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## Subsurface detection of fossil fuel pollutants by photoionization and gas chromatography/mass spectrometry

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## ABSTRACT

This paper describes analysis of environmental pollutants at depth without bringing sample to the surface. It is based on an improved 3-stage Peltier freeze trap, which efficiently pre-concentrates volatile coal tar and petroleum hydrocarbons, and an integrated system for detecting pollutants on-line, in real-time by photoionization detection and quantitation by gas chromatography/mass spectrometry (GC/MS) as the probe is advanced into the subsurface. Findings indicate measurement precision and accuracy for volatiles meet EPA criteria for hazardous waste site investigations. When a Teflon membrane inlet is used to detect contaminants in groundwater, its 140 °C temperature limit restricts analyte collection in soil to C<sub>2</sub>-phenanthrenes. Two case studies demonstrate the probe is well-suited to tracking petroleum and coal tar plumes from source to groundwater.

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### 1. Introduction

Hazardous waste site investigations are best carried out when sensor arrays provide continuous subsurface information, with 3-dimensional conceptual models produced quickly, accurately, and cost-effectively. In this context, cone penetrometers and geoprobes advance piezoelectric sensors to depth to collect geological and hydrological data. Chemical sensors have also been deployed to obtain spatial information on pollutants (Aldstadt and Martin, 1997). These include laser induced breakdown (Miles and Cortes, 1998), gamma (Palmer and Tepper, 2001), and X-ray fluorescence (Elam et al., 2000) spectroscopy for metals; laser induced fluorescence (Robbat et al., 1998a; Kram et al., 2004), Raman (Rossabi et al., 2000), and infrared (Garcia-Gomez et al., 2004) spectroscopy; and electron capture (McAndrews et al., 2003) and photoionization (Griffin and Watson, 2002) detectors for organics.

None of these analytical tools provide information on the wide array of organic pollutants targeted by forensic investigators. For example, although direct measuring thermal extraction mass spectrometry has been used to detect volatile organic compounds (VOCs) successfully, semivolatiles (SVOCs) remain a challenge (Myers et al., 1998; Robbat, 2001; Rossabi et al., 2003). Nonetheless, the US Environmental Protection Agency (EPA) lauded the Navy for saving six-years and \$3 million employing this technique to detect chlorinated solvents in groundwater (USEPA, 2009). Until

recently (Considine and Robbat, 2008), no on-line detection system existed for SVOCs for three reasons: (1) lack of efficient extraction, transfer, and quantitation of all EPA targeted analytes, (2) when MS detectors saturate, recovery requires long bakeout periods, and (3) standard EPA methods, based on conventional analytical instruments and data analysis software, necessitate separate VOC and SVOC analysis, which means field personnel sit idle waiting for data.

Consistent with EPA's TRIAD program (Crumbling et al., 2003; USEPA, 2003), the aim of which is to reduce site characterization uncertainties; we systematically attacked the abovementioned problems. First, we developed the only sampling probe capable of thermally desorbing SVOCs at depth without bringing sample to the surface (Gorshteyn et al., 1999a,b; Gorshteyn and Robbat, 2000). At probe temperatures of 400 °C, soil-bound organics were volatilized, extracted, and transferred through a 30 m, 300 °C heated transfer line and trapped off-line in Tenax filled adsorbent tubes or frozen glass sleeves. The former efficiently trapped VOCs (70–100%); the latter SVOCs (40–95%). Optimum results were obtained when samples were analyzed off-line by thermal desorption gas chromatography/mass spectrometry (TDGC/MS). Second, a 4-fold reduction in analysis time was achieved by employing resistively heated GC columns (Robbat et al., 1999; Robbat, 2001). Third, the Ion Fingerprint mass spectral deconvolution algorithms quantified target compounds independent of matrix complexity (Gankin et al., 1998; Robbat, 2000). Findings showed results meet EPA data quality objectives for field investigations (Robbat et al., 1998b). Fourth, a photoionization detector (PID) was added to

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the probe to produce subsurface profile maps. The sensor served two purposes: (1) it provided continuous, real-time detection of organics as the probe was advanced into the subsurface and (2) it protected the MS by signaling the concentration at a specific depth.

Based on sensor response, organics were pre-concentrated on-line in a single-stage Peltier-cooled freeze trap prior to off-line analysis by GC/MS. Soil moisture limited sample collection to soils containing <15% water. For groundwater, a hydrophobic Teflon-impregnated stainless steel mesh inlet was used. At temperatures >140 °C, the membrane no longer excluded water, which limited PAH collection to C<sub>2</sub>-phenanthrenes in soil. Despite this shortcoming, a 0.92 correlation coefficient was obtained between the on-line PID response and GC/MS results (Considine and Robbat, 2008). In contrast, the correlation coefficient was 0.99 when the sensor was compared to EPA method 8270 data. Analysis revealed loss of benzene, naphthalene and their alkylated homologs, which passed through the freeze trap. Research showed the combination of *in situ* chemical sensing and confirmation by on-site GC/MS produced data of acceptable quality to determine contaminant boundaries and migration pathways.

