**Direct analysis of polyaromatic hydrocarbons in soil and aqueous samples
using condensed phase membrane introduction tandem mass
spectrometry with low energy liquid electron ionization**

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Keywords: polyaromatic hydrocarbons, condensed phase membrane introduction mass spectrometry (CP-MIMS), liquid electron ionization, rapid screening, green chemistry, contaminated soils

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Abstract:

Polyaromatic hydrocarbons (PAHs) are listed as priority pollutants by the US EPA. PAH contaminated samples often require extensive sample cleanup before analysis, with the method used dependent upon the sample matrix. We present condensed phase membrane introduction mass spectrometry with liquid electron ionization (CP-MIMS-LEI) as a sensitive and universal technique that can directly analyze both aqueous and soil samples for PAHs without the need for sample clean up or instrumental modifications for different matrices. The method uses a semi-permeable hollow fibre membrane immersion probe to transfer analytes from complex samples into a solvent acceptor phase that is directly entrained at nanoliter/min flows to an LEI interfaced mass spectrometer. The resulting aerosol is desolvated under vacuum leading to analyte vaporization and subsequent electron ionization. Electron energy and LEI vaporization capillary position were examined and optimized for PAHs. The CP-MIMS probe was directly immersed in complex aqueous matrices, demonstrating low ng/L PAH detection limits and response times of ≤ 1.6 minutes. For soil sample analysis, 2-propanol was found to be the optimal PAH sampling solvent. Soil samples were briefly sonicated in 2-propanol, followed by direct CP-MIMS measurement. Soil sample throughput was *ca* 15 samples per hour, with PAH quantitation successful at $\mu\text{g/kg}$ levels. The workflow is remarkably simple, fast, green, and leads to reproducible results that enable high throughput screening of heterogeneous soil samples.

Introduction

Polyaromatic hydrocarbons (PAHs) are ubiquitous, nonpolar compounds produced by both natural and anthropogenic sources, and are classified as persistent organic pollutants (POPs). PAHs are mutagenic, carcinogenic, and bio-accumulative, and as a result are listed as priority pollutants by the US EPA ¹. While all PAHs are highly hydrophobic ($\log K_{ow}$ 3-7) ², they are globally distributed throughout air ³, water ⁴⁻¹², sediments ¹³⁻¹⁹ and biota ²⁰. The complexity of samples contaminated with PAHs often requires extensive sample preparation and cleanup prior to analysis, with procedures that differ significantly depending upon the sample matrix. While recent research has improved the rapidity, robustness, and green chemistry aspects of analytical methods for PAHs, extensive sample handling/cleanup procedures still remain as a significant impasse. PAHs have been analyzed by liquid chromatography using fluorescence and ultraviolet absorbance detection ^{5-7, 13}, and gas chromatography flame ionization ^{17, 21}. Gas chromatography mass spectrometry (GC-MS) is generally the preferred PAH measurement method ²². However, GC-MS methods generally require time consuming sample extraction and cleanup steps.

Despite their low water solubility, aqueous PAHs are monitored because of their mutagenic and carcinogenic effects at low concentrations ². Aqueous sample analyses have traditionally used liquid-liquid extraction sample preparation ⁵⁻⁶, requiring significant time and quantities of hazardous solvents. Alternative aqueous extraction procedures have been developed, including solid phase extraction ²³, solid phase microextraction (SPME) ⁴, stir bar sorptive extraction ⁷, molecularly imprinted polymers ¹², and membrane extraction ⁹⁻¹¹.

Soils, sediments, and biota are often a sink for PAHs because of favourable organic partitioning behaviour. Soxhlet extraction has long been employed to isolate PAHs from complex solid samples due to high extraction recovery ^{14-15, 17-18}. However, the time (up to 16 hours) and large solvent quantities required has lead to alternative, greener techniques, including microwave ¹³⁻¹⁴, sonication ¹⁵⁻¹⁶, super-critical fluid ^{17, 19}, and pressurized solvent extractions ¹⁸. While these techniques provide improvements, they still involve considerable sample pretreatment and cleanup in advance of analysis. These steps increase both the cost and time of analysis, limiting sample throughput. A rapid PAH screening approach for soils was developed by Frandsen *et al.* using field-portable, miniature mass spectrometers and a hot cell to heat the soil ²⁴, but as presented, this method suffers from inadequate detection limits (mg/kg levels), especially for larger, less volatile PAHs.

