Hydrocarbon Contaminated Soils and Groundwater

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Remediation

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11.3 The method detection limit calculated according to 40 CFR, Part 136, Appendix B was 0.5 μg/g gasoline for the methanol extraction of soils. The recommended Practical Quantitation Limit (PQL) is 5 μg/g.

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CHAPTER 9

A New Method for the Detection and Measurement of Aromatic Compounds in Water

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INTRODUCTION

In the introduction to his encyclopedic treatise, *Friedel-Crafts Alkylation Chemistry: A Century of Discovery*, Royston M. Roberts makes the statement, "Probably no other reaction has been of more practical value." Professor Roberts goes on to say, "Major processes for the production of high octane gasoline, synthetic rubber, plastics and synthetic detergents are applications of Friedel-Crafts chemistry."[1] It is fitting that, over a century after this monumental discovery, a technique for the analysis of environmental contamination caused by-products of this reaction has been developed which employs the same chemistry.

The analysis of organic compounds in aqueous solution has long been recognized as problematical for many reasons. Primary among them, of course, is the limited solubility of nonpolar compounds in such an extremely polar solvent. In a recent laboratory study undertaken for the American Petroleum Institute (API) on the solubilities of petroleum hydrocarbons in groundwater, it was pointed out that it was not possible to obtain linear response when trying to directly inject water standards of various aromatic hydrocarbons into a gas chromatograph.[2] This irreproducibility in analysis of water samples has been a source of consternation to proponents of gas chromatography for a long time. A fairly comprehensive review of the sort of problems associated with the gas chromatography of water samples is presented by Grob in Chapter 5 of *Identification and Analysis of Organic Pollutants in Water* in their argument for the use of capillary versus packed column GC. A statement from that reference is particularly appropriate, "Environmental chemistry includes probably the most extreme branch of analytical chemistry . . . environmental samples should be analyzed with means and methods to provide maximum separation efficiency and resolutions."[3]

Certainly chromatography of all types has proved to be a technique of "maximum separation efficiency and resolution." With the advent of capillary columns of thousands of theoretical plates of separation efficiency, the ability to resolve picogram quantities of substances is available. However, the problem of obtaining representative samples and their subsequent quantitative as well as qualitative analysis remains as perhaps the dominant problem in environmental assessment. Among the criteria involved in sampler design discussed by Johnson et al. in a recent article in *Ground Water* are those which would "prevent changes in the analyte concentration due to: (1) sorption or degradation in the well; (2) changes in temperature or pressure; (3) cross-contamination between monitoring wells due to the sampling equipment."[4]

Each of these criteria might also be applied not only to the collection of samples but to their analyses as well. In the subsequent laboratory analysis of a sample which may have been very well collected, preserved, and transported to the laboratory, each of the above factors plays an analogous role: (1) sorption or degradation in the sampling container and analytical transference device, e.g., syringe, pipet, or beaker; (2) changes in temperature or pressure (particularly applicable to the extreme pressure/temperature changes occurring in the syringe and then the GC itself); (3) cross-contamination of syringes, purge and trap devices, sample lines, injectors, columns, and detectors.

The problem of sorption of organics in sampling devices and in the passage of samples through analytical tubing was addressed in an article by Barcelona et al. in *Analytical Chemistry.*[5] In that discussion, the sorption of various organic liquids in different organic materials is well documented. This problem is seemingly one of a particularly Sisyphean nature; i.e., the containment of a substance within a like substance is akin to rolling a stone up a hill only to have it immediately fall down the other side. Certainly the problems encountered by the industry in attempting to contain petroleum products in unlined fiberglass tanks attest to this dilemma. The development of permeation tube calibration systems is based on the phenomenon.[6]

The present method addresses all of the problems mentioned in that, put most succinctly, it combines immediacy and simplicity of analysis. That is, it is easily transportable to the field, which eliminates problems of sample transfer and storage, and it provides an immediate analysis of a large volume of sample that speaks generally to the problem of representativeness.

THE EXTRACTION/COLORIMETRIC TECHNIQUE FOR AROMATICS

The Hanby Field Test Method for aromatics in water, described here, comes in the form of a kit complete with necessary reagents and apparatus to perform immediate analyses at the groundwater well site. It is contained in a rugged plastic case with enough reagents to perform 30 field analyses. Within the case are contained: a 500 mL separatory funnel, a tripod ring stand, a 10 mL graduated cylinder, 2 reagent (liquid) bottles, one desiccant jar with 30 reagent (powder) vials, a color chart depicting test results for 11 typical aromatics, plastic safety glasses, and 12 pairs of gloves. Upon arrival at the site, the kit is opened and the tripod ring stand is assembled. A 500 mL water sample is introduced into the separatory funnel, which is placed in the ring stand. Next, 5 mL of the extraction reagent is poured into the separatory funnel using the 10 mL graduated cylinder. The sample is vigorously extracted for two minutes with occasional release of the slight pressure buildup which occurs. The funnel is placed back in the ring stand and the extraction phase is allowed to separate to the bottom for five minutes. After phase separation is complete, the lower extraction layer is drained into a test tube, allowing a small amount of the extraction solvent to remain in the separatory funnel. Then one of the reagent vials is opened and the contents immediately poured into the test tube. The tube is shaken for two minutes, allowing the catalyst to be dispersed well throughout the extraction reagent so that color development, which is concentrated in the powder, will be uniform. Hue and intensity of the color of the catalyst which has settled in the tube is now compared to the standard aromatics pictured in the color chart.

