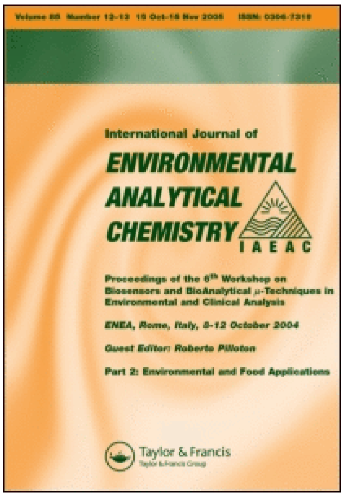

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Sensing of Petrochemical Fuels in Soils Using Headspace Analysis with Photoionization-Ion Mobility Spectrometry

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Photoionization-Ion Mobility Spectrometry (PI-IMS) was used to distinguish among common petrochemical fuels including leaded gasoline, unleaded gasoline, kerosene, and diesel fuel through sampling of headpsace vapors over liquid samples. Positive ion mobility spectra obtained in air at ambient pressure were comprised of 3 to 5 peaks which were tentatively identified as benzene, alkylated benzenes, naphthalene and alkylated naphthalenes. The simple mobility spectra from PI-IMS analysis, due to selective ionization of aromatic hydrocarbons, were contrasted with the complex chromatographic patterns for the same fuels from scanning GC/MS analysis. Discrimination between unleaded gasoline and diesel fuel in fuel mixtures was possible using PI-IMS across a broad range of gas-phase concentration ratios.

Fuels were also detected in soil using PI-IMS analysis of headspace vapors at 25°C. Unleaded gasoline in soil was detected from 0.16 to 16 mg/kg for only 0.1 g of sample with nearly linear response. Reproducibility in preparation and analysis of soil samples was 10 to 60% RSD for individual components while instrumental PI-IMS reproducibility with toluene alone was 5% RSD. Water vapor had no effect on PI-IMS response for fuel vapors alone, but increased moisture content in soils caused enhanced response. Drilling mud from a natural gas reserve pit was used to demonstrate environmental application of PI-IMS in sensing a water-saturated sample. Qualitative inspection of results showed no serious complication to PI-IMS response from water. Effects on sensor sensitivity from weathering and other environmental alterations of fuels in soils and groundwater were not explored.

INTRODUCTION

Dispensing of petrochemical fuels from underground storage tanks (USTs) has been a common practice in the United States for automotive service stations, refineries, other industries, and private residences. Particularly troublesome is uncontrolled, and usually unrecognized, leaking of hydrocarbon liquids such as gasoline, diesel fuel, jet fuel, and kerosene into nearby soils and groundwater. While 3 to 5 million USTs exist nationally (including those for hazardous industrial chemicals), 100,000 USTs are leaking presently and an estimated 350,000 additional USTs will begin leaking in the next 5 years.[1] In November 1984, the U.S. Resource Conservation and Recovery Act (RCRA) was amended[2] to regulate construction, installation, use, and documentation for certain USTs. A principle component of the RCRA amendment was development of capabilities and standards by 1987 for detecting fuel leaks from USTs through inspection of nearby soil, air, and water. Approaches to chemical sensing of environmental contamination for such fuels should be distinguished by rapid analysis, high sensitivity, and some measure of discrimination for fuel-types in situations where several USTs with different contents may be suspect. For practical logistics, determinations should be reasonably routine and inexpensive.

Surprisingly, detection of petroleum fuels in soils has not been widely investigated regarding leaking USTs. Since these fuels can be highly complex mixtures with hundreds of components,[3,4] existing chemical characterizations have been based on traditional separation techniques, typically gas chromatography (GC).[3-11] Detectors in these analyses have included flame ionization detectors,[7] mass[3,4,6] and FT-IR[5] spectrometers, and more importantly here, photoionization detectors.[10,11] Since many components in fuels have appreciable vapor pressures, pretreatment of samples can be speeded through the direct use of headspace vapors over soil[9,12] in contrast to lengthy liquid-solid extractions.[7] Thus, analytical approaches to this sensing problem may be simplified to sampling gases in soils under USTs for determination of volatile components in fuels.

Photoionization detectors (PID), with vacuum ultraviolet (UV) wavelengths, in combination with GC have been the subject of two recent reviews[13,14] and several independent investigations.[10,11,15,16] Promising characteristics which favor PID use in fuel-sensing are high selectivity to certain chemical classes such as aromatic hydrocarbons,[14] tunable selectivity with complex hydrocarbon mixtures,[10] and high sensitivity.[16] Although sensitivities in direct analysis of air by GC/PID compared favorably with those for more conventional adsorbent preconcentration methods, irregular response was observed for higher alkylated benzenes[16] and for organic vapors in high humidity.[17] Photoionization detection might be used alone as a sensor based upon some degree of selectivity from ionization, but response for fuels will be very complex still without additional means of discrimination. The combination of photoionization (PI) with ion mobility spectrometry (IMS) provided a second basis (e.g. ion mobility) for resolution of chemical information,[18] although operation was limited initially to nitrogen atmospheres due to oxygen quenching of UV photons.