Recent research has targeted the development of simpler analytical methods for PAHs and other similar compounds in complex matrices. Zenobi *et al.* analyzed aqueous pesticides and POPs using online SPME coupled with

photo and dielectric barrier discharge ionization sources with MS^{4, 25}. The Amirav and Cappiello groups have analyzed liquids for non-polar compounds with electron impact sources and MS, using a molecular beam interface²⁶ and liquid electron ionization (LEI)^{11, 27-28}, respectively. All are more universal with respect to the analyte, but without additional extraction techniques, they have generally been restricted to solution phase samples as presented.

Condensed phase membrane introduction mass spectrometry (CP-MIMS) typically uses a hollow fibre polydimethylsiloxane (PDMS) membrane mounted on a direct sampling probe. The PDMS membrane is permeable to hydrophobic analytes, which are often transferred in an organic solvent acceptor phase to an atmospheric pressure ionization source²⁹⁻³⁰. The membrane rejects charged solutes and particulate matter, while hydrophobic analytes (such as PAHs) permeate through the PDMS. Direct sampling CP-MIMS probes are applicable with a variety of different sample matrices, and can be paired with different ionization sources compatible for specific analyte classes. For PAHs, CP-MIMS may be coupled to electron ionization through the use of liquid electron ionization (LEI). In LEI, a nanoflow of liquid forms an aerosol in a heated helium stream under modest vacuum, followed by desolvation and solute (analyte) vaporization. The gas phase analytes are then ionized in an EI source. The coupling of CP-MIMS to LEI represents an ideal pairing of on-line membrane extraction and ionization for hydrophobic, neutral compounds, such as PAHs. Recent work in our group employed CP-MIMS coupled to an early variant of LEI (termed direct EI, DEI) for the measurement of PAHs in a variety of aqueous samples¹¹. The study presented here represents a significant advancement for the direct measurement of PAHs in complex heterogeneous samples (*i.e.* soils) with minimal sample handling.

Experimental

Standard and Sample Preparation

Aqueous PAH samples were prepared in 18 M Ω -cm de-ionized water (Model MQ Synthesis A10, Millipore Corp., Billerica, MA, USA), seawater (unfiltered, collected from local industrial area), and surface water (unfiltered, collected from local river). Aqueous standards were prepared at 0.80, 5.0, 25, and 50 μ g/L for pyrene and naphthalene, and at 0.80, 5.0, and 25 μ g/L for anthracene. Further details are available in the supporting information.

For prepared soil samples, clean sandy loam (Sigma Aldrich, 5.96% organic matter by mass, PAH free) was used. 4.0 g of soil was pre-wetted with 1500 μ L of 2-propanol, and spiked with PAHs to yield dry soil concentrations of 500, 1000, 1500 and 2000 μ g/kg each for anthracene, pyrene, and benzo[a]pyrene. The prepared soil samples were left to air dry at ambient

conditions for 5 days before analysis. PAH contaminated soil samples were obtained from the Ontario Ministry of Environment and Climate Change.

For all organic and aqueous sample measurements, the CP-MIMS probe was directly immersed into magnetically stirred (900 RPM) 38 mL samples (40 mL glass vials). Unless otherwise noted, analyte signals were allowed to reach steady-state, and were background subtracted using the signal from an appropriate matrix blank. For all soil sample measurements, samples (0.5 g) were suspended in 7 mL of 2-propanol in 8 mL glass vials, and spiked with 280 µg/L internal standard (pyrene-*d*₁₀ in 2-propanol). The slurry was then sonicated (FS140 ultrasonic bath, Fisher Scientific, 135 W) while heating at 75°C (Precision Scientific Co. Porta Temp, Chicago, IL, USA) for 3 minutes. The CP-MIMS probe was then directly immersed in the 2-propanol/soil suspension for 2 minutes immediately after sonication, with no further sample cleanup. During measurements, soil slurries were stirred at 900 RPM. Following all measurements, the probe was rinsed in stirred 2-propanol for 2 minutes to return the signal to baseline levels.