The wide range of intense colors produced in Friedel-Crafts reactions has been observed since the discovery of this reaction. A brief description of the chemistry of the reaction, as well as the color involved, is given by Shriner et al. in their widely used book.[7] In this novel adaptation of Friedel-Crafts alkylation chemistry, one of the reactants, the alkyl halide, is used as the extractant. The alkyl halide extractant plus the aromatic compound present in the water sample are caused to form electrophilic aromatic substitution products by the Lewis acid catalyst which is added in great enough amount to also act as the necessary dehydrant to allow the Friedel-Crafts reaction to proceed. These products are generally very large molecules; i.e., phenyl groups clustered around the alkyl moiety, which have a high degree of electron delocalization. These two factors are the principal reasons for the extreme sensitivity of this procedure; that is, large molecules are produced which are very intensely colored.

In the field conditions where this procedure is by and large carried out, the reaction is exposed to sunlight. This means that there will be a "window" in which to observe the color that is produced. This is due to the general instability of the reaction products to photochemical oxidation. Strong sunlight will cause most of the colors produced to fade to various shades of brown within just a minute or two; therefore, it is advisable to perform the test in a shaded area.

PURGE AND TRAP GC COMPARISON STUDIES

Comparison of the Field Test Kit method versus analyses performed with a purge and trap GC were made using standard solutions of benzene, toluene, ethyl benzene, and o-xylene (BTEX). The purge and trap/GC used for this study was a Tekmar LSC-3 and a Hewlett-Packard 5890, Supelcowax widebore capillary 60 meter column, programmed from 45°C (for 3 min.) to 120°C at 8°C/min. A 5 mL aliquot of the standard concentrations: 0.2, 1.0, and 10.0 ppm was injected into the purge vessel of the Tekmar. The sample was purged with helium for 10 minutes and desorbed for 4 minutes at 180°C. Purge flow was 20 mL/min helium. Two separate preparations of the BTEX standards were analyzed by the Field Test Kit and by purge and trap GC. Peak areas were compared for all chromatograms, and these results were normalized with regard to the theoretical response ratio of 0.2, 1.0, and 10.0. This simple average error calculation showed a typical purge and trap GC variation in analysis of ±9.1%.

The results of the Field Test Kit method, judging by comparison to the color chart are, of course, somewhat subjective. Rigorous evaluation of color intensities are being conducted using exact quantities of reagent and further UV/VIS spectrophotometric reflectance readings. These studies are being continued on a Varian DMS 300 as well as on a Cary 2200 UV/VIS/NIR spectrophotometer.

The slide of ethyl benzene analyses performed with the Field Test Kit method at 0.02, 0.1, 0.2, 0.3, 0.4, and 1.0 ppm, and scanned with the DMS 300, are indicative of the visual accuracy obtainable with the kit. The largest contributing factor in the variation of these results is the imprecision in amount of catalyst addition (±20%).

APPLICATIONS OF THE METHOD

Obviously, this method will have a wide variety of applications in field investigations. In fact, utilization of the Hanby Field Test by an environmental testing company has been going on since August 1987. Site investigations of hazardous waste-containing landfills and underground storage tank leaks have been conducted in several states thus far, and use of the kit has greatly facilitated sampling site locations. The first field use of the kit was in the establishment of groundwater monitoring well locations at an organic chemical processing unit. An article describing this first field use of the method is in preparation.

Recent regulations for the monitoring of underground storage tanks require that soil/groundwater investigations be carried out regularly to ensure that no leakage has occurred. It is clear that the use of this technique, which is easily learned and can be performed at an extremely low cost, will provide an immediate and definitive answer to these requirements.

OHIO RIVER STUDY

In the evening of January 2nd, 1988, the collapse of a tank containing approximately 3.5 million gallons of diesel fuel precipitated one of the worst inland oil spills in the country's history. Approximately one million gallons of the oil washed in a huge wave over the containing dikes around the tanks at the Ashland Oil plant at West Elizabeth, Pennsylvania and into the Monongahela River.