Ion mobility spectrometry is an atmospheric pressure based technique for separation and detection of gaseous molecules as ions.[19,20] Neutral analyte is ionized and injected into an electric field gradient where ion velocity is proportional to gaseous mobility. Mobility is inversely related to collisional cross-sections and separation is based largely on size and shape of charged analytes. While the potential use of IMS with chemical ionization sources for air sensing of contaminants was recognized as early as 1974,[21] such development occurred only recently.[22] Prior PI-IMS instrumentation was restricted to operation with inert atmospheres,[18] but a vacuum UV discharge lamp with reconfigured ionization chamber for PI-IMS has been successfully used for chemical sensing directly in air.[23] Thus, PI-IMS may have promise for rapid sensing of fuels in soils. The objectives of this work were to (A) characterize and describe PI-IMS response for complex petrochemical mixtures (i.e. fuels) as vapors in air; (B) evaluate PI-IMS behavior with fuel mixtures; and (C) explore sensitivity, linearity, and selectivity of response for hydrocarbon mixtures in soils. The goal of this study was evaluation of PI-IMS as a sensor for leak-detection with USTs.

EXPERIMENTAL

Instrumentation

An ion mobility spectrometer, built at NMSU and described in detail,[24,25] was modified through addition of a vacuum UV (10.2 eV) hydrogen discharge lamp (HNU Systems, Boston MA) to the repeller electrode.[23] The drift gas was breathing air from a compressed gas cylinder and was cleaned with a 13X molecular sieve (Alltech, Deerfield, IL). Conditions for operation of the IMS were: drift gas flow, 300 mL/min; temperature, 149°C; drift length, 9 cm; total tube voltage, 3000 V; electric fields in drift region, 243 V/cm; amplification, 2 to 8×10^{10} V/A; scans per spectrum, 500 or 1000; frequency of operation, 28 Hz; and atmospheric pressure, 660 mm Hg. Samples of liquids or soils were stored in 2 mL Wheaton glass minivials (Southland Cyrogenics, Carrollton, TX) and headspace vapors from vials were delivered to the IMS using a gentle stream of nitrogen gas at about 10 mL/min. Gases were passed from the vial to the IMS through 20 cm long sections of fused silica tubing with 0.2 mm ID.

A Hewlett-Packard model 5992A gas chromatography/mass spectrometer (GC/MS) was used in supporting chemical analysis of fuels. The GC/MS was equipped with dual disc drives, X–Y plotter, jet separator, and 2 m long packed column (glass) containing 3% OV–1 on 100/120 mesh Chromosorb W. Chromatographic conditions for analysis were initial temperature, 90°C; initial time, 3 min; temperature program rate, 5°C/min; final temperature, 250°C; injection port temperature, 250°C; and carrier gas flow, He at 25 mL/min Mass spectrometer conditions for scanning analysis were mass range, 45 to 600 amu, scan rate, 690 amu/s; scan delay, 0.1 s; electron multiplier voltage, 1400 V; and detection threshold, 100 linear counts.

Materials and Chemicals

Samples of leaded and unleaded gasoline, diesel fuel, and kerosene were obtained fresh from local filling stations in Las Cruces, NM. The samples were stored in glass test tubes with screw caps. Standards of aromatic hydrocarbons were benzene (distilled in glass grade, Burdick and Jackson, Co., Muskegon, MI), toluene (Photrex grade, J.T. Baker, Co., Phillipsburg, NJ) and p-xylene (Baker Grade, J.T. Baker, Co.). The soil was Glendale soil from Dona Ana County in Southern New Mexico.[26] Fuels were added to 5 g of soil which were then shaken vigorously and stored for 30 to 60 minutes before 0.1 g portions were removed for analysis. Microliter amounts of liquid fuels were discharged onto the soil so estimated total concentrations were 0.00, 0.16, 0.8, 1.6, and 16 mg/kg of fuel in soil. Concentrations of individual components could be calculated using fractional concentrations and estimated headspace losses from vaporization.

Procedures

Several separate studies were completed in the evaluation of IMS sensing of fuels in soils. These investigations were:

A) Direct Analysis of Fuels. Headspace vapors over liquid samples of four fuels were analyzed individually using scanning GC/MS and using the PI-IMS. Fuels were used as received. The injection volume for GC/MS analysis of fuels was 50 μL of headspace vapor at 25°C. Flows for carrier gas, used to sweep headspace in closed mini-vials into the PI-IMS, were adjusted to provide stable response with high signal to noise ratios. Standards of selected aromatic hydrocarbons were also analyzed by PI-IMS to aid in the assignment of peak identities.

B) Discrimination between Fuels by PI-IMS. Diesel and unleaded fuels were added to the PI-IMS at the following ratios for average vapor pressures of unleaded to diesel: 0.05, 0.1, 0.16, 0.44, 1.20, 1.32, 2.40, 2.96, 4.10, 7.05, 14.09, and 28.19. Average vapor pressures for fuels were estimated using a weighted equation of vapor pressures for content of benzene, toluene, xylene, and naphthalene with alkylated cogeners.