Condensed Phase Membrane Introduction Mass Spectrometry – Liquid Electron Ionization (CP-MIMS-LEI) System

Figure 1 provides a schematic diagram of the CP-MIMS-LEI instrumental apparatus. A triple quadrupole mass spectrometer (Agilent Technologies Inc. 7010B GC-MS/MS, Santa Clara, CA, USA) equipped with a high-efficiency source (HES) was used for tandem mass spectrometry (MS/MS) with a 500 ms dwell time. Analyte MS/MS parameters are presented in Table 1, and their respective physicochemical properties presented in Table S-1. Custom yttria coated yttria/rhenium alloy filaments (Scientific Instrument Services Inc., Ringoes, NJ, USA) were used for all studies, operated at 20 eV with a 100 µA emission current. A source temperature of 280°C was used.

An 8.0 cm length of 170 µm thick (0.30 mm i.d., 0.64 mm o.d.) PDMS hollow fibre membrane (Silastic brand, Dow Corning, Midland, MI) was coil mounted on a CP-MIMS immersion “J-probe” (Fig. 1), with construction details previously described³¹. A capillary HPLC pump and degasing module (1100 series, Agilent) was used to supply acceptor phase at 50 µL/min through the lumen of the hollow fibre membrane. To achieve stable pump flows, a 10 cm of fused silica capillary flow restrictor yielded *ca* 50 bar operating pressures. All fused silica capillaries for this study were polyimide coated and not deactivated (Polymicro Technologies, Phoenix, AR, USA). Our previous studies have shown that organic co-solvents present in the acceptor phase form *in situ* polymer inclusion membranes with PDMS that improve membrane permeability³². For all presented studies, a 15:85 heptane:methanol (v/v) acceptor phase was used to increase sensitivity and shorten analyte response times.

A zero dead volume stainless steel tee junction was used as a passive flow splitter (Fig. 1) post-membrane, reducing the acceptor phase flowrate to ~300 nL/min for optimal signals²⁸, and to minimize internal pressure within the PDMS membrane. Flow rate measurements were made off-line using a Sensirion SLG-0150 flow meter (Stäfa, ZH, Switzerland). Both rough and high vacuum pressures were monitored as an indicator of stable LEI performance (typically 1.3×10^{-1} and 9.5×10^{-5} torr, respectively). Neither are ideal measures for the ion source region pressure, which is more relevant for LEI performance monitoring. Thus, an in-house built stainless steel flange was mounted on the source end of the MS manifold (Fig. S-1), and equipped with an ion gauge (Hewlett Packard 59864A Ionization Gauge and Controller, Palo Alto, CA, USA). Stable LEI performance resulted in source region pressure measurements of 1.0×10^{-4} torr.

A modern LEI interface has been described in detail by Termopoli *et al.*²⁸. In our presented system, the acceptor phase was flowed post-splitter into 30 cm of a fused silica capillary (150 μm o.d., 30 μm i.d., referred to subsequently as the LEI capillary) towards the MS. The LEI capillary extended through a stainless steel tee into a fused silica capillary liner (800 μm o.d., 400 μm i.d.). A capillary column gas chromatograph (Agilent 7890B GC) was used to supply 0.5 mL/min helium flow to the tee (Fig. 1). In this way, helium is flowed coaxially within the capillary liner, around the liquid flow in the LEI capillary. The transfer line of the GC-MS/MS system was maintained at 400°C for all studies. The liner capillary extended through the transfer line, and the tip of the liner capillary extended 2 mm past the end of the transfer line into the MS source. The liner capillary helps to prevent analyte degradation/loss within the heated zone by preventing analyte contact with the transfer line metal surfaces. Negligible performance degradation occurred over weeks of daily use. The LEI capillary extended 6 mm into the transfer line unless otherwise specified. A 3 cm gap between the entrance of the transfer line and the helium tee was used to separate the tee from the heated zone, preventing premature vaporization in the LEI capillary. Acceptor phase exiting the LEI capillary was subsequently nebulized, desolvated and vaporized in the heated coaxial helium flow, pneumatically transferring neutral analytes and vaporized acceptor phase solvent to the MS source.

