

Speciation of Subsurface Contaminants by Cone Penetrometry Gas Chromatography/Mass Spectrometry

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A thermal extraction cone penetrometry gas chromatography/mass spectrometry system (TECP GC/MS) has been developed to detect subsurface contaminants in situ. The TECP can collect soil-bound organics up to depths of 30 m. In contrast to traditional cone penetrometer sample collectors, the TECP extracts organics from soil without bringing the soil to the surface or into a collection chamber. Results show that polychlorinated biphenyls, polycyclic aromatic hydrocarbons (PAHs), chlorinated pesticides, and explosives can be recovered (60–95%) from wet or dry soil, with extraction efficiency compound-specific. The data are in remarkable agreement with closed cell thermal desorption (TD) experiments, where no organics are lost to the environment during heating. TECP GC/MS results also compare favorably with solvent-extracted GC/MS analyses and can be used to delineate the presence and extent of contamination at hazardous waste sites. Data illustrating TECP dependence on probe temperature and soil moisture as well as carrier gas linear velocity and volume (modified Reynolds number) are shown along with sample analysis data from two hazardous waste sites. The total ion and reconstructed ion current chromatograms are shown for PAHs collected by TECP from a coal tar contaminated soil obtained at a manufactured gas plant in Massachusetts. TECP and TD results are within 15% for nonvolatile PAHs and within 50% of the solvent-extracted data.

Introduction

The ability to rapidly assess the disposition of environmental contaminants at purported or existing hazardous waste sites is an essential component of the nation's environmental restoration program. Each site, whether owned by the public or private sector, must be evaluated to determine whether risk to human health or the environment exists. If the data obtained supports the notion that either no risk or an acceptable level of risk exists for the intended land usage, then no further action is required. If, on the other hand, sufficient risk is determined to require a full site characterization, the site investigation effort must delineate the nature, extent, direction, concentration, and rate of movement of the contamination. Field analytics can support dynamic investigations when data are produced quickly enough to

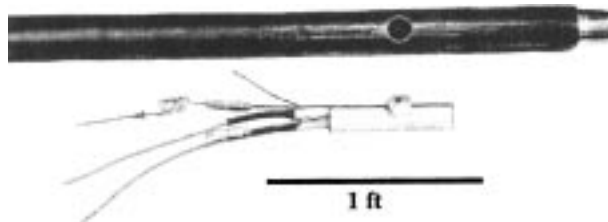


FIGURE 1. TECP probe and pipe housing.

make next step decisions on site. This requires that neither sample collectors nor analysts sit idle waiting for one another.

Cone penetrometry (CP) has become the most often used tool to rapidly determine subsurface geology and to collect soil samples at depth (1). More recently, CP has evolved into an effective means for detecting organics in situ by laser-induced fluorescence (2–5), Raman and infrared spectroscopy (6, 7), and thermal extraction mass spectrometry (8). CP has also been used in the detection of metals by laser-induced breakdown (9, 10) and γ (11) and X-ray fluorescence (12–14) spectroscopy. Myers et al. have described the detection of volatile organic compounds (VOCs) by the so-called site characterization and analysis penetrometer system (SCAPS) (8). In their device, the sampling chamber is opened by pneumatically releasing locking lugs once the CP is pushed to depth. A second, ~ 2 in., push results in the sampling chamber filling with soil (3.5–5 g). When the chamber, heated to $\sim 185^\circ\text{C}$, is purged by carrier gas, VOCs are swept to the surface for analysis. In contrast, we have built a CP sampling probe that is capable of thermally extracting (TE) soil-bound semivolatile organics as well as VOCs (15). The TECP collects organics in situ without bringing soil into the collection probe. Initial experiments indicate 50–90% recoveries can be obtained for polycyclic aromatic hydrocarbons (PAHs) on a compound-specific basis in dry soil. In this paper, results for explosives, polychlorinated biphenyls (PCBs), organochlorinated pesticides (OCPs), and PAHs are reported. Extraction efficiency versus applied temperature for dry and wet soils as well as distance from the probe window are discussed. Also described are the electronics and plumbing used to control the TECP sample collection system. The data were produced under fast, viz., 12 min versus 35 min, gas chromatography/mass spectrometry (GC/MS) conditions without the need of additional sample cleanup (16, 17).

Explosives data obtained from soils at Joliet Army Ammunition Plant (JAAP, IL) and PAH data from a coal-fired gas manufacturing plant in Massachusetts illustrate the quality of data that can be produced under typical site conditions. Cost savings of more than 50% have been demonstrated during site investigation studies at JAAP and Hanscom Air Force Base (HAFB, Bedford, MA) (18, 19). In these projects, samples were collected by hand (surface to 2 ft) or by traditional cone penetrometry (surface to 20 ft), where each sample was brought to the surface for analysis. Combining in situ sample collection with fast, on-site GC/MS analysis should provide the site owner and regulators with compound-specific site information while further reducing the per sample collection and analysis costs as well as the overall site investigation cost.