This paper reports the results of a newly-designed 3-stage Peltier freeze trap that overcomes the deficiency reported earlier as well as the integration of an on-line GC/MS detector. Coal tar seams, which are dense non aqueous phase liquids, as narrow as 5 cm were detected and confirmed by GC/MS at the same location. Characterization of contaminated soil surrounding an underground storage tank containing industrial heating oil confirmed this conclusion, since field vs. lab data were consistent with EPA precision and accuracy requirements despite high concentrations of matrix interferences.

## 2. Experimental section

### 2.1. Chemical sensor design

Construction of the heated probe, transfer line, and direct measuring photoionization sensor and GC/MS are shown in Fig. 1. The materials used to ensure safe operation have been described previously (Considine and Robbat, 2008). For field work, the 30-m heated transfer line (1) was threaded through 1.2-m, 35-mm OD, 22-mm ID steel pipes (2). The heated transfer line consisted of a resistively-heated Silicosteel tube sheathed in multiple layers of thermal, electrical, and water resistant insulation. The transfer line was held at 280 °C to prevent condensation in the transfer line. A 33-cm pipe (3) housed the sample collection port (4). For unsaturated soil, the pipe could be heated to 400 °C by high temperature cartridges (6). At this temperature soil was 300 °C after 5 min. Silicosteel outlet and inlet tubes were drill-fitted through the pipe to inject nitrogen into soil and to collect sample. A vacuum pump attached to the inlet tube reduced the pressure and facilitated sample collection at the inlet. In contrast, Teflon-impregnated stainless steel mesh (5, Geoprobe, Salina, KS) served as the collection port for saturated soil and groundwater. The hydrophobic mesh, heated to 140 °C, excluded water/steam and prevented damage to the transfer line. In this study, the membrane inlet probe (MIP) was used to obtain data for coal tar and petroleum hydrocarbons.

Nitrogen (7) swept sample from the collection port through a six-port valve (8) held at 300 °C to either the PID or GC/MS for on-line analysis. Carrier gas flow was calculated based on the modified Reynolds equation:  $Re_m = ReV_0 = \omega^2 \rho \tau d / \mu l = 256$ ; or  $5.5 \text{ mL min}^{-1}$  (at 5.45 kPa). Equation variables included transfer line length ( $l$ ), diameter ( $d$ ), carrier gas velocity ( $\omega$ ), density ( $\rho$ ), and viscosity ( $\mu$ ), collection gas to dead volume ratio ( $V_0$ ), and sample transport time ( $\tau$ ) from the collection port to the sensors.

When the PID spiked, flow was switched to a 3-stage Peltier freeze trap (FT, 9), which was designed by stacking the Peltier chips (Ferrotec, Bedford, NH) and cementing a 30 cm × 0.8 mm OD, 0.53 mm ID spiraled Silicosteel tube. By incorporating a heat sink and fan, the freeze trap achieved temperatures of −30 °C despite sitting on the GC. The new design improved volatile collection efficiency compared to the single-stage Peltier trap (−8 °C). The freeze trap also served as the thermal desorber (TD, 10), since the tube was resistively heated to 280 °C in less than 10 s. Helium (11) carried vapor from the TD to the GC/MS. The GC's pneumatics controlled the flow rate and pressure (1.0 mL min<sup>−1</sup> and 4.96 kPa).

### 2.2. Gas chromatography/mass spectrometry

A Gerstel (Mulheim an der Ruhr, Germany) modular accelerated column heater (MACH) and Agilent models 5890/5972 GC/MS (Santa Clara, CA) were modified for field work. The MACH resistively heated the GC column, which provided fast temperature programming and cool down. Agilent's GC oven heated the transfer lines from injection port to the GC/MS. A Shimadzu (Columbia, MD) 17A/QP5050A GC/MS was used to confirm field data. Listed in Table S1 (Supplementary material) are field and lab operating conditions. All GC/MS data was analyzed using the Ion Signature Technology Quantitative Deconvolution software (North Smithfield, RI). Target compound response factors were calculated as the ratio of  $A_x C_{is} / A_{is} C_x$ , where  $C_x$  was the amount of target analyte introduced into the GC/MS,  $A_x$  its observed signal, and  $C_{is}$  and  $A_{is}$  the internal standard concentrations and corresponding signal responses.

### 2.3. Reagents and standards

HPLC grade methylene chloride was used as received (Fisher Scientific, Pittsburgh, PA). Organic Standards Solutions International (Charleston, SC) made a custom mix of benzene, toluene, ethyl benzene, xylenes (BTEX), PAH and internal standards. A Piano aromatics standard was obtained from AccuStandard (New Haven, CT).