Data Analysis for CP-MIMS-LEI

All measurements were conducted in triplicate unless otherwise noted, with standard deviation error bars. The signal to noise ratios (S/N) presented in Table S-3 and Figure 2 were calculated using unsmoothed data. Standard deviations for the signal to noise ratios were calculated using steady-state signal measurements (*i.e.* not baseline noise). A 7-point moving boxcar smoothing function was applied to all other presented data. Detection limits were calculated as 3 times the standard deviation of the baseline for the appropriate matrix blank, divided by the calibration curve slope, given by equation 1:

$$DL = 3 SD_{Baseline} / Slope \quad (1)$$

For the direct quantitation of PAHs present in soil samples, naphthalene, anthracene, pyrene and benzo[a]pyrene response factors were calculated relative to pyrene-*d*₁₀, utilizing 100 µg/L PAH standards prepared in 2-propanol, (6 replicates, Table S-2). Relative response factors were observed to be constant for up to 5 mg/L of all target PAHs in 2-propanol. Soil sample quantitation results are presented as dry soil PAH concentrations for specific isomer classes based upon precursor *m/z* values (Table 1). Given that the response factors are calculated for specific PAHs (described above), PAH isomer class concentrations are represented as 'equivalent concentration units' for the respective model PAHs used to generate the response factors.

Results and Discussion

LEI Optimization for PAHs

A parametric investigation of PAH vaporization efficiency for various LEI capillary insertion positions inside the heated transfer line was conducted (Fig. 2A). S/N for naphthalene and anthracene, which have the highest vapour pressures of the analytes studied, were essentially independent of the LEI capillary position. However, less volatile pyrene and benzo[a]pyrene had significant sensitivity effects dependent upon capillary insertion depth. Vaporization is likely aided for these less volatile analytes because of the higher temperatures and reduced pressures experienced with deeper insertion into the heated zone²⁸. An optimum LEI capillary insertion depth of 6 mm was determined for the PAHs examined, and used for all subsequent studies.

Historically, 70 eV electron energy has been used for most EI experiments, as electron ionization cross section for many analytes is maximized at 70 eV³³. Lower electron energies may be desirable to limit fragmentation and preserve the molecular ion for tandem mass spectrometry (MS/MS). The HES used for these studies allowed the examination of lower electron energy use. In Figure 2B, electron energy was varied from 20-70 eV, demonstrating optimal S/N for all the PAH MS/MS transitions at 20 eV. Less extensive fragmentation at 20 eV resulted in greater parent ion abundance, and consequently signal improvements. The HES design uses an extended electron collision zone, coaxial with the analyzer ion beam path, and is further compressed by concentric magnetic fields to increase efficiency³⁴. This is unlike the typical Nier-type EI source design used in most EI systems³³, which has the electron beam perpendicular to the ion beam, and a truncated electron collision volume. The trends observed in Figure 2B are of particular interest with regard to PAHs, which typically do not display extensive EI fragmentation at 70 eV. Although beyond the scope of this study, we speculate the observed trend should be more pronounced

for compound classes experiencing increased fragmentation at higher electron energies. An alternative contribution to the observed trend in Figure 2B may also relate to the reduced ionization efficiency for the acceptor solvent at lower electron energies, resulting in reduced intra ion source space charge effects³⁵.