Experimental Section

Thermal Extraction Cone Penetrometry. Described below is the construction of the heated transfer line and sampling probe assembly. A typical cone penetrometer pipe was machined to house the heated aluminum (10 cm \times 1.75 cm

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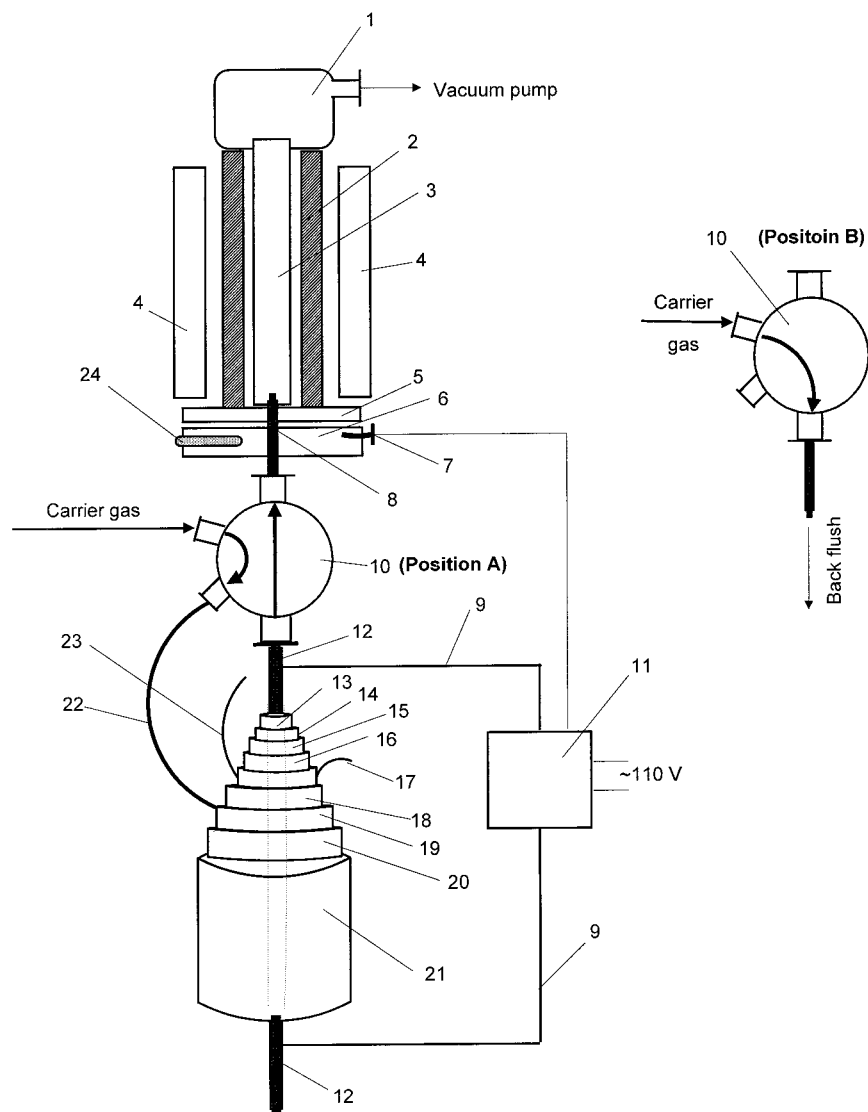


FIGURE 2. Schematic of transfer line materials and trapping system: (1) removable cap, (2) metal body of adsorber, (3) glass sleeve, (4) Peltier cooler, (5) ceramic heat and electrical insulation platform, (6) aluminum heat sink, (7) thermocouple, (8) Silcosteel tube, (9 and 23) high-temperature electrical wire, (10) four-port valve, (11) temperature and power controller, (12) Silcosteel collection tube (electrically heated), (13) aluminum foil with silicone adhesive, (14) Nextell 312 thermal insulation sleeving, (15) heat shrinkable Teflon tubing, (16) polyimide tape, (17) thermocouple, (18 and 20) fiberglass cloth, (19) high-temperature silicone tape, (21) heat shrinkable polyolefin sleeve, (22) Viton carrier gas tubing, (24) heater cartridge.

o.d.) sampling probe window (2 cm o.d.), see Figure 1. Connected to the sampling probe is the 30 m transfer line used to transport organic vapor to the surface. The transfer line is threaded through 1 m steel pipes, with the number dependent on the sampling depth. The probe contains a heater cartridge model L4A712, 240 V/1000 W (Omega, Stamford, CT), two 20 cm deactivated fused silica lined stainless steel tubes (Silcosteel, Restec Corp., Bellefonte, PA), and thermocouples. Each probe component is connected to its counterpart in the heated transfer line and pulled into the pipe. The collection window is force-fitted into the wall of the pipe and attached to the probe body. The collection and exit lines are pulled through channels etched in the sampling window. The window provides heat transfer to the soil and supports the collection and carrier gas lines at the pipe/soil interface. Figure 2 lists the transfer line materials and shows schematically the sample collector, gas flow control system, and transfer line heating system. The transfer line was fabricated from the following materials: 30 m \times 1 mm, i.d. 0.76 mm, Silcosteel (12) was used to transfer organics from the probe to the sample collector through the valve in position A (10). The Silcosteel was wrapped with an aluminum foil