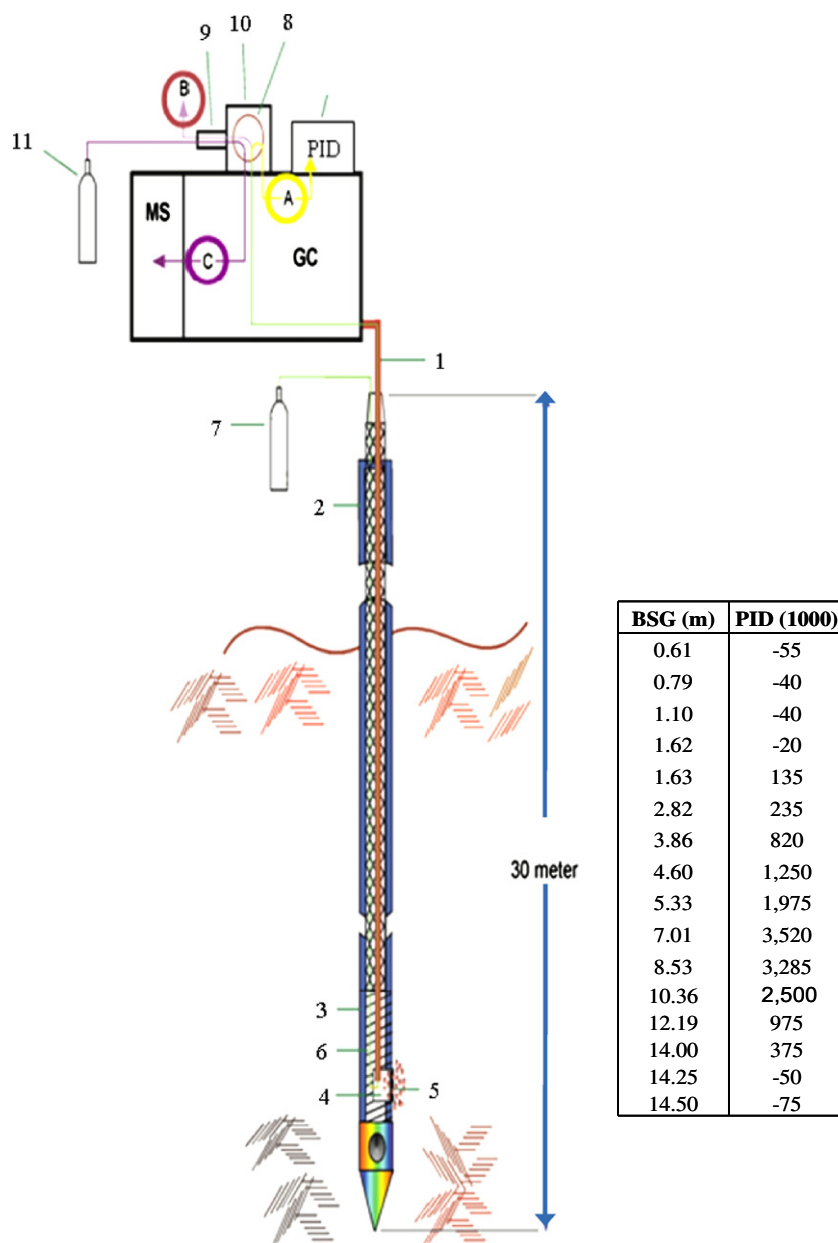
### 2.4. Samples

The chemical sensing system was tested at a former manufactured gas plant (MGP) in North Carolina. A cone penetrometer was used to advance the probe and to collect soil and groundwater samples for lab analysis. Soil contaminated with fuel oil was collected from an underground storage tank in Massachusetts and analyzed by advancing the sensor by hand.

## 3. Results and discussion

### 3.1. Coal tar

The question of whether on-line, subsurface chemical detection can be used to find hot spots, boundaries, and migration pathways continues to be the focus of this research. Several questions are posed. First, is it possible to detect contaminants in real-time without bringing soil/groundwater to the surface? Second, once detected, can the probe speciate pollutants and provide estimates of their concentration? If so, can data be compared to conventional sample collection and analysis methods? Finally, are data produced quickly enough so field personnel do not sit idle? Although earlier work showed PAH could be detected on-line, the instrument was unable to detect VOCs because they broke through the freeze trap during pre-concentration when analyzed by GC/MS. A newly-designed 3-stage Peltier freeze trap obviates this problem.



**Fig. 1.** Chemical sensor schematic and PID readings. Components: (1) heated transfer line, (2) 1.2-m steel pipes, (3) 0.33-m sample collection pipe, (4) sample collection port, (5) MIP, (6) heater cartridges, (7) nitrogen, transfer line carrier gas, (8) heated six-port valve, (9) freeze trap, (10) thermal desorber and (11) helium, GC/MS carrier gas. PID readings at below surface grade (BSG) locations: negative values indicate absence of organics; positive values indicate presence of organics.

This paper is not intended to provide large scale site characterization data. It is, however, aimed at providing the reader with concrete examples of how best to use the probe to address site-specific questions. A second aim is to prove volatile coal tar and petroleum hydrocarbons can be quantitatively identified in the same sample as SVOCs and high levels of chemical noise.

Forensic investigators know coal tar can migrate from source material to groundwater in seams as small as 5–10 cm. When this occurs, coal tar poses significant remedial challenges. A cone penetrometer tube is shown in Fig. 2. The location of the 6 cm coal tar seam was detected by the photoionization sensor as the probe was pushed into the subsurface, see Fig. 1 in Supplementary material for illustration. The sensor recorded no detectable organics until it hit the vein.