C) Sensitivity in Soil Analysis. Even though a simple headspace inlet system was used, measurements were possible using small amounts (0.1 g) of soil at 25°C. A flow of 10 mL/min of gas was sufficient to sweep headspace from the sandy soil without dispersing particles. The concentrations of fuels in soil were from 0.08 to 16 mg/kg.

D) Effects of moisture. Samples of soil with 2 mg/kg of unleaded gasoline were analyzed with moisture content of roughly 7, 15, and 25%. A final sample was analyzed under mud conditions (>50% water). The flow into the PI-IMS was not altered between analyses. Effect of water vapor directly on PI-IMS response was determined by metering unleaded gasoline and various amounts of water vapor into the IMS.

E) Reproducibility. Seven samples for 2 mg/kg of unleaded gasoline in soil were prepared and analyzed by PI-IMS. Spectra for individual samples were acquired and analyzed for peak heights of major components in spectra. Six repetitive measurements were made on liquid unleaded gasoline and toluene separately to eliminate variation from soil preparation and handling from instrumental variance.

F) Application. A sample of drilling muds from a reserve pit in northwest New Mexico was used to evaluate an actual environmental sample which was contaminated with a persistent hydrocarbon odor.[27] The sample had an estimated 30% water content and 0.5 grams were used for analysis by PI-IMS.

RESULTS AND DISCUSSION

PI-IMS Response to fuel vapors

Results from PI-IMS response to vapors from four petrochemical fuels are shown in Figure 1 as mobility spectra for positive ions and in Table I as tabulations of the same spectra. The IMS spectra for these fuels were reasonably simple with 4 to 5 major peaks and were distinguished by differences in intensities and mobility values for peaks from particular fuels. This simplicity contrasted sharply with GC/MS results shown in Figure 2 where over 25 major components in vapors from diesel fuel and unleaded gasoline were resolved on a packed column. Based on known composition of the headspace vapors from GC/MS analysis and from known ionization potentials for chemical classes in the fuels, major peaks in the mobility spectra should be aromatic hydrocarbons. Selectivity in ionization should result in formation of product ions for benzene, alkylated benzenes, and naphthalene (ionization potentials from 8 to 10 eV) while alkanes and alkenes (ionization potentials > 10 eV) should be unionized, and pose no interference in spectra. Consequently, the aromatic content of the individual fuels should be the principle variable in controlling the characteristics of PI-IMS response and spectra. The aromatic content of vapor from these same fuels is listed by compound in Table II. A reasonably good parallel between molecular weights (sizes) of predominant aromatic compounds in the fuels and the mobilities (and relative abundance) of peaks in PI-IMS spectra as shown in normalized abundances in Tables I and II.

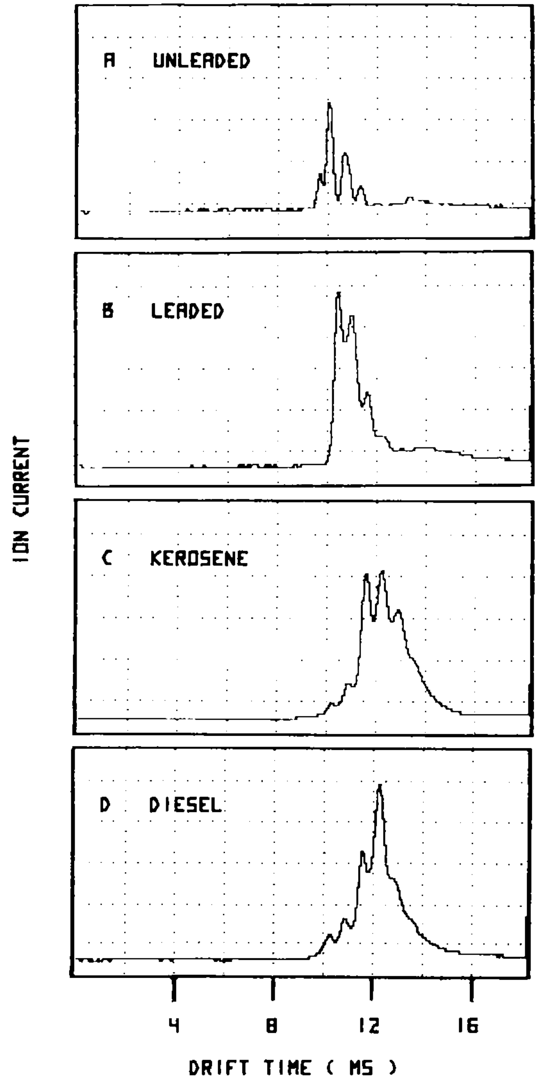

FIGURE 1 Ion mobility spectra for common fuels using Photoionization-IMS. Fuels were (A) unleaded gasoline, (B) leaded gasoline, (C) kerosene, and (D) diesel fuel. Spectra were collected from headspace vapors at 25°C with IMS in positive ion mode of operation.