siliconbacked adhesive (13, Fisher Scientific, Pittsburgh, PA) followed by thermal insulation sleeving (14, Nextell 312, Omega), and sealed by heat shrinkable Teflon tubing (15, Patriot Plastics, Woburn, MA). The line was wrapped with polyimide moisture insulation tape (16, Newark Electronics, Chicago, IL), thermally insulated fiber glass cloth (18, Fisher Scientific), and an adhesive-backed high-temperature silicon tape (19, Newark Electronics). A final layer of fiber glass cloth tape (20) was wrapped around the bundle before encapsulating with a heat shrinkable polyolefin sleeve (21, Comco, Somerville, MA). Electrical lines (9, 23), thermocouples (17), and Viton tubing (22, Omega) were inserted between layers as shown in the figure. Viton tubing was used for the carrier gas line.

The surface end of the Silcosteel (12) was inserted into a glass sleeve (3) lined GC injection port (2). The injection port was mounted on a ceramic disk (5) and insulated from the heated aluminum block (6; cartridge (24) model CII5, 110 V/60 W, Omega), whose purpose was to prevent condensation at the end of the transfer line. Tenax adsorbent tubes can be used in place of the glass sleeve when collecting volatile organics. Semivolatile organics are freeze-trapped by Peltier

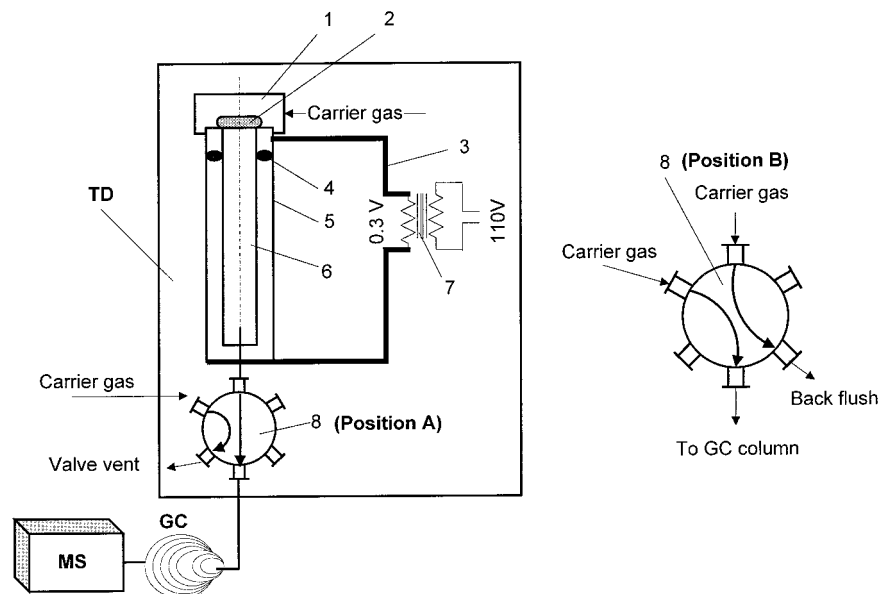


FIGURE 3. Schematic of the thermal desorber and six-port valve positions: (1) removable cap, (2) septum, (3) electrical leads, (4) O-ring, (5) metal body of thermal desorber, (6) glass sleeve, (7) step down electrical isolation transformer, (8) six-port heated valve.

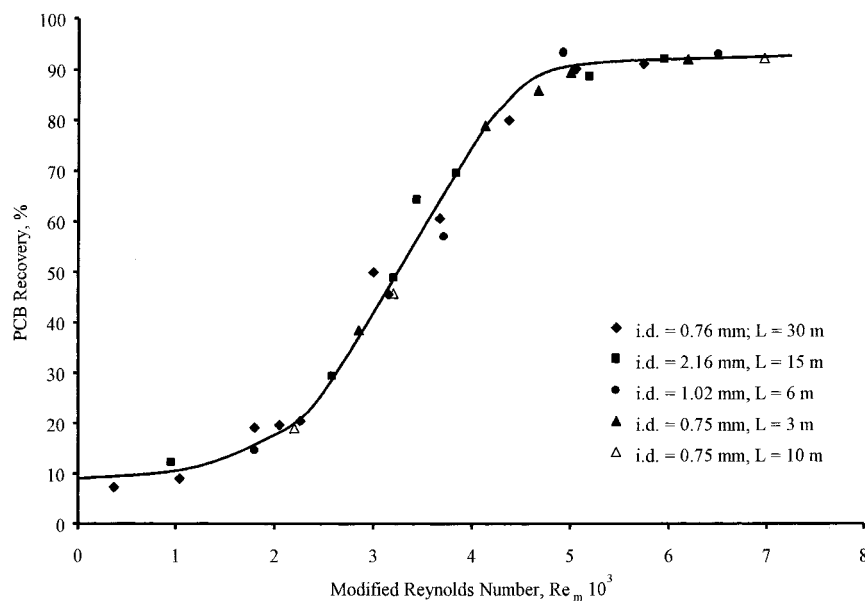


FIGURE 4. PCB recovered as a function of modified Reynolds number using a Silcosteel transfer line.

cooling (4). Both semivolatiles and volatiles can be collected in series if an empty glass sleeve is placed in the injection port with the Tenax tube connected to the outlet of the sample collector cover (1).

