Environmental Applications of Thermal Extraction Cone Penetrometry and Ultrafast Gas Chromatography/Mass Spectrometry

Albert Robbat, Jr.

Center for Field Analytical Studies and Technology, Chemistry Department, Tufts University, Medford, Massachusetts 02155

Abstract: This article describes the collection and analysis of organic contaminants at depth without bringing soil to the surface. A thermal extraction cone penetrometer (TECP) probe was used to extract soil-bound semivolatile organics, transferring them to the surface for analysis by ultrafast gas chromatography/mass spectrometry (GC/MS). Findings showed that polychlorinated biphenyls, polycyclic aromatic hydrocarbons, chlorinated pesticides, and explosives could be collected and analyzed in 5 min when the soil-water content was <20% and in 15 min when it was between 20 and 35%. When the TECP was directly connected to the GC/MS, trinitrotoluene (TNT) and four of its synthetic precursors were speciated in 20 sec. Moreover, 51 VOCs were detected by membrane-inlet mass spectrometry in ~10 sec. Organics were "sniffed" from a vial and identified using the Ion Fingerprint Detection™ software. The algorithms provide the means to untangle complex mass spectra making real-time, electronic nose detection and identification by MS possible. © 2001 John Wiley & Sons, Inc. Field Analyt Chem Technol 5: 60–68, 2001

Keywords: thermal extraction cone penetrometry; gas chromatography/mass spectrometry

Introduction

Field analytics can play a central role in environmental assessment, control, and monitoring. The closer the instrument is to the sample, the better (more representative) the data, and the faster information can be obtained about the site. Site-directed sample collection and analysis programs translate into lower site characterization, cleanup, and monitoring costs.[1–3] One of our goals was to develop a system that could collect subsurface soil contaminants quickly, without bringing the sample to the surface. A second goal was to match (as closely as possible) the sample-collection rate with the analysis rate, while minimizing human involvement as much as possible. Several different and ultimately integrating technologies were developed and presented at the 2000 Pacifichem Conference in the session entitled "Recent Developments in Field Analysis."

Results produced by a thermal extraction cone penetrometer (TECP) sample collection and analysis system were described. The sampling probe is capable of extracting soil gas and soil-bound volatile and semivolatile organic compounds (VOC and SVOC) at depths of up to 25 m. An ultrafast gas chromatography/mass spectrometry (GC/MS) system was described. The GC module is temperature programmable from 0.03 to 100 °C/s. Sample introduction is made by syringe injection, TECP probe, or directly from soil or solid-phase adsorbent without changing the GC inlet with the use of a ballistically heated thermal desorption (TD) unit. Finally, the resolving and quantitative application of new mass spectrometry data-analysis software was illustrated. The deconvolution algorithms imbedded in the software uniquely identify structurally different organics in the presence of each other as well as other matrix interferents. Results were presented comparing data produced by the TECP, TD, and soil-solvent extraction methods. Findings showed that the quality of data was as good as that required by EPA standardized methods and that the rate samples can be collected from the subsurface is dependent on geology and soil moisture, whereas the rate of analysis is dependent only on whether structural isomers must be distinguished.

Experiment

The thermal extraction cone penetrometer was initially developed as a stand-alone unit; see Figure 1(b). It consists of a 20–40-ton truck, hydraulically lifted over 3-ft pipe sections. The weight of the truck pushes the pipe into the earth's surface. The collection probe reaches sampling depth by means of threading together the appropriate number of pipes. The TECP heated transfer line is woven through the pipe prior to operation. It is connected on one end to a heated sampling probe and on the other to the collection chamber of the controller unit; see Figure 2. Details of the TECP system have been published elsewhere.[4,5] The probe temperature was maintained at 400 °C, which produced soil temperatures of ~300 °C. The system was operated at slightly reduced pressures. Nitrogen was used as the carrier gas to help transport the collected vapors to the surface, where they were freeze trapped at −10 °C in the collection chamber, and to backflush the system. All experiments were carried out with the following system parameters: modified Reynolds number, $Re_m = 6000$; ratio of carrier-gas collection volume to system dead volume, $V_0 = 32$; and carrier gas linear velocity $\omega = 1.8$ m/s.