While the analytical benefits of 20 eV operation are apparent, there were initial challenges with respect to the filament material. Commercially available rhenium filaments were found to erode and eventually fail after prolonged use, likely due to the high acceptor phase solvent vapour levels present in the ion source. By utilizing custom yttria/rhenium alloy filaments with a yttria coating, effective 20 eV operation was possible for months of daily use. Images of both rhenium and yttria coated filaments after 50+ hours of CP-MIMS-LEI operation are given in Figure 3. Therefore, yttria-coated filaments were used for all presented studies.

Aqueous PAH Calibration Studies

Aqueous calibration curves for naphthalene, anthracene and pyrene were obtained at low $\mu\text{g/L}$ levels in de-ionized water, seawater, and river water. All PAHs examined demonstrated good linearity ($R^2 > 0.996$), low ng/L detection limits and fast $t_{10-90\%}$ signal response times (≤ 1.6 mins.) for these aqueous sample matrices (Table 2). These results represent over an order of magnitude sensitivity improvement and significantly shorter response times than presented in our earlier studies¹¹. Faster response times are attributed to greater analyte permeability, facilitated by the heptane:methanol acceptor phase, consistent with earlier work³². The sensitivity improvements are due to both the greater permeability and ion source optimization. Interestingly, the PAH calibration slopes presented in Table 2 for river water and seawater are comparable to that of de-ionized water, despite the significant differences in matrix composition. The results presented are consistent with other findings, which suggest that matrix effects in LEI are significantly reduced when compared to other liquid – mass spectrometry couplings²⁷, particularly electrospray ionization (ESI)³⁶⁻³⁷. While the PDMS membrane rejects salts, ionized species and particular matter from the sample, co-permeating compounds have still been observed to cause significant ionization suppression in ESI based CP-MIMS measurements presented in earlier studies³⁸. The low ng/L aqueous detection limits demonstrated by this study may prompt future studies on expanding aqueous analyses to larger, less water soluble PAHs.

Solvent Selection for Direct Soil PAH Measurements

A series of common organic solvents (acetonitrile, dichloromethane, ethanol, ethyl acetate, N,N-dimethylformamide, methanol, and 2-propanol) were evaluated for their compatibility with PDMS membranes and their suitability as an analysis solvent for direct soil PAH measurements. The solvent choice must sufficiently aid PAH solubility and extraction from solid sample matrices, but not

excessively swell the PDMS membrane. If the solvent-PDMS solubility is too large, a soft, less robust membrane results, which is more prone to physical damage. Table S-3 summarizes the observed S/N ratios for the direct analysis of representative PAHs (100 µg/L each) utilizing various sampling solvents. Dichloromethane, a common PAH extraction solvent⁵⁻⁶, demonstrated poor analytical performance with CP-MIMS-LEI and excessively swelled the PDMS membranes. Hexane, another common PAH extraction solvent⁵, was not investigated, since it similarly causes excessive PDMS swelling. Ethyl acetate and 2-propanol demonstrated the best analytical performance for the solvents studied, with 2-propanol exhibiting the best overall performance (Table S-3).

The differences in sensitivity for the tested sampling solvents may be evaluated by examining factors influencing membrane transport. For a given analyte concentration and membrane thickness, the steady-state signal intensity in a CP-MIMS experiment is directly related to the membrane permeability (P), which can be expressed as the product of a partitioning term and a diffusivity term as given in Equation 2:

$$P = K_{m-s} D_m \quad (2)$$

where D_m is the analyte diffusivity in the membrane, and K_{m-s} the relative solubility of the analyte in the membrane and sample (a partition constant). Sample solvent can therefore affect P (and consequently sensitivity) by affecting either or both K_{m-s} or D_m . In part, increased solvent solubility in the membrane may cause the membrane to swell, making the membrane more permeable due to an increase in analyte diffusivity through the membrane (D_m)^{32, 39}. In addition to the degree of swelling, solubility parameters (e.g. Hansen, Hildebrand; derived from cohesive energy densities) may be used to predict solvent-polymer membrane solubility and D_m , as phases with similar solubility parameters are generally more soluble with each other⁴⁰. Solubility parameters (in MPa^{1/2}) for the sampling solvents examined here are given in Table S-4. The parameter for ethyl acetate (18.2) is reasonably close to that of PDMS (14.9), consistent with an increased PAH diffusivity in the swelled PDMS, and therefore a greater permeability.