The table in Fig. 1 lists below surface grade (BSG) signals for a different boring between 0.61 m and 14.5 m. Background response



**Fig. 2.** A standard cone penetrometry sampling tube was used to collect coal tar contaminated soil after it was found by the photoionization sensor as the probe was advanced into the subsurface.

was determined using the 5–10 cm signals, which were recorded, averaged, and subtracted from each subsequent reading. Negative

PID readings indicated no detectable organics. In contrast, positive responses were a measure of the relative coal tar concentration at that depth. The presence (PID = 135 at 1.63 m) and absence (PID = -50 at 14.25 m) of organics provided the information to produce the conceptual site model. For MGP sites, where excavation of source material is often the selected remedy, the volume of contaminated soil and, thus, cost, is best estimated by making continuous, real-time measurements confirmed by GC/MS. The example above illustrates how *in situ* sensing can be used to identify hot spots, define boundaries, and track coal tar migration in the subsurface.

Field and lab GC/MS data at  $8.53 \pm 0.30$  m are compared in Table 1. Field results are based on three discrete *in situ* measurements collected over 60 cm. Probe precision, as measured by percent relative standard deviation (%RSD), was excellent for all analytes, which should be considered in the context of how standard EPA

**Table 1**

Coal tar contaminated soil, concentration in  $\text{mg kg}^{-1}$ .

Compounds	Lab	Sensor, n = 3 Ave. (% RSD)	% Recovered
Benzene	11	9 (24)	82
<i>C</i> <sub>1</sub> -Benzene	328	228 (35)	70
<i>C</i> <sub>2</sub> -Benzenes	639	559 (6)	87
Naphthalene	1439	2255 (28)	157
<i>C</i> <sub>1</sub> -Naphthalenes	913	914 (38)	100
<i>C</i> <sub>2</sub> -Naphthalenes	1033	904 (33)	88
Acenaphthylene	224	173 (18)	77
Acenaphthene	144	110 (29)	76
Fluorene	380	170 (27)	45
Phenanthrene	640	275 (22)	43

**Notes:**

1. Samples were collected by the probe and conventional cone penetrometry from the same boring at  $8.53 \pm 0.3$  m.
2. Lab and sensor samples were extracted by methylene chloride and heat, respectively.
3. % Recovered = (sensor/lab)  $\times$  100.

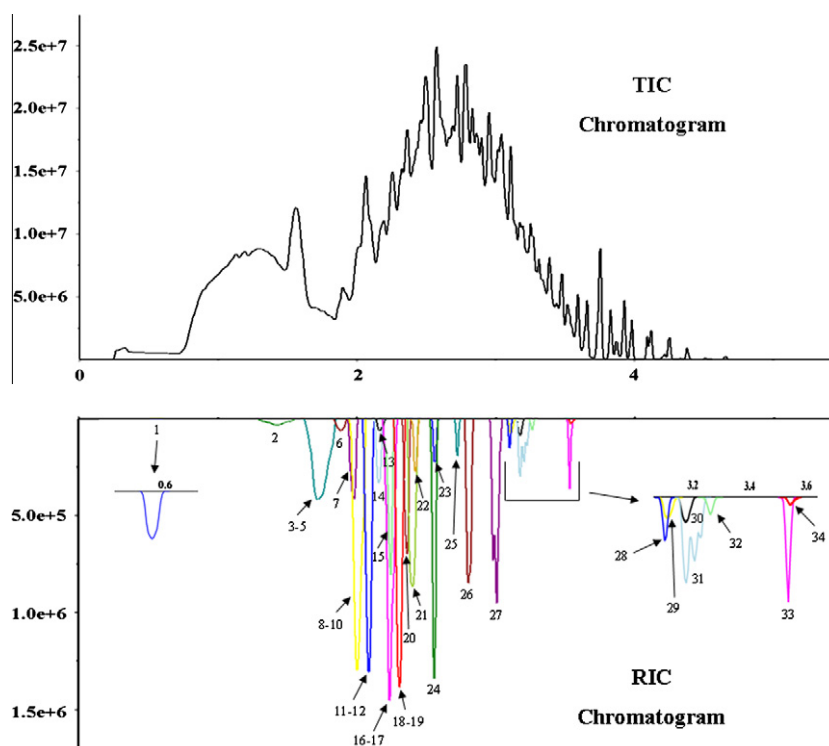
lab analyses are carried out. For example, the lab data is based on a composite soil sample collected in a 120 cm tube at the same approximate depth and boring. Sub-samples from the tube were homogenized, extracted, and analyzed according to EPA methods. In contrast, measurement accuracy was acceptable except for naphthalene (overestimated), fluorene and phenanthrene (underestimated). MIP probe temperature constraints limit the extraction efficiency and thus, the amount of high molecular weight compounds that can be collected.

### 3.2. Petroleum hydrocarbons

The total ion current (TIC) and reconstructed ion current (RIC) chromatograms for soil contaminated with fuel oil are shown in Fig. 3 (probe) and S2 (lab, Supplementary material), see corresponding peak identities in Tables 2 and 3. Absent is the well-defined hydrocarbon profile in the probe chromatogram compared to the solvent extracted analysis. Inspection of the former reveals the absence of aliphatic and polar compounds.