The thermal desorber (300 °C < 10 s) and ultrafast GC were made at Tufts.[4] Organics were swept onto the capillary column by helium at 2 ml/min. The GC column was Restek's 15-m MXT-5 (0.28-mm i.d., with 0.5-μm film thickness of 5% diphenyl, 95% dimethyl polysiloxane), which was resistively heated from 10 to 250 °C in 20 s. Column cool-down time was ~5 s. The GC module was connected to an Agilent model 5972 mass spectrometer. The MS was scanned from 50 to 450 amu at 3 scans/s. Agilent's Chemstation software was used to control the MS and to acquire data. The Ion Fingerprint Detection™ (IFD) mass spectrometry data analysis software was developed at Tufts and commercialized by Ion Signature Technology. IFD was used to identify and quantify target compounds. Details of how the deconvolution and quantitation algorithms work were previously published in this journal and elsewhere.[2,6]

All samples were introduced through the same inlet; therefore, the same 5-point calibration curve was used for all analyses. TD analysis was made by packing known quantities of soil into an empty glass tube. The sleeve was inserted into the desorber by lifting the pressure-fitted lever that held the syringe injector in place; see Figure 3. HPLC-grade solvents were used as received by the manufacturer.
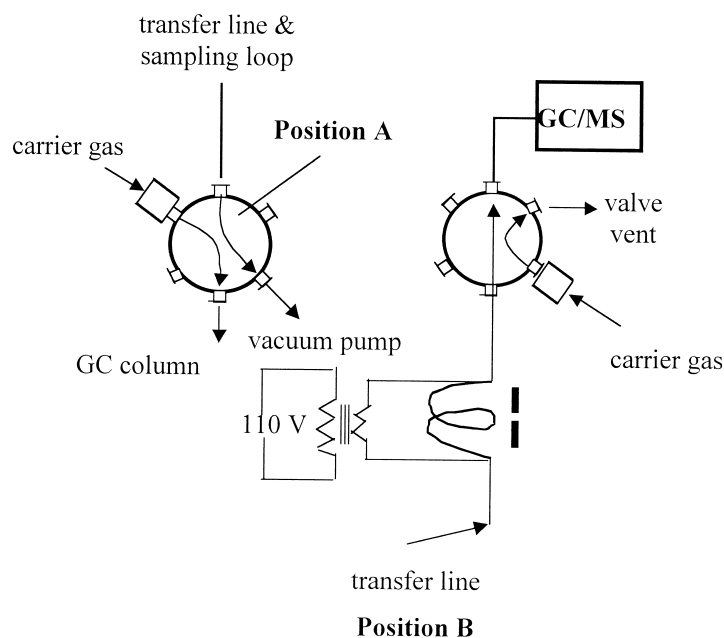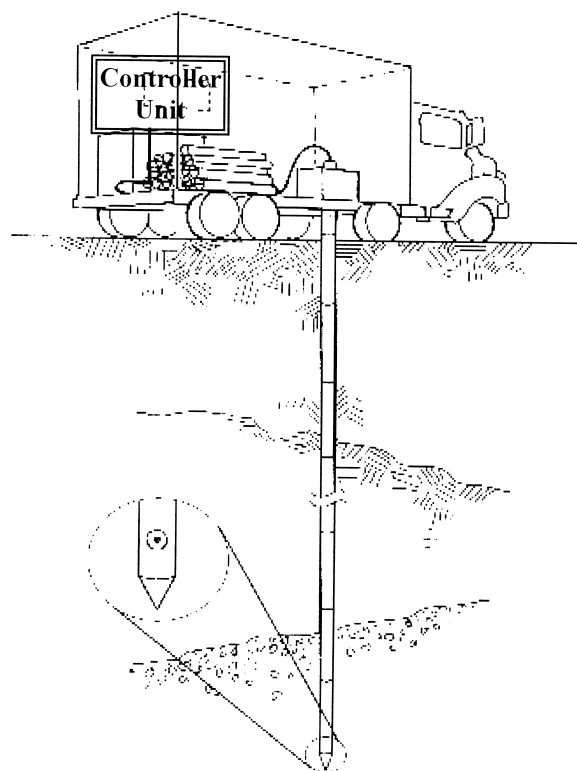

