MONITORING THE EVOLUTION OF ORGANIC COMPOUNDS FROM THE THERMAL TREATMENT OF CONTAMINATED SOIL SAMPLES USING SHORT COLUMN GC/MS

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INTRODUCTION

Incineration is an effective technology for the remediation of organic chemical contaminated wastes. For solid wastes, such as contaminated soils, processes involving separate stages of a primary desorber and secondary afterburner are particularly useful. The desorption stage is currently being modeled using a particle-characterization reactor (PCR, 0-500 g capacity), a bed-characterization reactor (BCR, 0.5-5 kg), and a rotary kiln simulator (2-15 kg) to study fundamental processes such as mass transfer, heat transfer, and volatilization of contaminants [1,2]. This paper describes the analytical methods and preliminary results from monitoring the evolution of organic compounds in these and smaller reactors.

The samples are soil contaminated with a broad range of polynuclear aromatic (PNA) hydrocarbons such as those derived from coal tars. The analytical methods primarily involve mass spectrometry (MS) with a variety of sample introduction techniques. The on-going analyses include solvent and thermal extractions of soil before and after various thermal treatments as well as on-line monitoring of vapors during desorption.

EXPERIMENTAL

Samples - Contaminated and uncontaminated clay soil samples were obtained from an undisclosed site. The samples were received air dried and simply designated as "soil A" and "soil B". The soils were analyzed for approximate mineral content by Fourier Transform Infrared (FTIR) spectroscopy of standard KBr pellets. Extracts were prepared from mg to g size samples by ultrasonification with repetitive aliquots of methylene chloride (CH_2Cl_2). Further, standard solutions of PNA's from naphthalene through dibenzoanthracenes were prepared for calibration purposes at 1, 23 ng/μl and 200 ng/μl in methylene chloride.

Extract Gas Chromatography/Mass Spectrometry (GC/MS) - GC/MS analyses of the extracts (procedure described above) were performed using a Hewlett-Packard 5890 chromatograph with a 15 m x 0.25 mm i.d. x 0.25 μm film thickness DB-5 column (J&W Scientific). Extracts were injected either by split injection or by flash vaporization in a Curie-point pyrolysis GC inlet [3] using 358 C Curie-point wires in an inlet set at 250 C. For the Curie-point injection, 2 to 10 ul of CH_2Cl_2 extract were concentrated on the pyrolysis wire with only limited loss of the smaller PNA's. The column was temperature programmed from 40 to 300 C at 15 C/min. An Ion Trap Detector (ITD, Finnigan MAT) was scanned from m/z 50 to 350 at 2 scans/sec.

Solids Probe MS - Soil samples were analyzed directly by use of a solids probe on a Ion Trap Mass Spectrometer (ITMS, Finnigan MAT). 1-3 mg samples were

placed in aluminum vials with 0.1 mm diameter holes in the press fit caps. The probe tip was then heated from 40 to 500 C at 60 C/min to desorb the organics directly into the ion trap maintained at 120 C. The mass spectrometer was scanned from m/z 50 to 350 at 2 scans/sec. PNA standards were deposited from CH_2Cl_2 solutions into the vials with and without soil substrate. Both uncontaminated and previously desorbed soils were used as substrates for the standards in separate experiments.

On Line Short Column GC/MS - The desorbing organic vapors were monitored during thermal treatment using a newly designed vapor sampling inlet with short column GC on a miniaturized ITMS (MINITMASS) all of which is described in detail elsewhere [4,5,6]. The system used a 1 m x 0.18 mm i.d. x 0.4 µm film thickness DB-5 column (J&W Scientific) in the standard ITD transfer line for isothermal operation. For these analyses the MINITMASS was operated in electron ionization mode with software features for enhanced sensitivity [6,7]. Retention time standards for various PNA's were acquired by direct injection of micro liter volumes of PNA standard solutions. Various inlet and column temperatures were used.

Thermal Treatment Reactors - Preliminary micro scale heat treatments (5-60 mg) were performed by thermogravimetry (TG) (Perkin Elmer TGA 7). In initial vapor sampling tests, 1 µg each of naphthalene and acenaphthylene were added to 10 mg of clean soil and then heated at 50 C/min to 600 C while the 125 or 200 C vapor inlet sampled the TG furnace outlet at 30 s intervals. In other tests, 50-60 mg portions of soil A were heated at 100 C/min to 250, 350 or 450 C, held for 5 min and then cooled at 50 C/min under He. The thermal treated soils were then analyzed by the extraction GC/MS and solids probe MS techniques.