The Silcosteel tubing was resistively heated from ambient temperature to 300 °C. Electrical current was supplied to the transfer line and probe by a step-up isolation transformer (11, Grainger, Haverhill, MA), with the power (Watlow model DCIP-50245-F00) and temperature (Watlow model 988A-10FD-AARG) electronically controlled. Equation 1 was used to determine the total amount of heat, Q_{total} , needed to achieve 350 °C soil temperatures from the heating cartridge to the collection window

$$Q_{\text{total}} = B[m_p c_{p,p}(T_{2,p} - T_1) + m_s c_{p,s}(T_2 - T_1) + m_w c_{p,w}(373 - T_1) + \Delta H_v m_w + m_w c_{p,g}(T_2 - 373)] \quad (1)$$

where the assumed heat loss, B , from the probe to the environment is 50%; the probe body mass, m_p , is 2350 g and

its specific heat capacity, $c_{p,p}$, is 0.79 J g⁻¹ K⁻¹; the soil mass, m_s , 1 mm from the collection window is 1.44 g with a specific heat capacity, $c_{p,s}$, of 0.92 J g⁻¹ K⁻¹; 20% soil/moisture has mass, m_w , of 0.36 g and specific heat capacity, $c_{p,w}$, of 4.18 J g⁻¹ K⁻¹; at 373 K the specific heat capacity of the water vapor, $c_{p,g}$, is 1.87 J g⁻¹ K⁻¹ and enthalpy, ΔH_v , 2259 J/g; with T_1 (283 K), T_2 (623 K) and $T_{2,p}$ (673 K) the initial subsurface, soil/vapor, and final probe temperatures, respectively. To volatilize soil-bound organics, approximately 2400 J of heat must be transferred from the probe to the soil.

Heat flow from the probe to the soil was calculated by the Newton–Fourier equation, $Q = kF(T_2 - T_1)$ or 9.3 kJ/h, when the heat transfer coefficient, k , is approximated by λ/δ , and the soil heat conductivity coefficient, λ , is 0.11 kJ m⁻¹ h⁻¹ K⁻¹, soil thickness, δ , is 1 mm, and collection window surface area, F , is 2.53 10⁻⁴ m². For soils containing 20% water, 15 min should be sufficient time to achieve 350 °C soil temperature; $Q_{\text{total}}/Q = 2.4$ kJ/9.3 kJ/h. From this, the estimated power required is ~1 kW. The transfer line and

TABLE 1. Thermal Desorption and Thermal Extraction Cone Penetrometry Material Balance

compound	TD (closed cell), %				TECP, %, recovery, <i>r</i>	RPD $100(r_{\max} - r)/0.5(r_{\max} + r)$
	recovery, r_{\max}	soil	column	total		
Aroclor 1248	96	3	PCBs ^a 0.2	~99	95	1
			CI Pesticides ^a			
α-BHC	91	7	ND ^b	98	77	17
β-BHC	88	11	ND	99	72	20
δ-BHC	82	13	ND	95	71	15
γ-BHC	84	13	ND	97	72	15
Aldrin	88	10	1	99	77	14
4,4' DDD ^c	65	25	2	92	59	10
4,4' DDE	82	13	2	97	72	13
4,4' DDT	83	12	2	97	73	13
dieldrin ^c	73	19	1	92	63	15
endosufan I	82	18	1	100	68	19
endosufan II	73	18	1	92	62	16
endosufan sulfate	71	26	2	99	63	12
endrin ^c	67	22	1	90	59	12
endrin aldehyde ^c	61	31	1	93	56	9
endrin ketone ^c	60	30	1	91	55	9
heptachlor	85	9	2	96	76	12
heptachlor epoxide	90	8	1	99	77	16
			Explosives ^d			
DNT	92	6	ND	98	77	18
TNT	88	9	ND	97	75	16

^a $T_{\text{soil}} = 350\text{ }^{\circ}\text{C}$; $T_{\text{tr.l.}} = 300\text{ }^{\circ}\text{C}$; $Re_m = 6000$; $V_0 = 32$; $w_g = 1.8\text{ m/s}$. ^b ND = nondetectable. ^c Thermally unstable. ^d $T_{\text{soil}} = 250\text{ }^{\circ}\text{C}$, all other experimental conditions are the same as PCBs and CI pesticides.