FIG. 1.   Thermal extraction cone penetrometer (TECP) connected to the GC/MS (a) and as a separate unit (b).
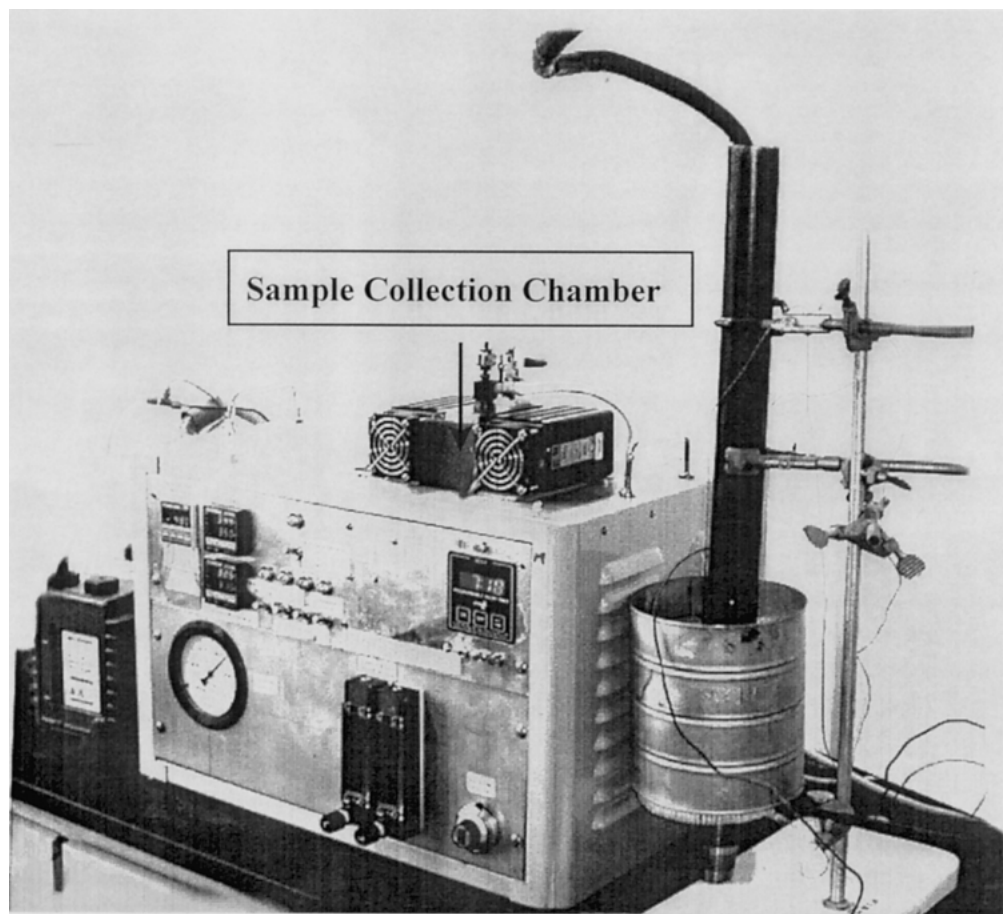
FIG. 2.   TECP controller unit and transfer line.

Results and Discussion

The dependence between the TECP sample collection efficiency and soil temperature as a function of soil type, water content, and collection time was studied.[4,7] Experiments showed that the "effective" soil extraction temperature varied somewhat with soil type but more so with moisture content, distance from the probe, and operating procedures. For soils containing up to 20% water, only 5 min were needed to collect organics within the EPA-acceptable soil-solvent recovery range (see Table 1), whereas 15 min were needed for soils >20% and <35%. Soils this wet reach a maximum temperature of 100 °C 1–2 mm from the probe, which is insufficient to volatilize and extract soil-bound SVOCs. Further research showed that the water vapor produced during heating must be pushed away from the collection window to improve SVOC recoveries. This led to a change in the procedure for collecting VOCs. For example, if the sample-collection system was turned on during the first 5 min of heating, VOC recoveries increased by >80% over the concentrations shown in the table. Then, SVOCs were collected after back-flushing the "local" environment for 5 min. Soil

temperatures 1–2 mm from the collection window increased to ~300 °C over the next few minutes. These findings suggest that the 5- and 15-min data are independent of water content, except for those compounds susceptible to thermal degradation in the presence of metallic material or steam (e.g., DDT), as long as the specified procedure was used.

TECP linear dynamic range experiments were carried out between the concentration range of 0.5 to 50 ppm for PCBs, PAHs, chlorinated pesticides, and nitrated toluenes. Aroclor 1248 was used to study PCB response, with congener detection and quantification made by chlorination level. No attempt was made to separate PAH isomers phenanthrene and anthracene, chrysene and benzo(a)anthracene, and the benzo(b and k)fluoranthenes, because the goal was to match the analysis time with the dry soil collection time. Regression analysis revealed $r^2 > 0.99$ for all compounds.

The TECP and ultrafast TD-GC/MS were brought to a manufactured gas plant and evaluated for field ruggedness and data quality. Pushes were made, with samples collected and analyzed at several locations. Soil was also brought to

the surface from several sampling points and analyzed by TD-GC/MS and by a commercial laboratory. A laboratory control check sample was prepared from soil obtained at the site to simulate one of the low-level coal-tar samples; see Table 2. Measurement accuracy for the TECP and TD results was generally <10%, whereas for the TECP and lab results the accuracy was <15%; well within the data-quality objective of <60% RPD established by the EPA for hazardous-waste site investigations. Similarly, the fortified sample data fell inside the 70–130% recovery range required by EPA for PAH compounds. These results are based on the TECP and TD-GC/MS systems operating as two separate units.