TABLE I

Tabulated ion mobility spectra for petrochemical fuels from photoionization IMS

Sample	Drift time (ms)	(K_0)	Peak height (V)	(%)	Normalized abundance
Unleaded	9.64	2.16	0.71	14.9	29.2
	10.00	2.08	2.43	50.9	100.0
	10.64	1.96	1.21	25.3	49.8
	11.28	1.84	0.43	9.0	17.7
Leaded	10.42	1.99	3.86	43.2	100.0
	10.92	1.91	3.29	36.8	85.2
	11.57	1.79	1.43	16.0	37.0
	12.14	1.71	0.36	4.0	9.3
Kerosene	10.85	1.92	0.43	4.9	13.7
	11.57	1.80	3.07	34.7	97.8
	12.21	1.70	3.14	35.5	100.0
	12.85	1.62	2.21	25.0	70.4
Diesel	10.21	2.04	0.21	3.0	5.3
	10.85	1.92	0.64	9.1	16.3
	11.50	1.81	2.29	32.4	58.3
	12.21	1.70	3.93	55.6	100.0
Benzene	9.60	2.17			
	10.50	1.98			
Toluene	10.29	2.02			
	11.06	1.88			
Xylene	10.71	1.94			
	11.57	1.80			
Naphthalene		1.80			

Spectra were collected for standards of aromatic hydrocarbons found in the fuels and mobility values as shown in Table I matched favorably those in the spectra for fuels.

Ionization of aromatic hydrocarbons in air has been observed in prior PI-IMS studies and were among the most sensitive chemical classes tested.[28] Limits of detection (ppb) in air and sensitivities (pA/ppb) were reported for certain aromatic compounds as benzene, 2, 200; p-xylene, 5, 6; and naphthalene, 0.1, 155. The significance in these determinations is that PI-IMS spectra should be related quantitatively to composition when response factors are weighted

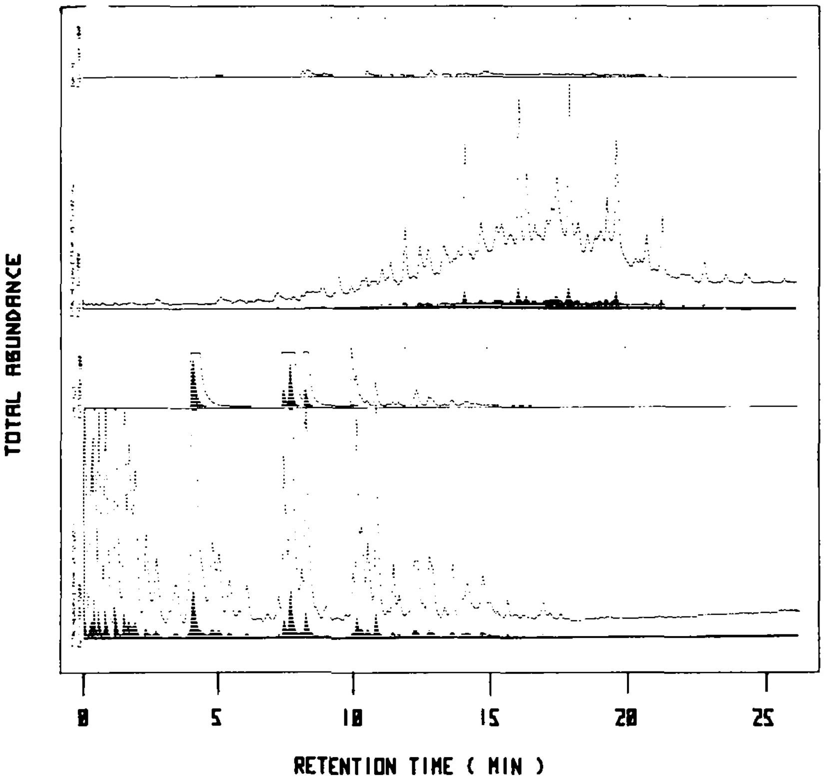

FIGURE 2 Chromatograms from scanning GC/MS analysis of headspace vapors for fuels. Plots shown were for (A) diesel fuel and (B) unleaded gasoline.

TABLE II

Content of aromatic hydrocarbons in fuels as determined using scanning GC/MS

Sample	Compound	Absolute abundance	Abudance normalized
Unleaded	Benzene	5719	56.4
	Toluene	9156	90.3
	Xylenes	10139	100
	Naphthalenes	1405	13.9
Leaded	Benzene	8778	100
	Toluene	8675	98.8
	Xylenes	4849	55.2
	Naphthalenes	859	9.9
Kerosene	Benzene	ND	0
	Toluene	ND	0
	Xylenes	1184	100
	Naphthalenes	542	45.8
Diesel	Benzene	ND	0
	Toluene	ND	0
	Xylenes	309	43.9
	Naphthalenes	704	100

into predictions. Unfortunately, exact semi-empirical predictions of relative ion intensities in IMS spectra using aromatic hydrocarbons in fuel vapors will be further complicated by charge-exchange reactions between mixtures of compounds with different ionization potentials.[29] For example, individual response factors may be distorted by the presence of compounds with lower ionization potentials and concentrations greater than for the compound of interest. Naphthalene at a fixed gaseous concentration caused the formation of a greater number of product ions when benzene was metered into the IMS at 20 to 100 fold excess concentrations than when naphthalene was alone detected. Despite all these complications and complexity of samples, various petrochemical fuels were clearly distinguishable as spectra from PI-IMS sensing. However, the suitability for resolution of mixtures of fuels using PI-IMS was uncertain.