The laboratory-scale reactors for particle and bed characterization, and the rotary-kiln simulator are described in detail elsewhere [1,2]. At the time of this writing, vapor sampling of test soils A and B was not completed. However, these results will be included in the oral presentation. A set of preliminary experiments in the bed-characterization reactor (BCR) have been conducted where "clean" clay soils were loaded with 0.5 wt% of either toluene, ethylbenzene, isopropylbenzene, or t-butylbenzene. In these runs, the tray of organic-loaded soil was placed beneath radiant heaters directly in the 536 C preheated air stream. The evolved gases were sampled at 60 s intervals for repetitive short column GC/MS analysis. The vapor inlet was operated at 160-175 C and the transfer line at 30 C isothermal.

RESULTS AND DISCUSSION

Extract GC/MS - Figure 1 shows a series of ion chromatograms from the flash vaporization GC/MS of the soil A extract. The total ion chromatogram is shown for the complete run (Figure 1a) and as an expanded short segment (Figure 1b). Single ion chromatograms are shown for m/z 228 (Figure 1c), 252 (Figure 1d) and 276 (Figure 1e). This data demonstrates the complexity of the chemical contaminants and the wealth of detailed qualitative and quantitative data that are available through this technique using a high resolution capillary column of normal length. Note that 5 or more isomers of benzofluoranthenes and benzopyrenes are distinguishable in the trace of m/z 252. The concentrations of compounds smaller than phenanthrene are underestimated in this chromatogram due to premature evaporation from the Curie-point wire.

Solids Probe MS - Figure 2 shows the solids probe MS analysis of soil A. The single ion chromatograms indicate that the PNA's were desorbed from the soil

into the MS high vacuum over a broad temperature range of 100 to 400 C when heated at 60 C/min. These ion traces suggest the strong interaction of the PNA's with the clay soil surface since these same compounds completely evaporate from a sample vial without the soil at temperatures less than 200 C. Note that there is no separation of the various isomers as was seen with the chromatography in Figure 1.

Vapor Sampling GC/MS - Figure 3 is a set of ion chromatograms from the vapor inlet short column GC/MS analysis of PNA standard solution. This figure illustrates how compounds eluting in the 9 min to 18 min portion of the chromatogram shown in Figure 1 are compressed into a 1 min analysis on the isothermal short column at 250 C. Although the chromatographic resolution is greatly reduced from that of Figure 1, there is still a clear separation of the benzofluoranthenes from the benzopyrenes as seen in the m/z 252 trace. The significant advantage is that the partial GC/MS analysis can be repeated each 60 sec versus the 20 min in Figure 1 and this analyses still gives some isomer information beyond that which can be obtained in direct MS methods such as seen in Figure 2.

Thermal Treatment Analyses - Figure 4 illustrates the monitoring of PNA evolution from thermal treatment of the soil using the short column GC/MS system on-line. In this analysis, the 4 min to 7 min portion of the chromatogram in Figure 1 has been compressed into a 30 sec segment of Figure 3. For this preliminary test, naphthalene and acenaphthylene were repetitively analyzed each 30 sec as they were evolved from 10 mg of soil in a thermogravimetry (TG) crucible. Note that the profiles of consecutive naphthalene (m/z 128) and acenaphthylene (m/z 152) peaks trace the evolution of these compounds from the soil at the TG temperatures indicated. The naphthalene is desorbed from the soil at higher temperatures than the higher boiling acenaphthylene possibly due to the fact that it was the first one coated on the soil and thus had first access to the strongest adsorption sites. Although equal amounts of each compound were placed on the soil, recondensing of the acenaphthylene in cold regions of the TG oven greatly attenuated its signal.