On-line measurements were made by connecting the transfer line directly to the GC/MS instrument; see Figure 1(a). Soil vapor was trapped in a Peltier-cooled Silcosteel sampling loop (120 cm × 1.56 mm, i.d. 1.02 mm) at 3 °C, which also served as the GC inlet. The sampling loop was ramped from 3 to 300 °C in <5 s. Figure 4 illustrates system reproducibility for eight consecutive analyses of a soil for-

tified with 50 ppm of nitrated toluenes. To obtain these data, the soil was heated for 2 min by the sampling probe until it reached 175 °C. Then, the soil was "sniffed" for 30 s, with the vapor collected and desorbed onto the column for analysis. After desorption, the probe was lowered ~0.5 cm, where the next depth location was sniffed. The total cycle time for sample collection and analysis was ~50 s. The sampling loop was cooled during analysis as the next soil depth was probed. The figure insert shows the expanded reconstructed ion current (RIC) chromatogram for each compound in peak 5. Despite the extremely fast temperature programming rate of 12 °C/s, target compounds were sufficiently separated and easily identified by the IFD software. As expected, analyte recoveries varied with probe temperature. At 175 °C, 2,4,6-trinitrotoluene was > 2,4-dinitrotoluene > 2- and 3-nitrotoluene nitrobenzene. At lower temperatures, the reverse order was observed. The average recovery for all compounds was 80 ± 35% when the temperature was between 150 and 175 °C. The results are remarkable given that
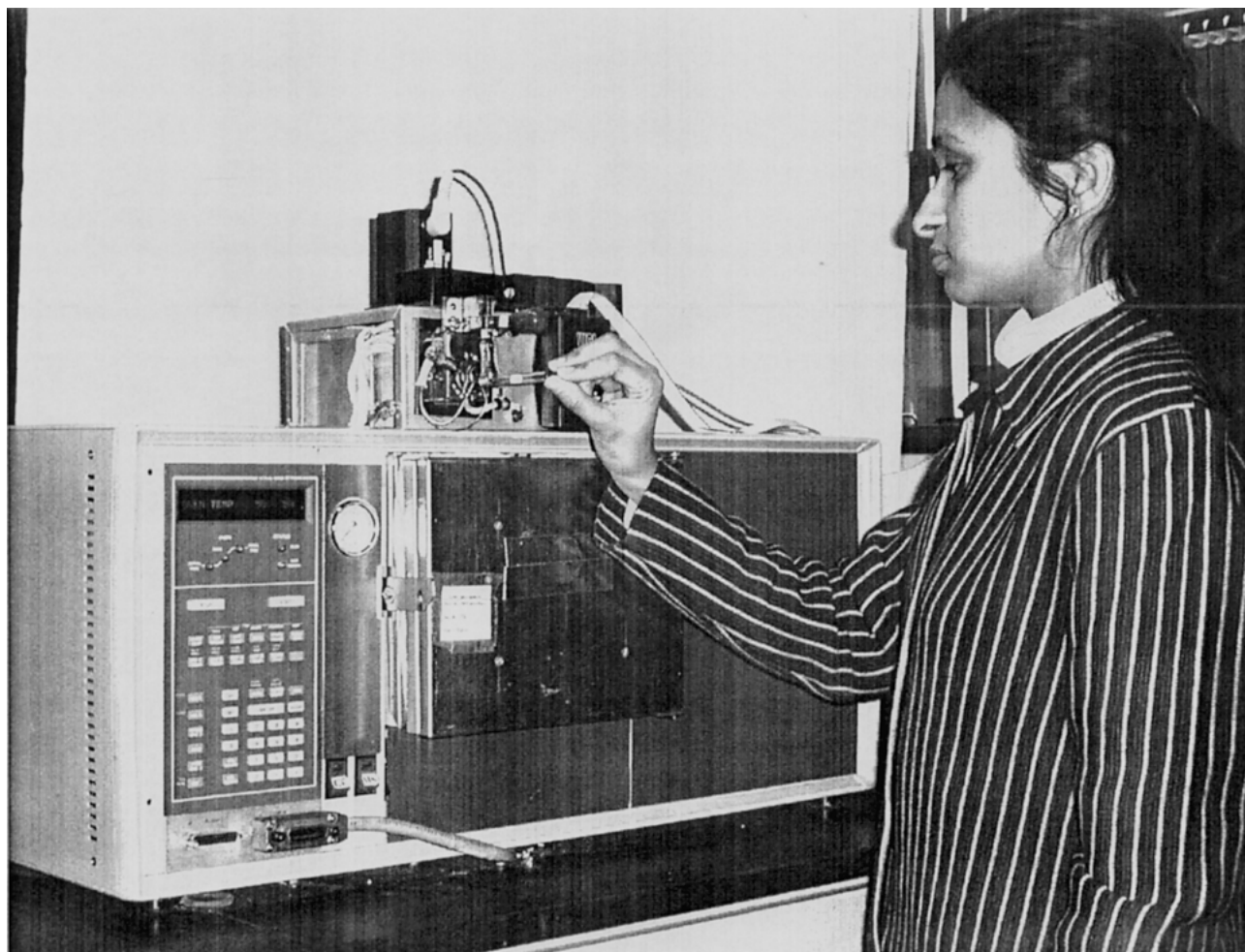

FIG. 3.   Ultrafast GC/MS system with thermal desorber unit.