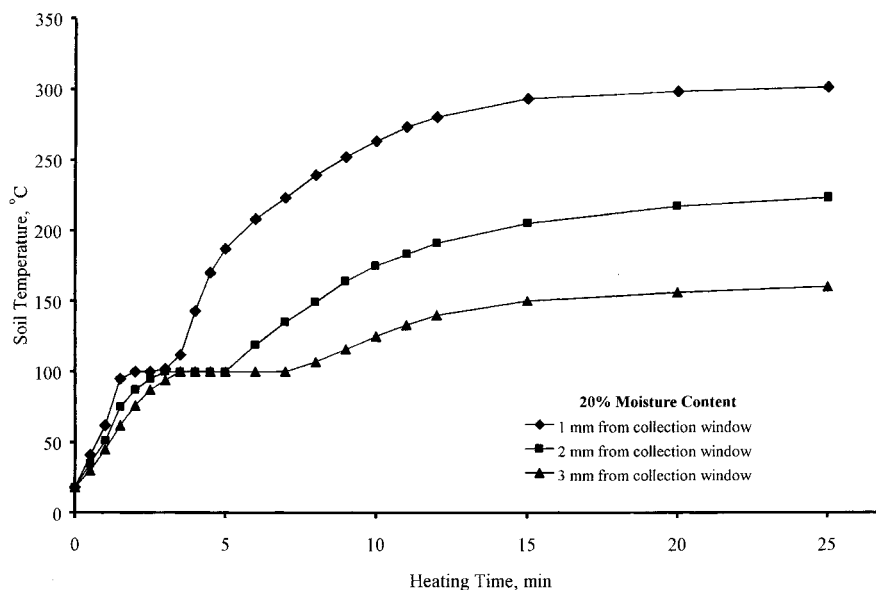


FIGURE 5. Soil temperature profile (20% moisture content) with probe temperature at 450 °C.

probe temperatures as well as the carrier gas flow rate and pressure within the collection system are all regulated and monitored by the instrument.

Nitrogen was used as the carrier and backflush gas. It also served to protect the Silcosteel from oxidation and deactivation at high temperature. The organic vapor was swept through the transfer line and then trapped in the TECP sample collector. The glass sleeve was placed into the thermal desorption (TD) GC sample injection port (5), see Figure 3. The TD was resistively heated by connecting the injection port to a step down isolation transformer (7) by a gold soldered copper strip (3). A standard inlet cap (1), with septa (2), was used when solvent-extracted soils or standards were syringe-injected into the glass liner (6). In contrast, a pressure cap without septa was used when soil or TECP extracts were

directly introduced into the GC/MS. An O-ring (4) was used to hold the glass liner in place. Calculations were made to estimate the power necessary to heat the thermal desorber to 350 °C. Equation 2 was used to determine the current, *I*.

$$Q = B(m_m c_{p,m} + m_g c_{p,gl})(T_2 - T_1) = \dot{I}^2 R \tau = \dot{I}^2 r L (\tau/S) \quad (2)$$

where the assumed heat loss, *B*, into the environment is 25%; the mass of the TD body, *m_m*, is 11 g and stainless steel specific heat capacity, *c_{p,m}*, 0.45 J g⁻¹ K⁻¹; mass, *m_{gl}*, of the glass sleeve is 4 g and specific heat capacity, *c_{p,gl}*, 0.71 J g⁻¹ K⁻¹; *T₁* (298 K) and *T₂* (623 K) are the initial and final temperatures; *R* is the electrical resistance ($R = rL/S$) with *r* the stainless steel specific resistance (0.181 Ω mm²/m); *τ*

TABLE 2. PCB Recovery for the TD and TECP with Varying Soil Moisture^a

% moisture	% recovery	
	TD	TECP
0	96	95
5	87	70
10	75	55
20	45	35
30	35	27

^a $\tau = 5$ min; $T_{\text{probe}} = 450$ °C; $Re_m = 6000$; $V_0 = 32$; $w_g = 1.8$ m/s.

(30 s) is the time required to heat the TD, with cross sectional area, S , 18.84 mm² and length, L , 0.075 m. When Q equals 3300 J, the current is 390 A. Thus, the power and voltage needed to heat the TD are 110 W and 0.3 V, respectively.

Organics were swept from the TD through the valve (8, position A) onto the GC capillary column by helium at 2 mL/min. Flow was maintained through the column at all times using a six-port heated valve (300 °C). After 1 min the valve was switched to position B at which time the GC temperature program began. The fused silica column, 15 m \times 0.32 mm i.d. with 0.25 μ m film thickness of 5% diphenyl, 94% dimethyl, and 1% vinylpolysiloxane (Supelco SPB-5), was held at 35 °C for 1 min then heated to 290 °C at 33 °C/min and held isothermal for 1.5 min. The GC was used in combination with a quadrupole mass spectrometer ruggedized for field application. The Ion Fingerprint Detection mass spectrometry software (IST, Cambridge, MA) searches each MS scan for a particular compound's mass spectral profile and then extracts the selected ion signals, computing their match against predetermined relative abundance error ratios. Quantitation is made by normalizing the least matrix affected target ion against the main ion for each compound's integrated ion signal. This approach decreases nonuniform matrix background signals and minimizes variances in the scan-to-scan chromatographic envelope (20).