Resolution of fuel mixtures

Since leaded gasoline soon will be less available in the U.S. and since unleaded gasoline and diesel showed IMS spectra distinctly different, unleaded gasoline and diesel fuel were selected for a fuel mixture study. Various mixtures of unleaded gasoline diesel fuel vapors were continuously introduced into the drift gas in the reaction region of the IMS. Results from varying the ratio of vapors from extremes of 0.05 to 28.19 for unleaded diesel are shown in Figure 3 and 4. At the ratio of 0.05, peaks at shorter drift times or higher mobilities were barely evident. These peaks, benzene and C_1 or C_2 substituted benzenes, were found at relatively high concentrations in unleaded gasoline but were not detected in diesel fuel. As the ratio was increased, these same peaks also increased in size. At a ratio of near 0.44, peak heights were comparable for components from individual spectra for diesel fuel and unleaded gasoline. Contributions of peaks in the mobility spectrum from diesel fuel were no longer seen at ratios greater than 14.

In Figure 4, peak heights for components in the mobility spectrum were plotted versus concentration ratios for fuel vapors. The curves showed regular and linear trends for peak heights as a function of the concentration ratio. This was preliminary evidence that PI-IMS may be a quantitative and linear sensor for fuels. These results also demonstrated that quantitative discrimination within fuel mixtures

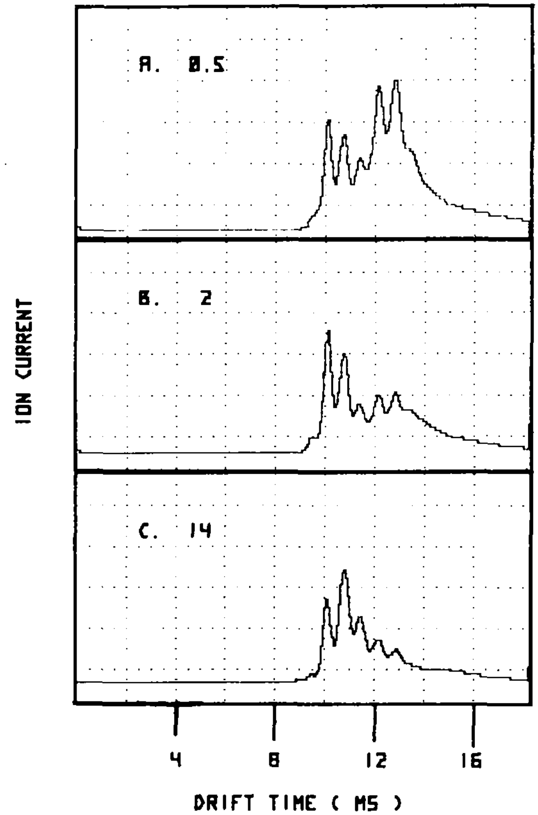

FIGURE 3 Mobility spectra for mixtures of unleaded gasoline and diesel fuel. Ratios of average vapor pressures for aromatic components were (A) 0.5, (B) 2, and (C) 14 for unleaded gasoline to diesel fuel.

was possible with PI-IMS. Other fuel combinations or other hazardous chemicals were not used in evaluation of resolution and interferences, although kerosene versus diesel fuel and leaded versus unleaded gasoline may be poorly resolved.

Sensing of fuels in soils

Response of PI-IMS was proportional to concentration of fuels in soils as shown in Figure 5 for unleaded gasoline. With the small