TABLE 1.   TECP recovery as a function of soil heating time and water content

| Compound (50 ppm each)	5 min <15% water %R_1 (%RSD)	5 min 25% water %R_2 (%RSD)	15 min 25% water %R_3 (%RSD)	R_3/R_1
PCBs, Aroclor 1248	95	35	93	98
PAHs				
Naphthalene	85 (15)	15 (19)	38 (25)	45
Acenaphthylene	88 (10)	24 (15)	46 (20)	52
Acenaphthene	88 (10)	20 (20)	51 (28)	58
Fluorene	87 (8)	28 (14)	70 (18)	80
Phenanthrene and Anthracene	86 (12)	22 (15)	76 (15)	88
Fluoranthene	81 (11)	22 (18)	85 (12)	105
Pyrene	86 (11)	28 (10)	84 (13)	98
Chrysene and Benzo(a)anthracene	82 (19)	21 (13)	76 (16)	93
Benzo(b and k)fluoranthene	92 (14)	18 (12)	87 (15)	95
Benzo(a)pyrene	81 (10)	18 (18)	83 (11)	103
Indeno(1,2,3-cd)-anthracene	80 (12)	10 (21)	88 (14)	110
Dibenz(a,h)anthracene	83 (10)	12 (23)	75 (18)	90
Benzo(g,h,i)perylene	80 (9)	10 (15)	82 (10)	102
Cl- pesticides				
Aldrin	70 (15)	30 (20)	66 (22)	95
α-BHC	87 (10)	25 (18)	84 (18)	97
β, γ-BHC	80 (15)	27 (20)	78 (15)	98
δ-BHC	82 (12)	25 (20)	85 (20)	103
Chlordane	65 (10)	17 (28)	58 (17)	89
4,4′ DDD	82 (17)	32 (18)	51 (25)	62
4,4′ DDE	75 (16)	26 (15)	71 (18)	95
4,4′ DDT	80 (20)	25 (20)	60 (25)	75
Dieldrin	70 (12)	35 (35)	42 (25)	52
Endosulfan I	72 (18)	25 (15)	68 (15)	95
Endosulfan II	88 (15)	25 (15)	92 (17)	105
Endosulfan sulfate	85 (18)	30 (27)	91 (17)	107
Endrin	83 (13)	27 (30)	33 (30)	40
Endrin aldehyde	87 (10)	35 (28)	44 (30)	50
Endrin ketone	90 (13)	29 (30)	38 (31)	42
Heptachlor	90 (15)	22 (25)	81 (14)	92
Heptachlor epoxide	88 (12)	29 (21)	89 (16)	101
Methoxychlor	80 (12)	35 (27)	67 (20)	87
Explosives				
Nitrobenzene	75 (18)	10 (35)	37 (33)	49
2-Nitrotoluene	85 (20)	9 (40)	34 (33)	40
3-Nitrotoluene	88 (18)	12 (33)	32 (30)	36
2,4-Dinitrotoluene	95 (12)	30 (25)	84 (22)	88
2,4,6-Trinitrotoluene	90 (10)	27 (22)	81 (15)	90
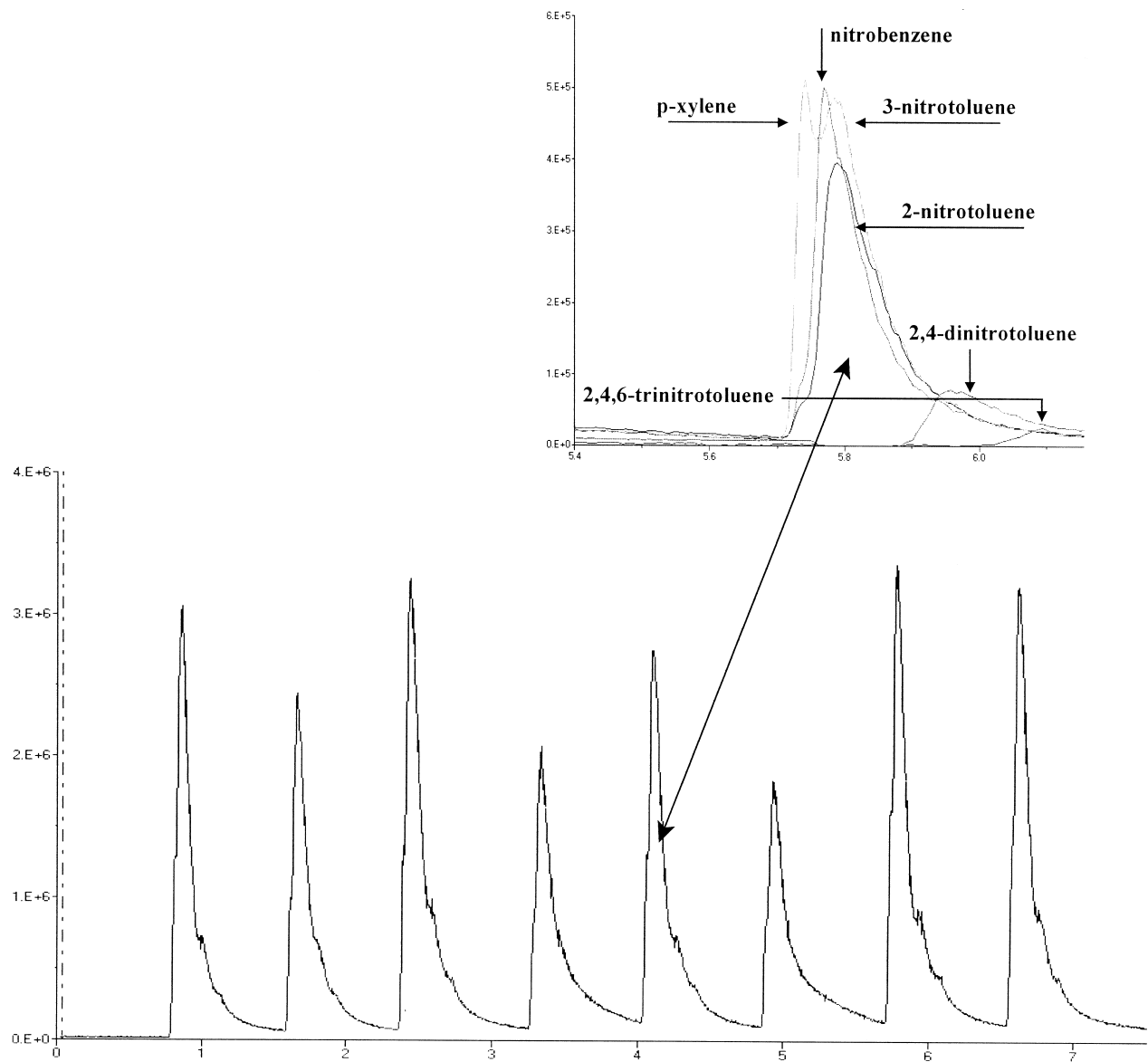
FIG. 4. TECP–TD GC/MS on-line chemical analysis of nitrated toluenes from soil; eight repetitive analyses. Insert shows the RIC chromatograms for target compounds in peak 5.