Reagents, Standards, and Soil Samples. Standard solutions of PAHs, PCBs, organochlorine pesticides, di- and trinitrated toluene (DNT and TNT), and pyrene- d_{10} were purchased from Ultra Scientific (North Kingston, RI) and used to prepare fortified soil samples. These soils were a poorly to moderately sorted fine to medium sand and an organically mixed loam collected from university property. Soils samples were analyzed before fortification and found to be free of contamination. Soil from Joliet Army Ammunition Plant (IL) consisted of sandy loam to loam, and when dry it was dark grayish brown (Munsell designation 10YR4/2). The manufactured gas plant (MA) soil was highly contaminated with coal tar. It consisted of carbonaceous gravelly sandy loam, whose color when dry was slight brown to black (Munsell designation 10YR2/1). Methylene chloride was used to extract all organics from soil except for the nitrated toluenes, which were extracted by acetone. All solvents were purchased as HPLC grade from Fisher Scientific and used as received.

Results and Discussion

The dependence of the TECP transfer line on length (3–30 m) and diameter (0.75–2.16 mm) as well as the carrier gas linear velocity (0.4–5 m/s) and collection volume was determined. These experiments were carried out by directly desorbing known concentrations of organics from soil using the thermal desorption GC inlet connected to the transfer line, with organics trapped via the TECP sample collector. The TD/transfer line simulates closed cell operating conditions, namely, no loss of organics to the environment. The

TABLE 3. TECP Percent Recovery from Wet and Dry Soil with Time^a

compound	dry soil 5 min, % r_1 (%RSD)	20% soil moisture		ratio r_3/r_1
		5 min, % r_2 (%RSD)	15 min, % r_3 (%RSD)	
PCBs				
Aroclor 1248	95	35	93	0.98
PAHs				
naphthalene	43 (23)	18 (22)	8 (31)	0.19
acenaphthylene	49 (18)	24 (14)	15 (18)	0.31
acenaphthene	53 (21)	22 (19)	18 (13)	0.34
fluorene	56 (13)	28 (9)	46 (12)	0.82
phenanthrene	64 (8)	31 (14)	60 (10)	0.94
anthracene	58 (11)	23 (10)	60 (14)	1.03
fluoranthene	58 (9)	22 (15)	63 (8)	1.09
pyrene	65 (12)	28 (8)	63 (4)	0.97
chrysene	46 (19)	21 (13)	48 (15)	1.04
benzo(a)anthracene	52 (4)	22 (11)	53 (7)	1.02
benzo(b)fluoranthene	41 (14)	18 (10)	40 (12)	0.98
benzo(k)fluoranthene	40 (14)	17 (11)	38 (12)	0.95
benzo(a)pyrene	48 (7)	21 (12)	48 (9)	1.00
indeno(1,2,3- <i>cd</i>)pyrene	29 (16)	8 (21)	28 (16)	0.97
dibenz(a,h)anthracene	26 (17)	9 (23)	27 (20)	1.04
benzo(g,h,i)perylene	18 (18)	6 (19)	17 (7)	0.94
Cl Pesticides				
α -BHC	73 (12)	27 (15)	69 (9)	0.95
β -BHC	66 (10)	25 (6)	64 (6)	0.97
δ -BHC	61 (10)	21 (10)	62 (12)	1.02
γ -BHC	61 (13)	23 (8)	59 (25)	0.97
aldrin	65 (9)	24 (12)	62 (10)	0.95
4,4' DDD	62 (27)	32 (18)	38 (23)	0.61
4,4' DDE	57 (16)	25 (11)	53 (10)	0.93
4,4' DDT	58 (18)	24 (13)	51 (14)	0.88
dieldrin	56 (30)	31 (34)	29 (22)	0.52
endosulfan I	54 (12)	19 (8)	55 (13)	1.02
endosulfan II	49 (9)	16 (8)	47 (13)	0.96
endosulfan sulfate	51 (14)	19 (11)	53 (10)	1.04
endrin	61 (29)	30 (32)	27 (28)	0.44
endrin aldehyde	58 (29)	33 (27)	28 (31)	0.48
endrin ketone	57 (26)	29 (30)	24 (33)	0.42
heptachlor	62 (11)	22 (9)	59 (8)	0.95
heptachlor epoxide	63 (8)	24 (13)	61 (12)	0.97
Explosives ($T_{\text{soil}} = 250^\circ\text{C}$)				
DNT	77 (6)	53 (9)	73 (10)	0.95
TNT	75 (13)	47 (15)	76 (16)	1.01

^a $T_{\text{soil}} = 300$ °C; $T_{\text{tr,l}} = 300$ °C; $Re_m = 6000$; $V_0 = 32$; $w_g = 1.8$ m/s; 50 ppm per compound.

data showed that the collection efficiency was independent of length and diameter but dependent on flow rate and collection gas volume. Figure 4 depicts PCB (Aroclor 1248) extraction efficiency from dry soil as a function of the modified Reynolds number,

$$Re_m = Re V_0 = w^2 d \rho \tau / \mu L \quad (3)$$

where V_0 is the ratio of the carrier gas collection volume to system dead volume, w is the linear velocity of the carrier gas, ρ is the carrier gas density and μ the viscosity, L is the length of the transfer line and d the diameter, and τ is the time it takes for the vapor to be transported to the sample collector. Maximum recovery was obtained when Re_m was >5700 and the collection volume was 30 times the dead volume.