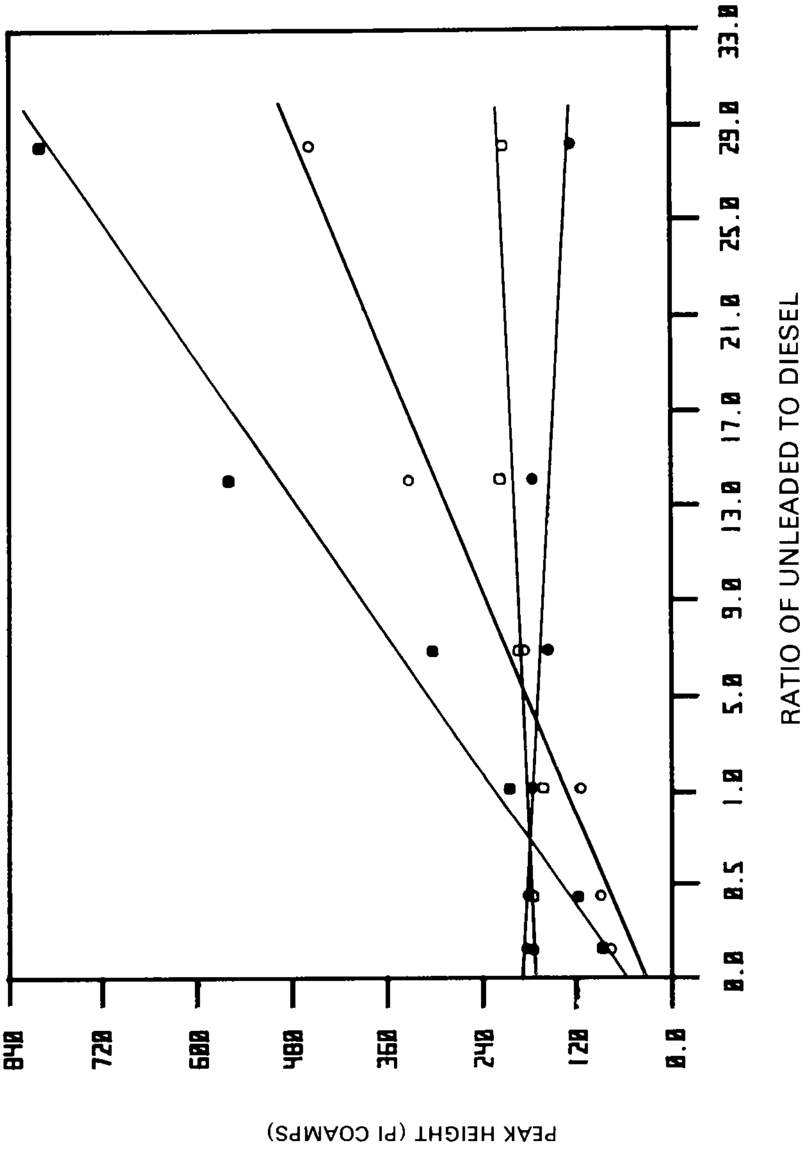

FIGURE 4 Plots of peak heights for components in mobility spectra from fuel mixtures. Plots correspond to major components in PI-IMS spectra in Figure 3, with drift times (ms) of: 10.8 (■), 11.4 (○), 12.1 (□), and 12.8 (●).

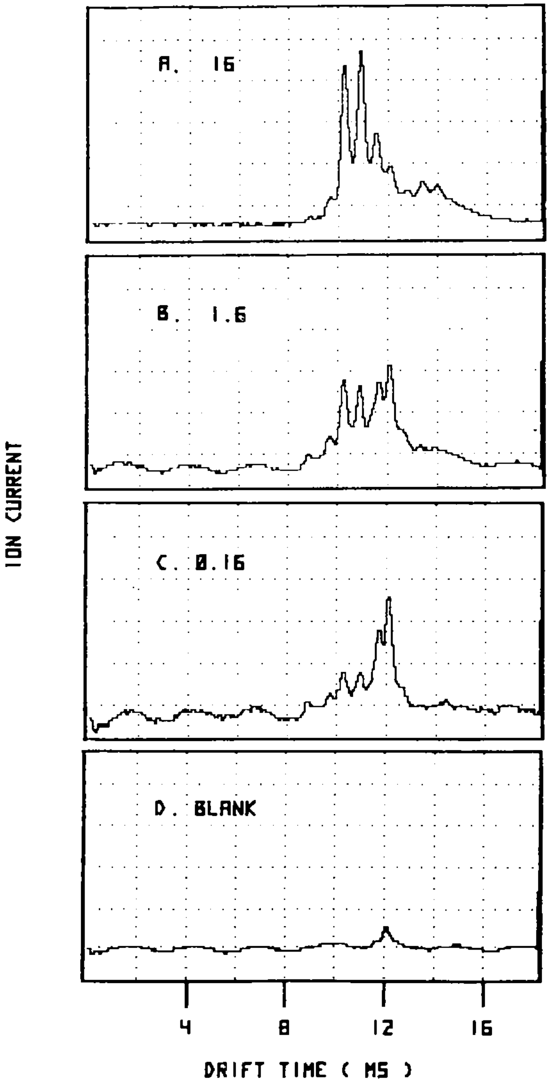

FIGURE 5 Mobility spectra from PI-IMS analysis of soil containing unleaded gasoline. Concentrations (mg/kg) were (A) 16, (B) 1.6, (C) 0.16, and (D) 0 (soil blank).

sample size and rudimentary headspace apparatus, the limit of detection (LOD) was estimated as 0.18 mg/kg for unleaded gasoline and 1.8 mg/kg for diesel fuel as calculated using total concentrations. The LOD values for the fuel could be reduced further using a refined sampling inlet in which soil greater than 0.1 grams could be sampled with better efficiency than that used here. Nevertheless, response was linear for peak height versus concentrations with correlation coefficients of 0.94 and 0.95 for plots from 0 to 14 ppm for the two largest peaks in spectra in Figure 5. No interferences from soil alone were observed. Since the PI-IMS has ultra-high sensitivity (<0.1 ppb in air) for gaseous aromatic hydrocarbons, LOD values for fuels in soils will be governed by soil to head-space partitioning. This last point is also significant in terms of prior IMS research using chemical ionization sources. Results obtained here strongly support Hill's contentions that elimination of reactant ions (used in chemical ionization-IMS) with a PI source would simplify both IMS spectra and interpretations. Since conventional reactant ions would have drift times near those for benzene and toluene which are major indicators in spectra for unleaded gasoline, practical operation is made possible by advantages from creation of product ions using photons.