TABLE 2. Comparison of TD, TECP, and solvent-extracted results for fortified and coal tar samples

|	Percent recovery						Coal tar sample method 8270	Com lab and TECP RPD
	Fortified sample[a]			Coal tar sample[b]				
PAHs	TD	TECP	RPD	TD	TECP	RPD		
Naphthalene	18	12	10	16	11	9	18	12
Acenaphthylene	69	60	3	57	50	3	60	5
Acenaphthene	79	70	3	66	55	5	75	8
Fluorene	77	69	3	62	50	5	70	8
Phenanthrene and Anthracene	85	70	5	65	41	11	60	9
Fluoranthene	0.46	0.46	0	0.48	0.57	−4	0.60	1
Pyrene	82	72	3	72	58	5	80	8
Chrysene and Benzo(a)anthracene	68	52	7	60	50	5	75	10
Benzo(b and k)fluoranthene	52	45	4	40	42	−1	50	4
Benzo(a)pyrene	64	57	3	49	42	4	55	7
Benz(a,h)anthracene	39	29	7	27	17	11	30	14
Indeno(1,2,3-cd)pyrene	39	25	11	26	18	9	30	13
Benzo(g,h,i)perylene	26	21	5	19	23	−5	22	−1

[a] Fortified soil sample made to the same approximate concentration as the coal tar sample.