Samples of soil A were heated in the TG to 250, 350, or 450 C (without on-line vapor analysis) and then analyzed by extraction GC/MS and solids probe MS. Preliminary analysis of these data indicate that there were virtually no PNA's left on the soil heated to 450 C in helium. The solids probe MS data on selected PNA's in the original soil and the 250 and 350 C thermal treated soils are listed in Table 1. Although these data show the expected reduction of these compounds from the heated soils, the actual solids probe ion profiles indicate that the remaining amounts are more tightly bound than the major portions of the original contamination. This result is readily explained if one simply assumes that the first monolayer of PNA's on the clay surface is more strongly adsorbed than additional layers. Further, a layer of black char began to form at 350 C (in helium), which might be a secondary binding site. At present it is unclear to what extent this char was formed from the PNA contaminants versus native soil humic substances.

Evolution profiles of selected compounds from .5 wt % toluene loading on a clay soil are presented in Figure 5. 600 g of soil was heated to 536 C in the BCR. Three secondary products are shown at concentrations of 1 ppb to 1 ppm (in air). In addition to the reaction products shown in the figure, the following were also detected at similar concentrations: benzylalcohol, bromotoluene, bromobenzene, quinone, benzonitrile, xylene, ethylbenzene, chlorotoluene, and dichlorobenzene. The benzaldehyde and benzylalcohol are expected as partial oxidation products. The exact sources of the other compounds are as yet

uncertain although it can be stated that these were not impurities in the original solvent and there was approximately 15 ppm chlorine found in the original soil. The quantity and diversity of these products gives some idea of possible secondary reactions and desorbtion characteristics expected with the PNA's.

CONCLUSIONS

These preliminary results clearly demonstrate the potential of mass spectral techniques for studying the effectiveness of thermal treatment in contaminated soil remediation. Solvent extraction followed by high resolution GC/MS is the method of choice for detailed examination of soils before and after treatment. Solids probe MS is a rapid technique for screening soils and can offer additional information on how the contaminant is bound to the soil. The vapor sampling short column GC/MS system is a powerful tool for on-line monitoring of the desorbed gas phase products which are important to identify for desorber optimization and afterburner design. Isothermal operation of the short column is a major limitation to the boiling point range of compounds which can currently be analyzed on a rapid repetitive basis and plans are underway for making it temperature programmable.

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TABLE 1
Approximate Concentrations in ng/mg (ppm) of Selected PNA's on "As Received" and TG Thermally Treated Soil A

	Concentration (ppm)		
Compound m.w.	Soil A	250 C	350 C
128	600	66	19
202	200	17	1
278	16	14	0

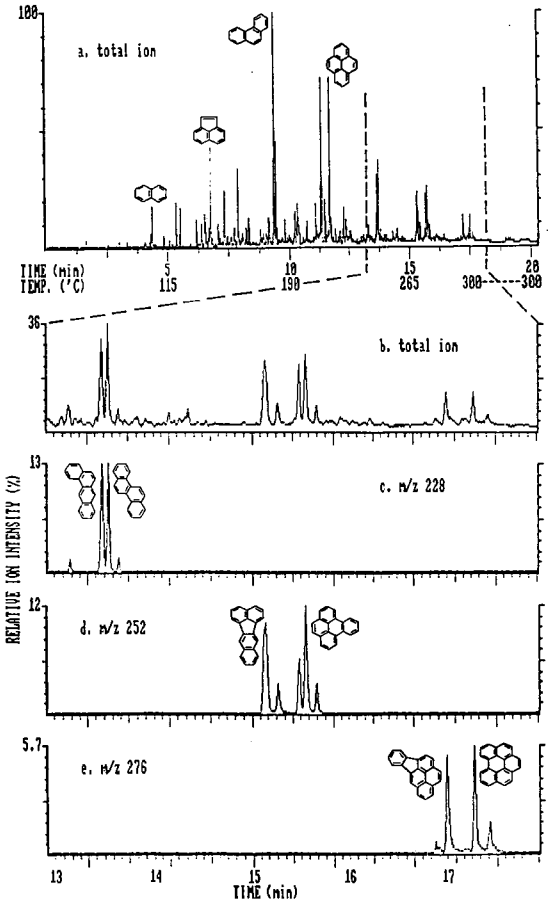

Figure 1. GC/MS ion chromatograms from the analysis of the soil A extract on a 15 m column.