Although measurement sensitivity is limited by the applied membrane temperature, reporting limits are equal to MIP detection limits for PAH standards. The data analysis software deconvolves target compound fragmentation patterns from matrix spectra compared to standard vendor software, where reporting limits are often 10–100 times higher than the lab's method detection limit. The deconvolution software obviates this problem by eliminating the need to dilute the sample, while producing data in as little as 5-min.

For example, no false positives or negatives were observed between GC/MS and lab data for VOCs. This finding is remarkable considering benzene, isopropylbenzene, and acenaphthylene are only a few hundred  $\mu\text{g kg}^{-1}$  in the sample. Although sensor precision was poorer compared to the lab, differences can be attributed to discrete vs. composite sample collection. Nonetheless, the average *C*<sub>0</sub> to *C*<sub>6</sub> benzene RSD was 26%, well within EPA's data quality



**Fig. 3.** Fuel oil contaminated soil collected by the probe and analyzed on-line by GC/MS in 5-min, see Tables 2 and 3 for compound identity.

**Table 2**  
Oil contaminated soil, concentration in mg kg<sup>-1</sup>, n = 3.

Number	Compounds	Lab ave. (% RSD)	Sensor ave. (% RSD)	EPA accuracy criterion	Acceptable RPD	RPD
1	Benzene	0.1 (34)	0.1 (35)	0.005	<60%	0
	C <sub>1</sub> -Benzene	1.6 (13)	0.9 (7)	1.5	<60%	56
2	Toluene					
	C <sub>2</sub> -Benzenes	6.5 (10)	7.8 (16)			-18%
3	Ethylbenzene			25	<60%	
4	m-, p-Xylene			2	<60%	
5	o-Xylene					
	C <sub>3</sub> -Benzenes	26.8 (6)	21.1 (23)			24
6	Isopropylbenzene	0.5 (7)	0.4 (23)	N/A		22
7	n-Propylbenzene	1.7 (4)	1.7 (22)	N/A		0
8	1-Methyl-3-ethylbenzene					
9	1-Methyl-4-ethylbenzene	11.8 (9)	10.1 (23)	N/A		16
10	1-Methyl-2-ethylbenzene					
11	1,3,5-Trimethylbenzene	12.8 (5)	8.9 (23)	N/A		36
12	1,2,4-Trimethylbenzene					
	C <sub>4</sub> -Benzenes	31.7 (5)	23.0 (27)			32
14	Tert-butylbenzene	1.5 (8)	1.9 (28)	N/A		-24
15	n-Butylbenzene	3.6 (4)	3.0 (27)	N/A		18
16	1-Methyl-3-n-propylbenzene					
17	1-Methyl-4-n-propylbenzene	7.3 (7)	5.3 (25)	N/A		32
18	1,3-Dimethyl-5-ethylbenzene	8.7 (2)	5.8 (24)	N/A		40
19	1,4-Dimethyl-2-ethylbenzene					
20	1,2-Dimethyl-3-ethylbenzene	4.2 (3)	2.6 (22)	N/A		47
21	1,2,4,5-Tetramethylbenzene	6.4 (4)	4.4 (34)	N/A		37
	C <sub>5</sub> -Benzenes	8.6 (3)	6.0 (28)	N/A		36
22	n-Pentylbenzene					
	C <sub>6</sub> -Benzenes	3.9 (33)	2.1 (48)	N/A		60
25	1,3,5-Triethylbenzene					
	PAH					
24	Naphthalene	4.4 (34)	3.5 (47)	10	<100%	23
28	Acenaphthylene	0.5 (4)	0.4 (50)	70	<100%	22
30	Acenaphthene	0.9 (4)	0.5 (43)	70	<100%	57
32	Fluorene	0.9 (4)	0.4 (32)	70	<100%	77
34	Phenanthrene	1.1 (2)	0.1 (50)	710	<100%	167

## Notes:

1. Compounds 13, 23, 29, and 33 are internal standards 1,4-dichlorobenzene-d<sub>4</sub>, naphthalene-d<sub>8</sub>, acenaphthene-d<sub>10</sub>, and phenanthrene-d<sub>10</sub>, respectively.
2. Analysis by GC/MS in the lab and sensor analysis was 56-min and 5-min, respectively.
3. Lab and sensor samples extracted by methylene chloride and heat, respectively.
4. EPA accuracy criterion = 2.5 × site-specific action level (AL). N/A = no soil screening data available for these compounds.
5. The acceptable relative percent difference (RPD) is dependent on analyte concentration in the sample: concentrations > 2.5 × AL, RPD < 60% and < 2.5 × AL, RPD < 100%.
6. RPD, accuracy = 100 ((lab - sensor)/0.5 (lab + sensor)).