[b] Coal tar soil sample collected from manufactured gas plant.
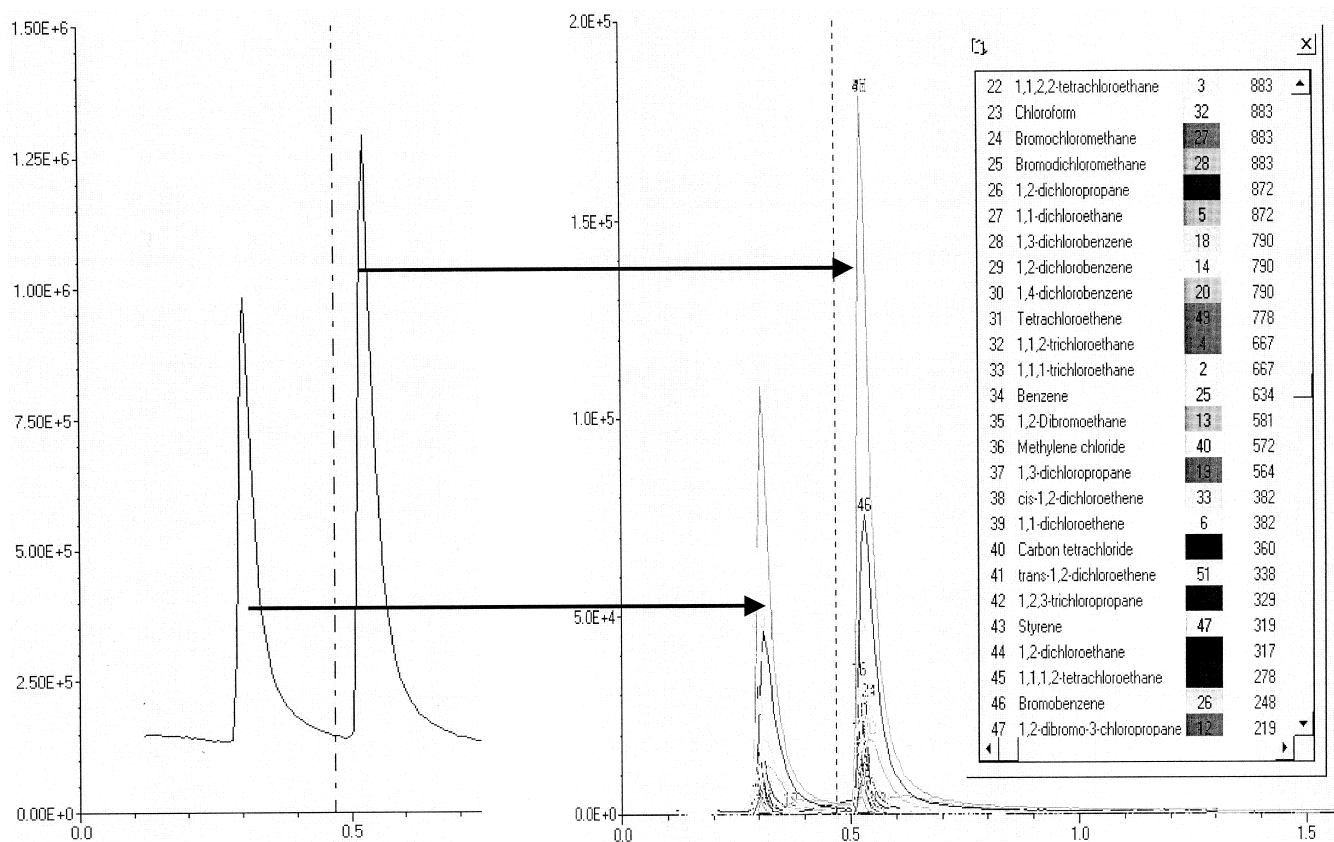
FIG. 5. Membrane inlet MS response of 51 VOCs. All compounds detected and analyzed in <10 s. Selected compounds shown in the figure.
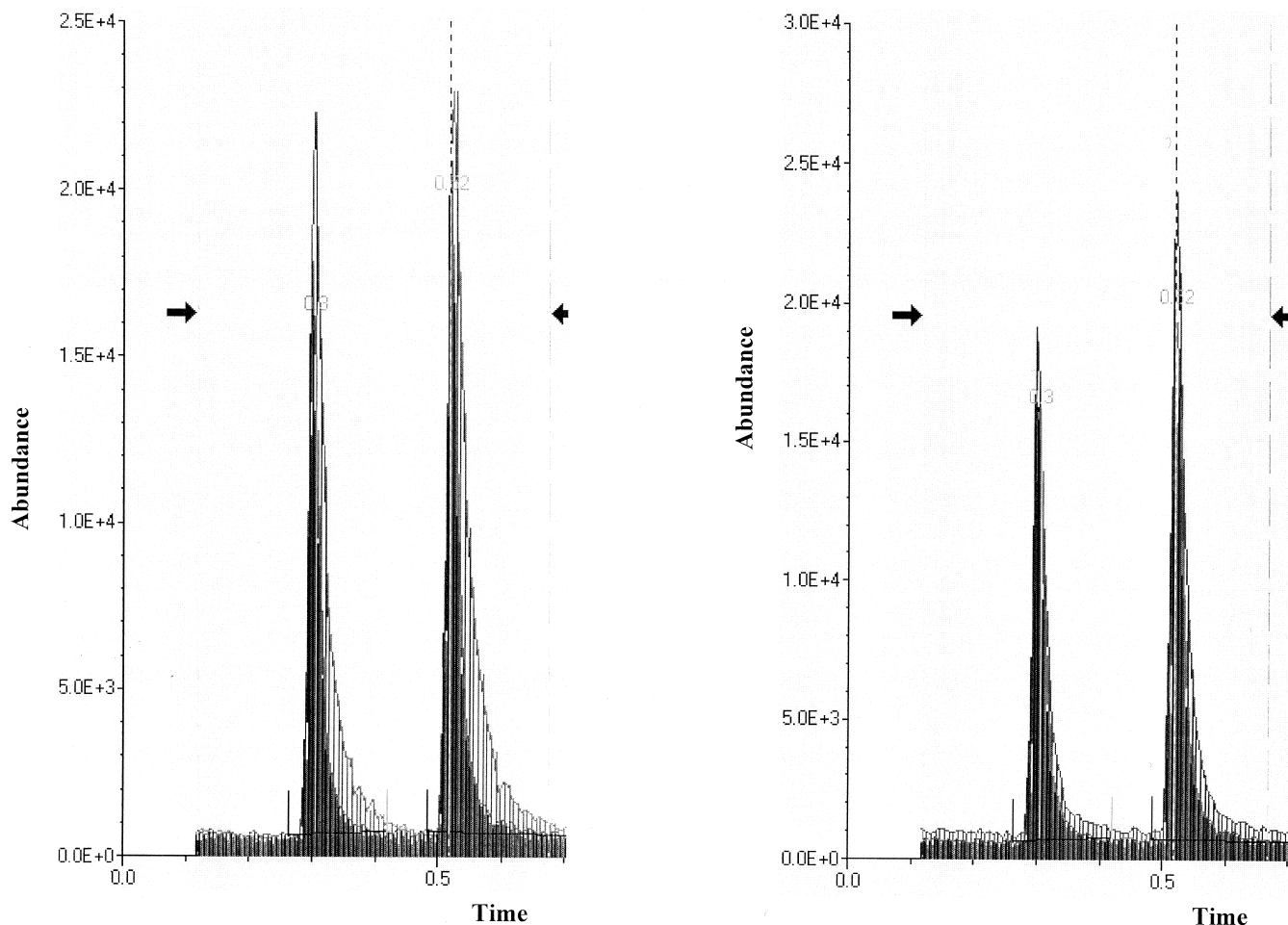
FIG. 6. The 1,1,1- and 1,1,2-trichloroethane isomers were identified from the RIC chromatograms by extracting and comparing the relative abundances of one different and two common fragment ions.