2-Propanol (solubility parameter of 23.5) is not excessively soluble in PDMS, indicated by solubility parameter comparisons and minimal membrane swelling. The optimal PAH performance observed must therefore come from an effect on K_{m-s} . This is supported by lower PAH solubilities in 2-propanol than ethyl acetate (Table S-5), suggesting a higher activity of PAHs in 2-propanol compared to ethyl acetate when present at equimolar concentrations. Consequently, we attribute the improved sensitivity of PAHs in 2-propanol solution compared to ethyl acetate to an increased K_{m-s} , leading to a larger concentration gradient in the membrane, and subsequently greater mass transport. It should be noted that

PAH solubility in 2-propanol is still sufficiently high to justify using 2-propanol as a sampling solvent for PAHs present in soil samples ($[\text{pyrene}]_{\text{sat}} = 7.69 \times 10^3 \text{ mg/L}$, $[\text{anthracene}]_{\text{sat}} = 9.60 \times 10^2 \text{ mg/L}$). Therefore, 2-propanol was chosen as the optimal sampling solvent for direct soil measurements. Furthermore, 2-propanol is now recommended as a green solvent alternative, a significant advantage over conventional PAH sample extraction solvents such as hexane or dichloromethane ⁴¹.

Figure 4 demonstrates an evaluation of 2-propanol suitability as a sampling solvent for the direct measurement of PAHs in soil samples. Panel A gives the signal chronograms of four representative PAHs (100 $\mu\text{g/L}$ each) spiked together into 2-propanol at $t = 3$ mins. Signals were allowed to rise to steady-state levels, and at $t = 7$ mins, 1.0 g of clean, sandy loam was added directly to the continuously stirred sample. Despite the high organic content of the soil (5.96 wt%), no significant change to the steady-state signal was observed, indicating that the PAHs remained free in solution rather than being sorbed by the soil. This behavior is in stark contrast to a similar experiment conducted in de-ionized water (panel B), where the MS signals for the solution phase concentration of naphthalene, anthracene and pyrene decrease dramatically within 5 mins of adding soil to the stirred water sample. The data suggests nearly complete PAH sorption on the soil when present in aqueous suspensions. Benzo[a]pyrene was not used in the de-ionized water study because of its limited water solubility. Based upon these sorption studies, 2-propanol demonstrated promise as an effective sampling solvent for direct soil measurements of the PAHs examined.

Prepared Soil Measurements

Prepared PAH soil samples (500-2000 $\mu\text{g/kg}$) were analyzed by CP-MIMS-LEI. The masses of PAHs extracted into 2-propanol were plotted against the masses of PAHs loaded, as shown in Figure 5. Linear relationships are observed ($R^2 \geq 0.992$), demonstrating that different PAH loadings correlate with their measured concentrations. Percent recoveries (represented by the slopes in Fig. 5) for anthracene, benzo[a]pyrene and pyrene were 62%, 76% and 76% respectively (average of 71%), with corresponding detection limits of 120 $\mu\text{g/kg}$, 70 $\mu\text{g/kg}$ and 60 $\mu\text{g/kg}$ (Fig S-2). Although the short, 3 minute sonicated extraction in hot 2-propanol is not exhaustive for soil PAHs, we believe the simplicity of the CP-MIMS-LEI work flow presented, bypassing any sample cleanup, provides significant advantages as a semi-quantitative, rapid screening method.