Reproducibility was measured with portions of six independently prepared samples of 5 mg/kg of unleaded gasoline in soil. While reproducibilities on peak heights were from 10 to 50% RSD, the variation included soil preparation, sampling of soils for analysis, and instrumental response; this represented more than PI-IMS reproducibility. Reproducibility of only the instrumental response for unleaded gasoline on 6 replicate spectra was 2 to 10% RSD which demonstrated that the majority of deviation was in the sample preparation and handling. During this study, decreases were observed in relative abundances for the first two components in the IMS spectra. This was preliminary evidence that weathering through volatilization of certain components in fuels may alter IMS signatures for various fuels. The reproducibility of peak heights for toluene alone was 5% RSD.

Effects of water on PI-IMS sensing

Effect of water concentration in soil on the response is shown in Figure 6 for unleaded gasoline in soil at several moisture levels. A

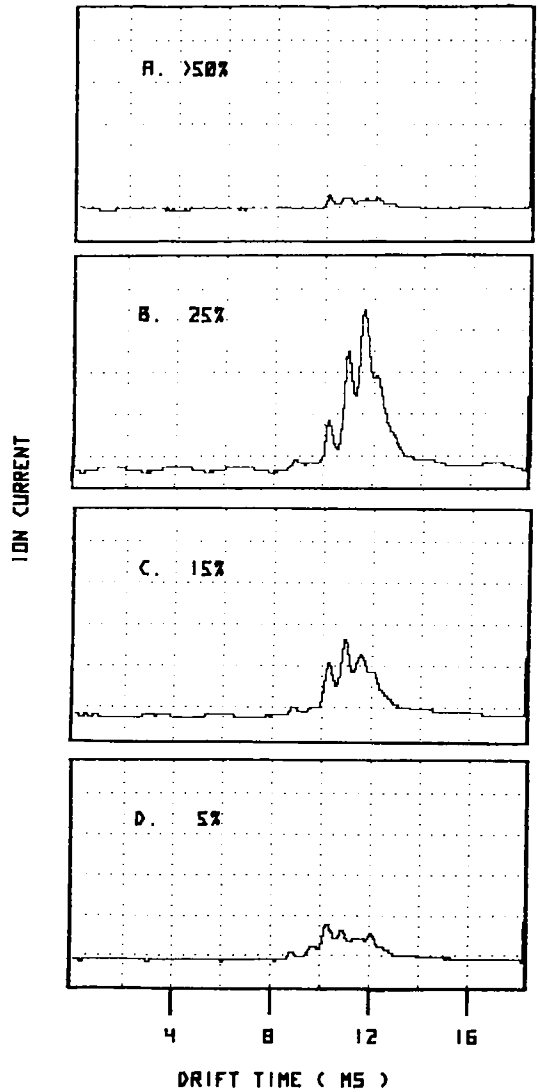

FIGURE 6 Mobility spectra from PI-IMS analysis of fuel contaminated soil at several moisture contents. The concentrations of diesel in soil was 2 mg/kg. The moisture content (by weight) was (A) >50%, (B) 25%, (C) 15%, and (D) 5%.

striking increase in response was observed with addition of slight to moderate amounts of water. However, complete deleterious response occurred when the soil was completely saturated. The trend from 7 to 25% moisture in soil was consistent with reports and predictions that increased water content will increase the rate of vaporization of organic compounds in soils[30] consistent with observed effects here. The formation of a mud with the sample resulted in poor performance perhaps due to physical restriction of solute transport from the soil to the vapor phase by a film of water over the soil. Otherwise, any sensitivity to moisture alone for PI-IMS sensing in soils near groundwater would be a serious limitation indeed. Effects from water vapor on PI-IMS response was determined by metering unleaded gasoline and water vapor into the PI-IMS drift gas. While water is known to promote formation of hydrated clusters for ions, peak heights and shapes in these spectra were insensitive to water content until extreme concentrations of water were used in the drift gas.

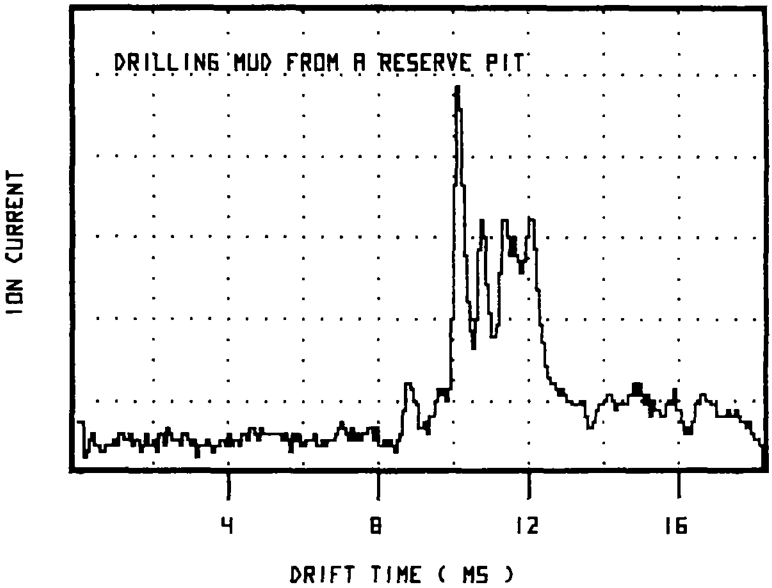

FIGURE 7 Mobility spectrum for PL-IMS analysis of drilling mud from a reserve pit.