**Table 3**  
Concentration of naphthalene homologs, concentration in mg kg<sup>-1</sup>, n = 3.

Number	Homolog	Lab					Sensor				
		MFP	SIE	Diff. (%)	SFP	Diff. (%)	MFP	SIE	Diff. (%)	SFP	Diff. (%)
26	C <sub>1</sub> -Naphthalenes		16.2		16.0			8.5		7.9	
27	C <sub>2</sub> -Naphthalenes	25.5	31.1	-22	4.0	84	12.6	17.8	-41	2.4	81
31	C <sub>3</sub> -Naphthalenes	17.9	20.2	-13	2.3	87	8.6	11.8	-37	1.9	84
	∑C <sub>1</sub> -C <sub>3</sub>		72.2		26.7			42.1		15.7	

## Notes:

1. Lab and sensor samples extracted by methylene chloride and heat, respectively.
2. MFP = multiple fragmentation patterns per homolog.
3. SIE = selected ion extraction.
4. SFP = single fragmentation pattern per homolog.
5. % Diff. (percent difference) = (MFP - (SIE or SFP))/MFP.
6. Absence of MFP values for C<sub>1</sub>-naphthalenes is due to the fact that only one fragmentation pattern is needed to identify these analytes.

objectives. Although poorer, the 45% RSD for PAH provides reliable concentration estimates when constructing conceptual models. The VOC/SVOC data were within the 50% criterion established by the EPA for field studies (USEPA, 1996).

Based on site-specific action levels as outlined in EPA's Soil Screening Guidance Document, measurement accuracy was also excellent (USEPA, 2002). Applying the most stringent action level, namely, when pollutants are in close proximity to shallow water

tables, fractured media, or have source sizes greater than 0.12 km<sup>2</sup>, the quantitation limit (QL) is set to one-half the action level. To meet the EPA criterion for accuracy, the relative percent difference (RPD) between sensor and lab must be <60% for target compounds whose concentrations are >5-times the QL. For concentrations <5-times the QL, the RPD must be <100%. The QL for benzene, toluene, and C<sub>2</sub>-benzenes are 0.001, 0.3, and 5 mg kg<sup>-1</sup>, respectively; ethylbenzene is 0.4 mg kg<sup>-1</sup>. The QL for naphthalene,

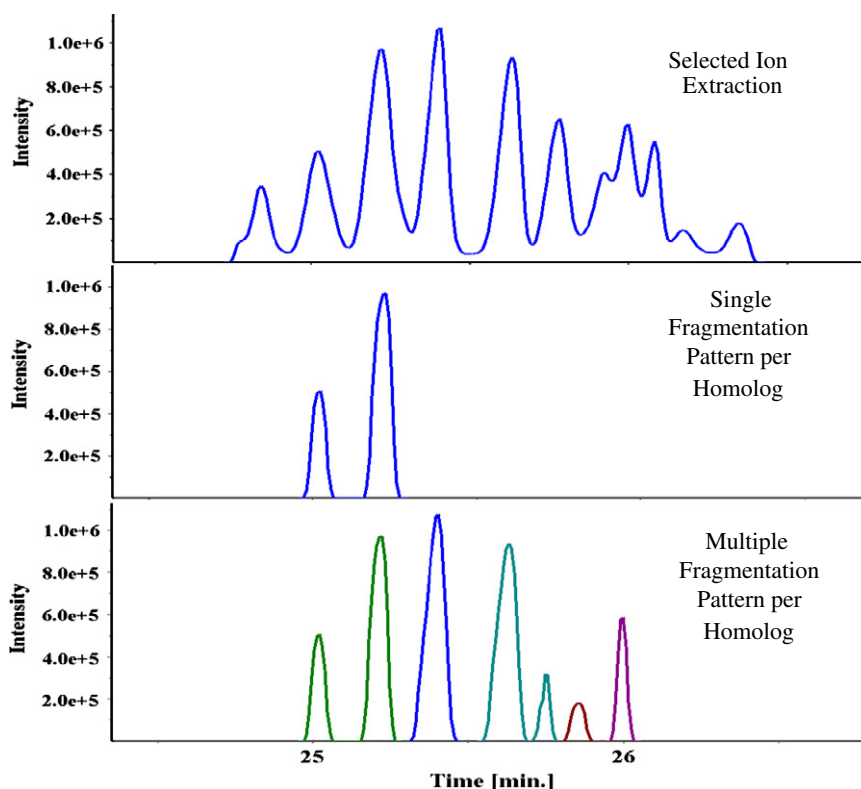


Fig. 4. Reconstructed ion current chromatograms for  $C_3$ -naphthalene based on selected ion extraction (SIE), single fragmentation pattern (SFP), and multiple fragmentation patterns (MFP).

acenaphthylene, and acenaphthene are 2, 14, and 14  $\text{mg kg}^{-1}$ , respectively. Based on these QL's, all compounds fall within EPA's criterion for accuracy, see Table 2. In contrast to our previous study, where the single stage freeze trap failed to retain volatiles, these results demonstrate that the new 3-stage Peltier efficiently captured VOCs. Work is in progress to evaluate long-term system performance under harsh environmental conditions. In this example, the probe was hand pushed or hammered to assess underground storage tank leakage. Findings indicated little to no oil was released from the tank to warrant extensive remedial action.

We showed when alkylated PAH patterns are used to assess fossil fuel weathering; the most often used forensic methods lead to erroneous findings (Zeigler et al., 2008). Evident from Table 3 are differences in alkylated PAH concentrations that occur when analysts rely solely on the molecular ion to determine peak area. These errors happen whether data are collected by selected ion monitoring (SIM) or obtained from selected ion extraction (SIE) of scanned data. If analysts rely on a single fragmentation pattern (SFP), underestimation of concentration occurs. If analysts rely solely on the molecular ion to estimate concentration, overestimation occurs. We propose multiple fragmentation patterns (MFP) be used to correctly identify and quantify alkylated PAH homologs. Fig. 4 illustrates the results for SIE/SIM, SFP, and MFP. Evident is the fact when all SIE/SIM peaks are integrated, the total peak area is much larger than SFP and MFP. Similarly, when only one fragmentation pattern is integrated the peak area is much smaller than SIE/SIM and MFP.