In the above example, Aroclor 1248 was used to model the behavior of the other test compounds. The mixture contains dichlorinated to heptachlorinated biphenyls, which approximate the volatility range of other EPA-targeted semivolatile organics. To further test the model, closed cell extraction efficiencies were determined for di- and trinitro-

TABLE 4. PAH Recovery from Coal Tar Contaminated Soil^a

PAHs	solution extraction, ppm	TD (closed cell)		TECP		RPD $100(r_{\max} - r)/0.5(r_{\max} + r)$
		conc'n, ppm	% recovery, r_{\max}	conc'n, ppm	% recovery, r	
naphthalene	1267	431	34	198	16	74
acenaphthylene	351	200	57	103	29	64
acenaphthene	297	196	66	108	36	58
fluorene	441	273	62	247	56	10
phenanthrene	865	562	65	566	65	-1
anthracene	866	563	65	533	62	5
fluoranthene	567	437	77	421	74	4
pyrene	1070	760	71	724	68	5
chrysene	536	322	60	301	56	7
benzo(a)anthracene	535	321	60	310	58	3
benzo(b and k)fluoranthene	284	114	40	131	46	-14
benzo(a)pyrene	427	209	49	226	53	-8
indeno(1,2,3-cd)pyrene	186	48	26	54	29	-12
dibenz(a,h)anthracene	187	49	26	56	30	-13
benzo(g,h,i)perylene	132	25	19	24	18	4

^a Wet = 16%; $\tau = 13$ min; $T_{\text{probe}} = 450$ °C; $T_{\text{soil}} = 300$ °C; $Re_m = 6000$; $w_g = 1.8$ m/s.