Although the inlet on the PI-IMS must be redesigned for sensing of soils on a routine basis, an immediate practical application of PI-IMS on very wet soils/solids was made. Drilling muds from a reserve pit were obtained from a prior project[27] and were analyzed directly. These muds contained a complex hydrocarbon mixture and should have been saturated with water, yet PI-IMS response was rapid and spectra were sharp and distinct as shown in Figure 7. While this test was not a systematic investigation, no salient interferences were observed qualitatively on PI-IMS response. Effects from other industrial chemicals as interferents remain a concern and must be addressed in a rigorous testing schedule.

References

1. EPA Brocure; EPA/530-SW-85-009. Anonymous (1985).
2. Federal Register, Public Law 98-616, 98 STAT. 3276 to 3288.
3. I. P. Karlin, S. A. Leont'eva, E. P. Semkin, V. A. Kvasonava, V. N. Galyashin and N. M. Kuz'min, *Sh. Anal. Khim.* **16**(8), 245 (1984).
4. E. Matisova, J. Krupcik, P. Cellar and A. Kocan, *J. Chromatogr.* **346,** 177 (1985).
5. J. R. Cooper and L. T. Taylor, *Appl. Spectrosc.* **38**(3), 366 (1984).
6. L. Schou, A. Moerk and M. Bjoroey, *Org. Geochem.* **6,** 513 (1984).
7. W. Garncarz, *Gaz. Woda Tech. Sanit.* **58**(4), 95 (1984).
8. H. Binder and L. Weis, *Z. Wasser Abwasser Forsch.* **17**(1), 20 (1984).
9. J. K. Whelan, Volatile C1-C8 compounds in marine sediments, In: *Gas Chromatogr./Mass Spectrom. Appl. Microbiol.* (G. Odham, L. Larsson and P-A. Maardh, eds.) (Plenum Press, New York, NY, 1984), p. 381.
10. V. O. Polotnyuk, I. A. Revel'skii, S. A. Leont'eva and A. A. Grinberg, *Zh. Anal. Kim.* **39**(3), 529 (1984).
11. V. O. Polotnyuk, I. A. Revel'skii, A. A. Grinberg and S. A. Leont'eva, *Zh. Anal. Kim.* **40**(3), 511 (1985).
12. N. N. Sirotkina and M. N. Marunyak, *Pochvovedenie* **3,** 127 (1985).
13. P. Verner, *J. Chromatogr.* **300**(2), 249 (1984).
14. J. N. Davenport and E. R. Adlard, *J. Chromatogr.* **290,** 13 (1984).
15. T. B. Aliev, *Zh. Anal. Khim.* **39**(1), 71 (1984).
16. A. I. Clark, A. E. McIntyre, J. N. Lester, R. Perry, *Int. J. Environ. Anal. Chem.* **17**(3 4), 315 (1984).
17. J. B. Barsky, S. S. Q. Hee, C. S. Clark, *Am. Ind. Hyg. Assoc. J.* **46**(1), 9 (1985).
18. M. A. Baim, R. L. Eatherton, H. H. Hill, Jr., *Anal. Chem.* **55,** 1761 (1983).
19. F. W. Karasek, *Anal. Chem.* **43,** 1982 (1971).
20. T. W. Carr, ed., *Plasma Chromatography* (Plenum Press, New York, NY, 1984).
21. F. W. Karasek, *Research and Development,* **25,** 32 (1974).
22. J. P. Carrico, A. W. Davis, D. N. Campbell, J. E. Roehl, G. R. Sima, G. E. Spangler, K. N. Vora and R. J. White, *American Lab.* **18**(2), 152 (1986).

23. C. S. Leasure, M. E. Fleischer, G. K. Anderson and G. A. Eiceman, *Anal. Chem.* **58**, 2142 (1986).

24. C. S. Leasure, V. J. Vandiver, G. Rico and G. A. Eiceman, *Analytica Chimica Acta* **175**, 135 (1985).

25. V. J. Vandiver, C. S. Leasure and G. A. Eiceman, *Intern. J. of Mass Spectrom. and Ion Process* **66**, 223 (1985).

26. G. A. O'Connor, R. S. Bowman, M. A. Elrashidi and R. Keren, *Solute Retention and Mobility in New Mexico Soils. I. Characterization of Solute Retention Reactions* (New Mexico State University, Agricultural Experimental Station, Bulletin 701, April 1983).

27. G. A. Eiceman and K. Lindley, 1986, in preparation.

28. C. S. Leasure, Ph.D. Dissertation, *Photoionization and Related Chemical Processes in Ion Mobility Spectrometry*, New Mexico State University, April, 1986.

29. G. A. Eiceman and V. J. Vandiver, *Anal. Chem.* **58**, 2331 (1986).

30. W. A. Jury, W. F. Spencer and W. J. Farmer, *J. Environ. Quality*, **13**(4), 567 (1984).