they include the thermal extraction collection efficiency from soil as well as the loss of volatiles between the time the soil was spiked and actually analyzed. The data are consistent with the findings shown in Table 1, with precision and accuracy within the EPA prescribed levels.

The resolving power of the software was illustrated in an experiment where 51 VOCs were identified in the presence of each other in seconds. The data were produced with the use of a membrane-inlet mass spectrometer from Bruker Instruments. A standard solution was prepared containing 52 VOCs, passed by the inlet and "sniffed" for ~10 s. The vial was removed and then sniffed again for 10 s. Figure 5 shows the total and reconstructed (quant) ion current chromatograms and a partial list of those compounds found in the vial. Figure 6 illustrates the overlapping RIC scan signal for the three ions used to identify 1,1,1- (117, 99, 97) and 1,1,2-trichloroethane (83, 97, 99). The algorithms extract the target ions and computed relative ratios, and compare the signal against library values. The output is shown in the figure. Identification is made when at least six consecutive scans through the chromatogram possess the correct relative abundances. In contrast, no ions were found for hexachlorobu-

tadiene, which produced a nondetect response by the software. Because no target ions were extracted from the total signal, it is presumed that this compound did not make it into the instrument. Research is in progress to determine the quantitative quality of the data.

In summary, the research presented illustrates two different applications of MS as an electronic nose. The TECP method makes remote, real-time chemical measurements of semivolatiles possible. The combination of a 25-m heated transfer line with ultrafast GC/MS makes speciation possible for an unprecedented range of target compounds. IFD, with either ultrafast GC/MS or direct MS, should provide opportunities when making real-time, on-line chemical measurements in environmental, forensic, national security, process, and quality control applications as well as the monitoring of freshness in food and beverages.

Acknowledgments

References

1. Robbat A, Jr., Smarason S, Gankin Y. Dynamic work plans and field analytics, the keys to cost-effective hazardous waste site investigations. Field Anal Chem Technol 1998;2(5):253–265.
2. Robbat A, Jr., Smarason S, Gankin Y. Fast gas chromatography/mass spectrometry analysis in support of risk-based decisions. Field Anal Chem Technol 1999;3(1):55–66.
3. Johnson R, Quinn J, Durham L, Williams G, Robbat A, Jr. Adaptive sampling and analysis programs for contaminated soils. Remediation 1997;2:81–96.
4. Gorshteyn A, Smarason S, Robbat A, Jr. Speciation of subsurface contaminants by cone penetrometry gas chromatography/mass spectrometry. Environ Sci Technol 1999;33:2474–2480.
5. Gorshteyn A, Kataenko Z, Smarason S, Robbat A, Jr. Subsurface detection of environmental pollutants. Instrum Sci Technol 1999;27(1):111–121.
6. Gankin Y, Gorshteyn A, Smarason S, Robbat A, Jr. Time-condensed analyses by mass spectrometry. Anal Chem 1998;70:1655–1663.
7. Gorshteyn A, Robbat A, Jr. Rapid in situ collection and analysis of semivolatile organics by thermal extraction cone penetrometry gas chromatography/mass spectrometry. Field Anal Chem Technol 2000;4(2–3):85–92.