SIE of on-line GC/MS data is underreported compared to the lab by  $\sim 40\%$  for the  $C_1$ – $C_3$  naphthalenes, which suggests little to no selectivity differences between target analytes that pass through Teflon at  $140^\circ\text{C}$ , extracted by heat, and those extracted by methylene chloride. Since 1- and 2-methylnaphthalenes have the same fragmentation patterns, we attribute differences in the  $C_2$ - and  $C_3$ -naphthalene concentrations to the fragmentation patterns used to identify corresponding isomers when SFP and MFP data are com-

pared. For example, the analyte concentration estimated by SIE and SIM includes matrix ion signals, since standard vendor data analysis software offers little ability to eliminate chemical noise. Consequently, the concentration is overestimated compared to MFP. In contrast, SFP ignores ion ratios of isomers whose relative abundances differ from the target analyte. For instance, the ion ratio signal for the molecular ion and primary qualifier ions for 1,3,6-trimethylnaphthalene, 1,4,5-trimethylnaphthalene, and isopropylnaphthalene are 140%, 80%, and 45%, respectively. If the 1,4,5-trimethylnaphthalene ratio is used to quantify the homolog, 1,3,6-trimethylnaphthalene and isopropylnaphthalene will be ignored, since their ion ratios differ from the target compound by more than 20%. In this case, the  $C_3$ -naphthalene concentration will be underestimated. Five fragmentation patterns are needed to correctly capture the dialkylated naphthalene peak area; 10 patterns for the trialkylated naphthalenes. Results showed all patterns but one was found in the sensor data compared to the lab data. These findings support the premise that differences in the alkylated PAH concentration are solely dependent on MIP temperature and collection time, especially since 80% of the alkylated benzenes passed through the mesh and were detected on-line by GC/MS. Nonetheless, data showed fuel oil weathering can be deduced based on the loss of the  $C_0$  and  $C_1$  analogs compared to the amount of  $C_0$ – $C_4$  naphthalenes detected. The absence of  $C_4$ -naphthalenes and the high concentration of  $C_0$  compared to total alkylated naphthalenes suggest a relatively new release occurred, which is consistent with the hydrocarbon backbone observed in Fig. 3. Work is in progress to develop a high temperature,  $310^\circ\text{C}$ , hydrophobic mesh so one system can be used to detect alkylated PAH in soil as well as groundwater.

#### 4. Conclusions

The work described herein demonstrates the on-line photoionization sensor can profile the absence/presence of pollutants as the

probe is continuously advanced into the subsurface. The combination of the on-line GC/MS sensor and spectral deconvolution software correctly quantifies target compounds in 5-min in fossil fuels. Although the current membrane limits the heat transfer from the probe to soil, no false negatives were observed even at low analyte concentrations. Data quality was consistent with EPA criteria for measurement precision and accuracy. Currently, the membrane-less probe can be used to detect a wide range of pollutants in soil, and the same can be said for the membrane inlet probe in groundwater. Our next step is the development of a high temperature membrane probe, to allow for detection of all VOC and SVOC of interest in both soil and groundwater, without having to change probes in between analyses. These recent and future developments in the field of *in situ* chemical sensing should greatly improve conceptual site models and reduce the uncertainties associated with site cleanup.

### Acknowledgements

The willingness of the utility companies, state regulators, and Electric Power Research Institute to support this work made the coal tar project possible. The cooperation of the site owner in Massachusetts for the fuel oil project is greatly appreciated. Agilent continues to support our work by providing instrumentation we modify for these studies.

### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2010.06.005.