Contaminated Soil Measurements

To examine the potential for direct PAH measurements in contaminated soil samples, three real world samples were analyzed by CP-MIMS-LEI. A suite of 21 individual PAHs were also previously measured in these samples by an

independent laboratory using accelerated solvent extraction in dichloromethane, workup and isotope dilution GC-MS⁴². For the CP-MIMS-LEI measurements, concentrations of PAHs in 2-propanol were quantified via predetermined response factors (Table S-2), and reported as mass ratios in the original soil sample (Table 3). Because PAH structural isomers are not resolved by CP-MIMS-LEI (*i.e.* there is no chromatographic separation), quantitative results in Table 3 are reported for isomer classes. These are expressed as equivalent amounts of naphthalene (m/z 128), anthracene (m/z 178), pyrene (m/z 202) and benzo[a]pyrene (m/z 252), based upon the MS/MS transitions in Table 1. The internal standard signal (pyrene- d_{10}), consistently present in each sample at 280 $\mu\text{g/L}$, had a percent relative standard deviation of 5% across all CP-MIMS-LEI measurements. Percent relative standard deviations for individual PAHs ranged from 1 to 47% (3 samples with 3 replicates each, see also Fig. 6).

Soil PAH concentrations observed by 2-propanol sonicated sampling followed by CP-MIMS-LEI measurements were generally less than those reported by accelerated solvent extraction - GC-MS (Table 3). The average percent bias of CP-MIMS-LEI relative to GC-MS was -30%, where individual biases ranged from -72% to +45% (negative in 11 out of 12 cases). These results are consistent with the recoveries observed for the prepared soil samples in Figure 5 (*i.e.*, non-exhaustive extraction, -29% average bias). Quantitation results from GC-MS, which were for individual PAHs, were similarly summed according to isomer classes for purposes of comparison to CP-MIMS-LEI data, as presented in Table 3.

As presented, the complete analytical duty cycle for direct PAH determinations in soil using CP-MIMS-LEI is *ca* 15 soil samples per hour, representing a significant improvement over existing analytical strategies, such as GC-MS. Although not examined, it is anticipated that the use of previously demonstrated, non-steady-state CP-MIMS measurement approaches would further reduce the analysis times³².

In spite of the fact that the lack of chromatography in CP-MIMS-LEI does not allow for the quantitation of individual PAH isomers, given the simplified green chemistry workflow, rapidity, reproducibility, and sensitivity of CP-MIMS-LEI, we propose this technique as a rapid screening tool for high throughput applications. Although beyond the scope of this study, we are actively exploring liquid reagent chemical ionization (CI) strategies for direct PAH isomer differentiation with our approach. Mosi *et. al.* demonstrated the use of halocarbon cations as CI reagents for PAH isomer differentiation⁴³. CP-MIMS-LEI can be readily adapted for use with a variety of liquids as sources for reagent ions, either by using a suitable liquid acceptor phase itself, or by admixing suitable dopants. Further, adapting the presented methodology for use with small MS systems may allow for onsite applications (*e.g.*, contaminated site remediation, critical incident

response, etc.), where obtaining reliable semi-quantitative information can be used to support decisions in the field, and inform adaptive sampling strategies for complimentary lab-based analytical determinations. Importantly, CP-MIMS-LEI measurements are time resolved, and may be used to monitor online processes, such as the adsorption and desorption phenomena presented herein. Ongoing work is being conducted to improve PAH extraction efficiency from soils, and to further increase sample throughput.

Conclusions

CP-MIMS-LEI represents a novel, sensitive and direct, rapid screening technique for PAHs from both aqueous and soil samples without any instrumental or sampling modifications. The rapid detection of PAHs in environmental samples has potential applications for protection of the environment and human health. Furthermore, this study represents novel soil analyses that completely obviate sample cleanup, allowing for significantly simpler sample handling and faster sample throughput.

Acknowledgements:

The authors would like to thank Lukas Miner and the AERL group members, Agilent Technologies for funding (UCR Grant# 4088) and providing the analytical instrumentation, Chunyan Hao at the Ontario Ministry of the Environment and Climate Change for graciously providing the contaminated soil samples and GC-MS results, and Achille Cappiello's research group for their LEI assistance. The authors acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC) for Discovery Grants Program funding (RGPIN-2016-05380), and also Vancouver Island University and the University of Victoria for their on-going support of both faculty and graduate students.