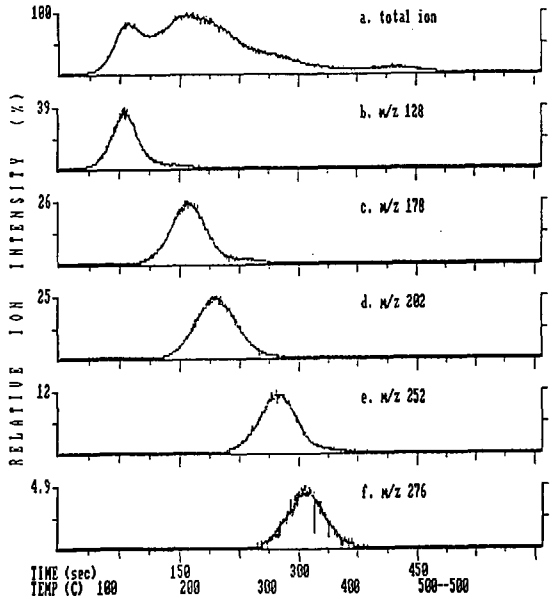

Figure 2. Solids probe MS ion chromatograms from the thermal desorption of soil A directly into the mass spectrometer high vacuum.

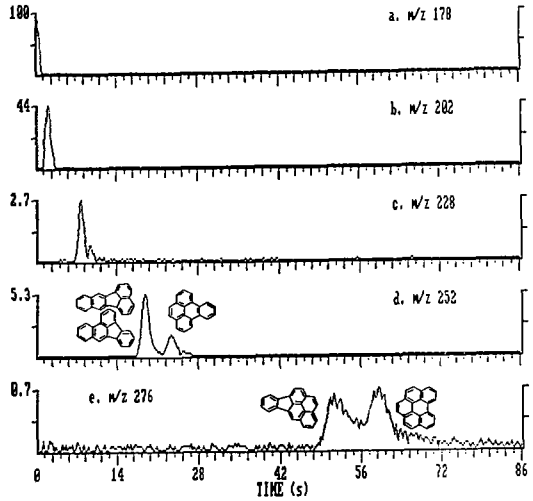

Figure 3. Selected ion chromatograms from the vapor sampling GC/MS analysis of a PNA standard solution.

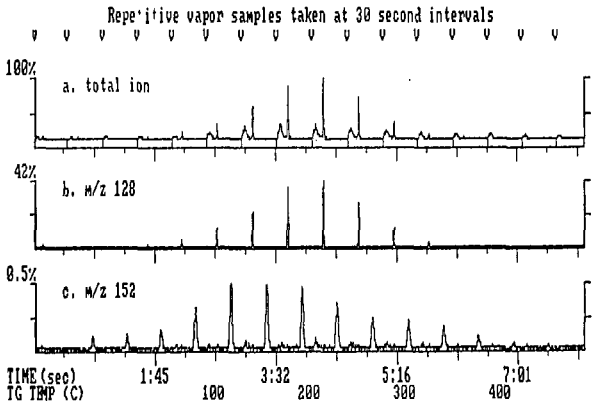

Figure 4. Ion chromatograms for repetitive on-line sampling using vapor inlet short column GC/MS during a TG soil desorption.

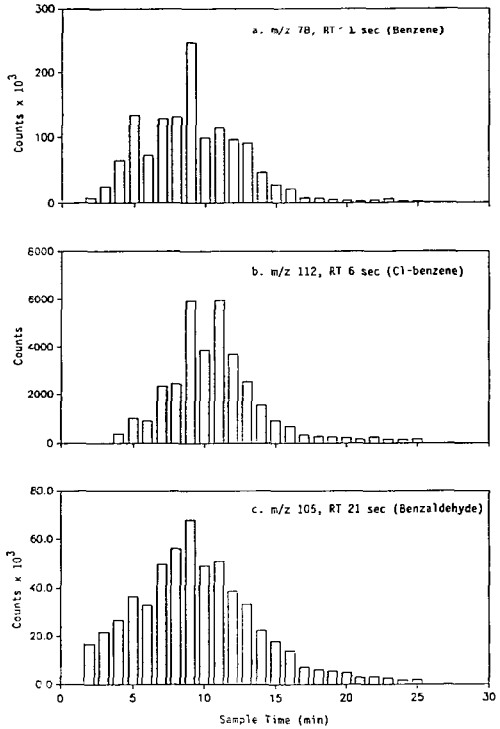

Figure 5. Peak area profiles for 3 selected reaction products produced from toluene desorbtion.