### References

- Aldstadt, J.H., Martin, A.F., 1997. Analytical chemistry and the cone penetrometer: *in situ* chemical characterization of the subsurface. *Mikrochim. Acta* 127, 1–18.
- Considine, T., Robbat Jr., A., 2008. On-site profiling and speciation of polycyclic aromatic hydrocarbons at manufactured gas plant sites by a high temperature transfer line, membrane inlet probe coupled to a photoionization detector and gas chromatograph/mass spectrometer. *Environ. Sci. Technol.* 42, 1213–1220.
- Crumbling, D.M., Griffith, J., Powell, D.M., 2003. Improving decision quality: making the case for adopting next generation site characterization practices. *Remediation* 13, 91–111.
- Elam, W.T., Adams, J.W., Hudson, K.R., McDonald, B.J., Gilfrich, J.V., Galambos, J., 2000. *In situ* environmental XRF. *Adv. X-ray Anal.* 42, 137–145.
- Gankin, Y.V., Gorshteyn, A., Smarason, S., Robbat Jr., A., 1998. Time-condensed analyses by mass spectrometry. *Anal. Chem.* 70, 1655–1663.
- Garcia-Gomez, R.S., Pandiyan, T., Aguilar-Iris, V.E., Luna-Pabello, V., Duran de Bazua, C., 2004. Spectroscopic determination of poly aromatic compounds in petroleum contaminated soils. *Water Air Soil Poll.* 158, 137–151.
- Gorshteyn, A., Robbat Jr., A., 2000. Rapid *in situ* collection and analysis of semivolatile organics by thermal extraction cone penetrometry gas chromatography/mass spectrometry. *Field Anal. Chem. Technol.* 4, 85–92.
- Gorshteyn, A.Y., Kataenko, Z., Smarason, S., Robbat Jr., A., 1999. Subsurface detection of environmental pollutants. *Instrum. Sci. Technol.* 27, 111–112.
- Gorshteyn, A., Smarason, S., Robbat Jr., A., 1999. Speciation of subsurface contaminants by cone penetrometry gas chromatography/mass spectrometry. *Environ. Sci. Technol.* 33, 2474–2480.
- Griffin, T.W., Watson, K.W., 2002. A comparison of field techniques for confirming dense nonaqueous phase liquids. *Ground Water Monit. R.* 22, 48–59.
- Kram, M.L., Keller, A.A., Massick, S.M., Laverman, L.E., 2004. Complex NAPL site characterization using fluorescence part 1: selection of excitation wavelength based on NAPL composition. *Soil Sediment Contam.* 13, 103–118.
- McAndrews, B., Heinze, K., DiGiuseppe, W., 2003. Defining TCE plume source areas using the membrane interface probe (MIP). *Soil Sediment Contam.* 12, 799–813.
- Miles, B., Cortes, J., 1998. Subsurface heavy-metal detection with the use of a laser-induced breakdown spectroscopy (LIBS) penetrometer system. *Field Anal. Chem. Technol.* 2, 75–87.
- Myers, K.F., Karn, R.A., Eng, D.Y., Hewitt, A.D., Strong, A.B., Brannon, J.M., 1998. *In situ* thermal desorption of VOCs in vadose zone soils. *Field Anal. Chem. Technol.* 2, 117–125.
- PA, U.S.E., 2009. Triad use at naval base San Diego saves an estimated six years and \$3 million for site investigation. *Technol. News Trends* 40, 1–2.
- Palmer, R.L., Tepper, G.C., 2001. Development of a high-pressure xenon ionization chamber gamma-ray spectrometer for field deployment in cone penetrometers. *J. Radioanal. Nucl. Ch.* 248, 289–294.
- Robbat Jr., A., 2000. Productivity enhancing mass spectral data analysis software for high throughput laboratories: simultaneous detection of volatile and semivolatile organics by GC/MS. *Environ. Test. Anal.* 9, 15–19.
- Robbat Jr., A., 2001. Environmental applications of thermal extraction cone penetrometry and ultrafast gas chromatography/mass spectrometry. *Field Anal. Chem. Technol.* 5, 60–68.
- Robbat Jr., A., Kenny, J.E., Smarason, S., Pepper, J.W., Wright, A.O., 1998a. Laser-induced fluorescence and fast gas chromatography/mass spectrometry with subsurface thermal extraction of organics: field analytical technologies for expediting site characterization and cleanup. *Remediation* 9, 95–111.
- Robbat Jr., A., Smarason, S., Gankin, Y., 1998b. Dynamic work plans and field analytics: the keys to cost-effective hazardous waste site investigations. *Field Anal. Chem. Technol.* 2, 253–265.
- Robbat Jr., A., Smarason, S., Gankin, Y., 1999. Fast gas chromatography/mass spectrometry in support of risk-based decisions. *Field Anal. Chem. Technol.* 3, 55–66.
- Rossabi, J., Riha, B.D., Haas, J., Eddy-Dilek, C.A., Lustig, A., Carrabba, M., Hyde, K., Belo, J., 2000. Cone penetrometer-based Raman spectroscopy for NAPL characterization in the vadose zone. In: Looney, B.B., Falta, R.W. (Eds.), *Vadose Zone Science and Technology Solutions*, vol. 1. Battelle Press, 505 King Avenue, Columbus, Ohio, pp. 431–444.
- Rossabi, J., Riha, B.D., Eddy-Dilek, C.A., Looney, B.B., Hyde, W.K., 2003. Recent advances in characterization of vadose zone dense non-aqueous phase liquids (DNAPL) in heterogeneous media. *Environ. Eng. Geosci.* 9, 25–36.
- USEPA, 1996. Region 1. EPA-NE Data Validation Functional Guidelines for Evaluating Environmental Analyses. Part II, Section VOA/SV – IX.
- USEPA, 2002. Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites: Appendix A. OSWER No. 9355.4-24.
- USEPA, 2003. Using Dynamic Field Activities for On-site Decision Making: A Guide for Project Managers, Office of Solid Waste and Emergency Response. OSWER No. 9200.1-40 EPA/540/R-03/002.
- Zeigler, C., MacNamara, K., Wang, Z., Robbat Jr., A., 2008. Total alkylated polycyclic aromatic hydrocarbon characterization and quantitative comparison of selected ion monitoring versus full scan gas chromatography/mass spectrometry based on spectral deconvolution. *J. Chromatogr. A* 1205, 109–116.