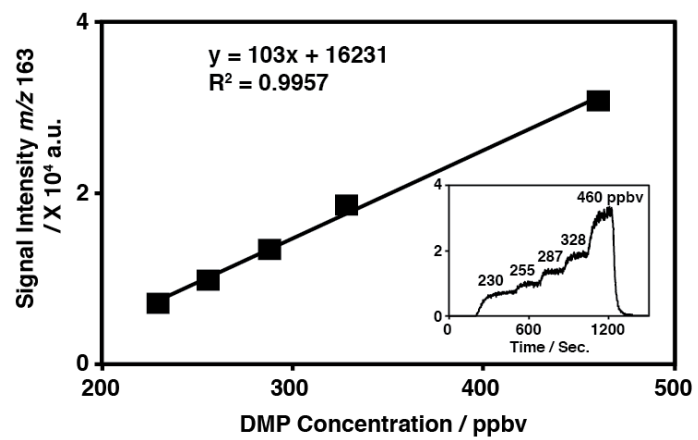


Fig. 3

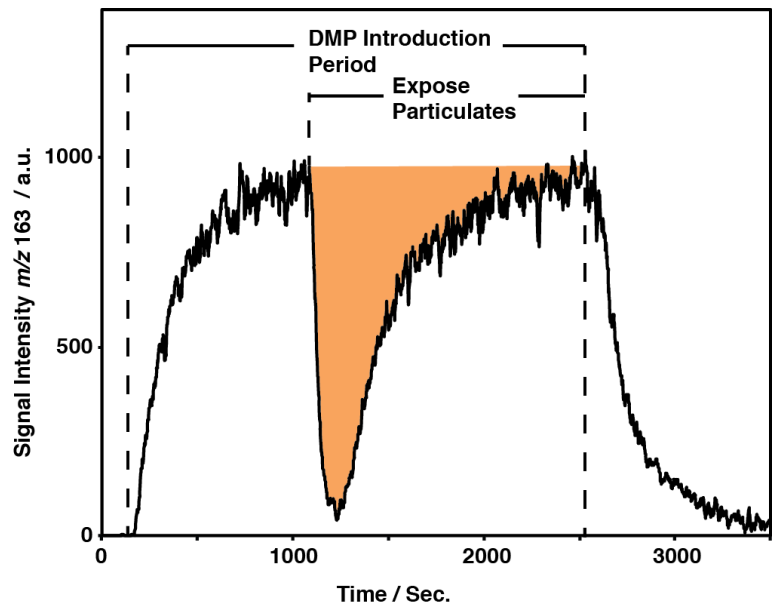


Fig. 4

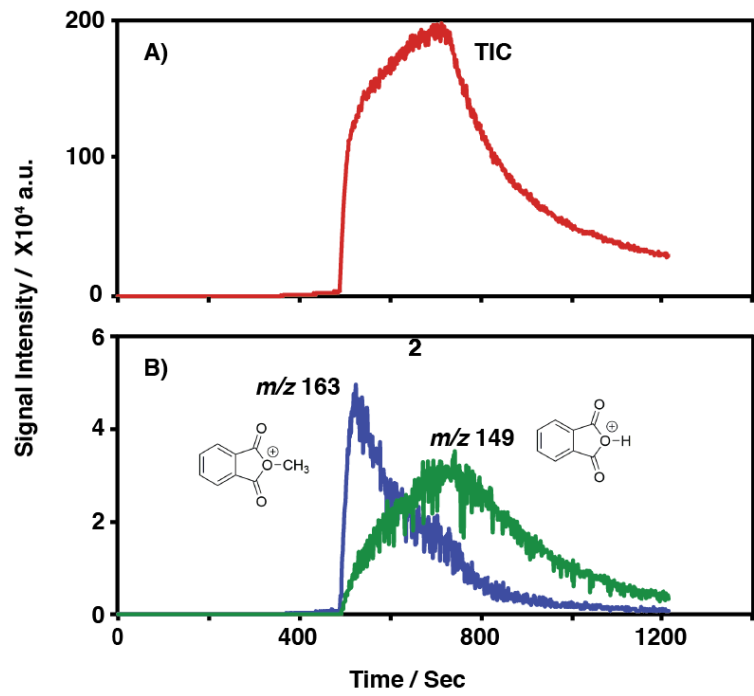


Fig. 5