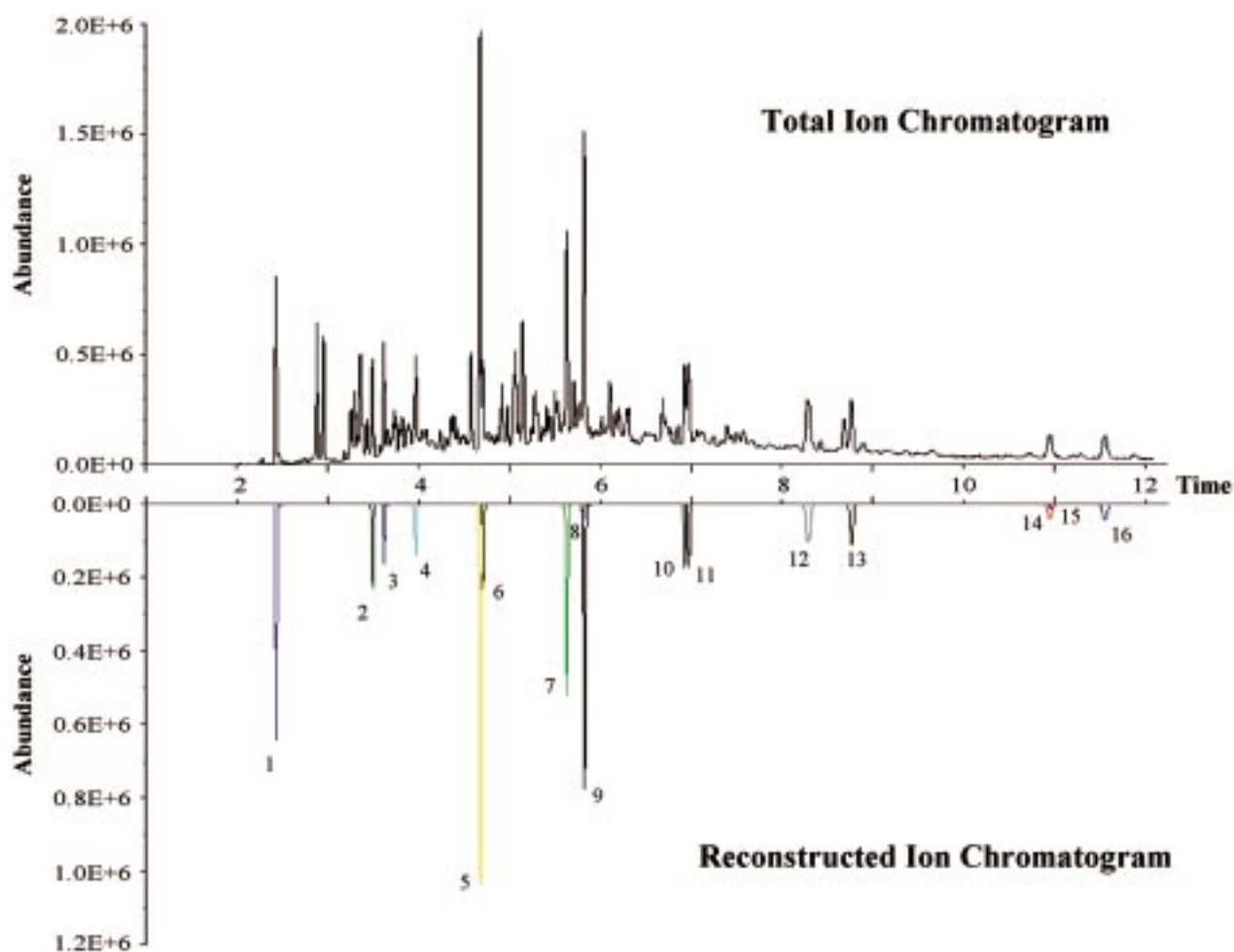


FIGURE 6. Analysis of a coal tar contaminated soil sample by GC/MS: (1) naphthalene, (2) acenaphthylene, (3) acenaphthene, (4) fluorene, (5) phenanthrene, (6) anthracene, (7) fluoranthene, (8) pyrene-*d*₁₀ (internal standard), (9) pyrene, (10) benzo[a]anthracene, (11) chrysene, (12) benzo[b&k]fluoranthene, (13) benzo[a]pyrene, (14) indeno(1,2,3-*c,d*)pyrene, (15) dibenz(a,h)anthracene, (16) benzo(g,h,i)perylene.

toluene, 16 PAHs, and 17 OCPs at $Re_m = 6000$. Although the recovery for each compound was different, see Table 1, the shape of the modified Reynolds curve was the same as that found for PCBs. These experiments were carried out under dry soil conditions, with the organics collected during a 5 min heating period. Backflushing the sample collection

system for 5 min reduced any adsorbed transfer line organics to nonmeasurable amounts.

The TECP in situ collection process was simulated by fortifying dry soil around the collection probe. Thermocouples were placed 1–3 mm out from the center of the probe. When the probe temperature was 450 °C, soil

temperatures reached 350 °C at 1 mm from the window and 265 °C at 2 mm. Table 1 also lists the TECP extraction efficiency as well as the percent difference between in situ and closed cell results. Impressive is the fact that TECP recoveries for all compounds were within 20% of the ideal, closed cell, thermal desorption data.

As soil moisture was increased, PCB recoveries decreased for both the TD and TECP systems, see Table 2. For example, when the water content was 20%, TD and TECP extraction efficiencies dropped from 95% (dry soil) to 45% and 35%, respectively. The temperature–time profile is shown in Figure 5 for this sample at distances of 1–3 mm from the collection window. After 5 min of heating, the soil within 1 mm of the window was 180 °C. No material change in temperature was observed from 100 °C at distances beyond 1 mm. Table 3 lists the recoveries under these conditions. If, on the other hand, the TECP is backflushed during the first 5 min of heating and then switched to valve position A for collection, extraction efficiencies are within statistical agreement of the 5 min dry soil results except for the thermally unstable pesticides and the more volatile PAHs. Soil 1 mm from the window reached 300 °C after 15 min of heating and as high as 200 °C at 2 mm. Presumably the volatile PAHs are lost to the surroundings as the vapor is swept away from the TECP during the first 5 min. It also appears that the TECP loses more heat than what was assumed in eq 1. In contrast, 10% soil moisture experiments showed no difference in measured organic recoveries between wet and dry soils, with soil temperatures maximizing at 350 °C after 12 min. Results suggest analyte concentrations should be calculated on a dry weight basis for soils containing more than 20% water.

Field experiments were performed to evaluate TECP ruggedness under typical site conditions. The TECP was pushed 10 m into the ground. The TECP passed both the mechanical and safety standard tests. TECP analyses were made from soil collected at a manufactured gas plant (MGP) that burned coal to produce electrical energy. The site contained extremely high levels of PAHs, with concentrations ranging between 10 and 2500 ppm. Table 4 shows the results for one sample where the soil was solvent-, TD-, and TECP-extracted. All extracts were analyzed with no sample cleanup. Note that the typical EPA SW 846 method 8270 GC/MS run time is 35 min preceded by a 1 hr sample cleanup procedure rather than the 12 min analysis used in this study. Although only PAHs were found in the MGP samples, the same instrument could quantify PAHs, PCBs, pesticides, and explosives discussed above. Solvent-extracted samples were preconcentrated by the TD. PAHs were trapped onto a precolumn as the solvent was vented into a carbon trap. The TD and TECP data are in remarkable agreement given that the moisture content in the sample was 16%.

The total ion current (TIC) and reconstructed ion current (RIC) chromatograms are shown in Figure 6. Although TIC signals were 10^6 , individual PAH signals were between 10^2 and 10^6 . The IFD software detected low-concentration PAHs in the presence of high-concentration interferences present in the coal tar extract. By “seeing through” the matrix, the algorithms increase confidence in surrogate, internal standard, and target compound identification and quantitation without the need for extensive sample cleanup (21).

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