Tables

Table 1: MS scan parameters

Analyte	MS/MS Transition	Collision Energy (eV)
Naphthalene	128 → 102	30
Anthracene	178 → 176	34
Pyrene	202 → 200	42
Benzo[a]pyrene	252 → 250	42
Pyrene- <i>d</i> ₁₀	212 → 208	42

Table 2: Calibration data, detection limits, and response times for PAHs in aqueous matrices

Analyte	Matrix	Equation of line	R ²	Detection Limit ^a (ng/L)	t _{10-90%} (min)
Naphthalene	De-ionized water	y = 41.5x + 21.2	0.9991	330	1.3
	Seawater	y = 40.7x + 20.5	0.9988	330	1.3
	River water	y = 49.3x + 15.0	0.9995	270	1.1
Anthracene	De-ionized water	y = 44.5x + 6.7	0.9997	83	1.4
	Seawater	y = 45.3x + 5.0	0.9996	85	1.4
	River water	y = 51.7x + 5.9	0.9995	70	1.3
Pyrene	De-ionized water	y = 68.1x + 16.4	0.9996	70	1.6
	Seawater	y = 62.7x + 52.3	0.9963	76	1.5
	River water	y = 78.9x + 44.3	0.9977	61	1.5

^a Estimated using Equation 3

Table 3: Soil analysis results for PAH isomer classes by GC-MS and CP-MIMS-LEI

Sample	Isomer Class (<i>m/z</i>)	CP-MIMS-LEI (mg/kg)	GC-MS (mg/kg)	% Bias ^h
1	128	0.7 ± 0.4 ^a	0.97 ^a	-29
	178	5 ± 2 ^e	8.77 ^b	-44
	202	10 ± 2 ^f	14.13 ^c	-31
	252	9.7 ± 0.4 ^g	10.36 ^d	-8
2	128	0.12 ± 0.06 ^a	0.41 ^a	-72
	178	4.9 ± 0.6 ^e	5.62 ^b	-14
	202	14.0 ± 0.9 ^f	16.86 ^c	-17
	252	21.1 ± 0.3 ^g	14.54 ^d	+45
3	128	1.2 ± 0.2 ^a	2.11 ^a	-43
	178	19 ± 2 ^e	38.56 ^b	-51
	202	26 ± 2 ^f	57.08 ^c	-54
	252	19 ± 1 ^g	34.08 ^d	-43

^a Concentration of naphthalene

^b Summed concentration of anthracene and phenanthrene

^c Summed concentration of fluoranthene and pyrene

^d Summed concentration of benzo[a]pyrene, benzo[b]fluoranthene, benzo[e]pyrene, benzo[k]fluoranthene and perylene

^e Reported as equivalent amount of anthracene

^f Reported as equivalent amount of pyrene

^g Reported as equivalent amount of benzo[a]pyrene

^h % Bias = (CP-MIMS-LEI Result – GC-MS Result) / GC-MS Result × 100%

Figures and Legends

Figure 1: Schematic diagram of the CP-MIMS-LEI experimental apparatus.

Figure 2: CP-MIMS-LEI system optimization. A) Optimization of capillary position in the transfer line for select PAHs. B) Electron energy optimization for select PAHs with LEI source.

Figure 3: Image comparing EI filaments operated for 50+ hours of CP-MIMS-LEI measurements. A) Custom yttria coated yttria/rhenium alloy filament operated at 20 eV. B) yttria/rhenium alloy filament operated at 70 eV. The red circle in panel B represents a filament failure.

Figure 4: Comparison of signal chronograms for target PAHs in A) 2-propanol and B) de-ionized water (both 38.0 mL) with the addition of clean, sandy loam using CP-MIMS-LEI. Inset picture is of the aqueous sample after the addition of the clean, sandy loam.

Figure 5: Investigation of PAH recoveries for direct CP-MIMS-LEI measurements of prepared soil samples.

Figure 6: Representative signal chronograms for three soil sample analyses by CP-MIMS-LEI, illustrating rapid sample throughput. Inset picture is that of a representative sample.

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