Monday morning, two days after the spill, I contacted Mike Burns of the Western Pennsylvania Water Company in regard to using the Hanby Field Test Kit at the company's water treatment facility on the Monongahela, south of Pittsburgh. Mike asked me to bring one of the kits to the plant. The next day I arrived in Pittsburgh and was met by Mike at the West Penn Water Works Treatment facility, where I demonstrated the use of the kit for the personnel at the plant. Mike suggested I call John Potter, the chief chemist at the Water Treatment Plant in Wheeling, West Virginia, which was the next major facility taking water from the Ohio river. John said the kit sounded like it would fill a real need for a rapid analysis of the river water at the plant's intakes. The next day, Wednesday, I was demonstrating use of the kit to the personnel at Wheeling. It was immediately put into use on an around-the-clock basis when they realized that in just a few minutes they could get visual indication down to 100 ppb of the diesel aromatic components.

The next morning I met with the West Virginia Department of Natural Resources personnel who were in Wheeling to monitor the oil spill. That afternoon I was invited by the office of the Environmental Protection Agency (EPA) in Wheeling to join EPA chemist Bob Donaghy, West Virginia Department of Natural Resources Inspectors Sam Perris and Brad Swiger, and the Ohio River Valley Water Sanitation Commission Coordinator of Field Operations, Jerry Schulte, on the river tugboat Debbie Sue to make a run up the Ohio River from Wheeling to try to locate the front of the spill.

The investigators met at the Debbie Sue at noon where it was tied up at the docks on the south side of Wheeling. A light snowfall had begun and the temperature was around 10°F as the boat pulled out into the Ohio, headed up stream.

Due to the fluctuating voltage from the tug's generator, the fluorometer readings exhibited a fairly wide swing during the ensuing measurements. As for the measurements performed with the Field Test Kit, I was primarily concerned with the sensitivity of the test in relationship to the near-zero temperature of the water. Reference to the API study of solubilities of petroleum hydrocarbon components in groundwater had indicated rather large decreases in partitioning of these components into water at lower temperatures.

There was no time, however, to spend worrying about these matters of close quantitation. The boat was soon into the channel and Jerry Schulte was bringing aboard the first bailer of water. On the first sample taken, just minutes after leaving the dock, an obviously detectable coloration was seen in the catalyst material of the Field Test. Reference to the color chart indicated presence of aromatic constituents at something less than 0.5 ppm diesel. Having no reference colors or data at these temperatures I arbitrarily chose this intensity to represent 0.1 ppm. The fluorometer was bouncing between zero and four on its movable dial indicator. (It was an old Turner model arbitrarily numbered from 0 to 100.)

We continued approximately 18 miles up the Ohio, taking samples from the surface and the bottom on the West Virginia side, mid-channel, and the Ohio side. As Table 9.1 indicates, the results from the EPA fluorometer and the Hanby Field Test Kit tracked each other fairly consistently at each point.

Table 9.1. Ohio River Sampling for Diesel Oil (January 7, 1988)

Ohio River Mile Point	Fluorometer Reading	Hanby Field Test (ppm)
89.0	4	0.10
85.5	8	0.15
85.5	9	0.15
85.5	6	0.20
85.0	8	0.20
85.0	11	0.20
84.5	6	0.20
84.5	10–15	0.50
84.5	10	0.20
82.0	20	1.00
81.0	25	1.00
80.0	30	1.50
79.0	33	2.50
77.0	57	10.00
76.0	43	8.00
75.0	35	7.00
74.0	48	5.00
70.0	29	3.00

VALDEZ OIL SPILL

At 12:04 A.M., March 24, 1989, the oil tanker *Exxon Valdez* ran onto Bligh Reef in Prince William Sound. Of the 1.26 million barrels of Prudhoe Bay crude oil the ship was carrying, approximately 10.1 million gallons immediately poured out of the ruptured tanks into the clear blue water of the sound. Of the series of unfortunate circumstances involved in this event, such as the unpreparedness of crew, port, and pipeline officials to immediately begin containment efforts, perhaps none was more critical than the imminent release of hundreds of millions of salmon fry which had been hatched and raised in the half dozen fish hatcheries in and around Prince William Sound.

On Monday, March 27, I contacted the Alaska Department of Environmental Conservation in regard to use of the test kit for onsite monitoring of aromatic contamination of the water caused by the crude oil. Prior analyses of Prudhoe Bay crude had revealed that in comparison to other sources of oil it was particularly high in aromatic content (25%), with the majority components of this fraction being naphthalenes (9.9%), phenanthrenes (3.1%), and pyrenes (1.5%). [Information supplied by the Alaska Department of Environmental Conservation (DEC).] David Kanuth of the Alaska DEC had obtained one of the test kits in January and had subsequently used it at a smaller oil release several weeks later. It was decided that the kit would be helpful at the Valdez incident and commissioner Dennis Kelso requested that I take a kit to three of the hatcheries which would probably be most impacted by the spill. On Thursday, March 30, at 8:30 A.M. Dick Fanell of the DEC, Mark Kuwada of the Alaska Fish and Game Department, and I took off in a pontoon-equipped Cessna 206 piloted by Ken Lobe, and flew SSW from the Valdez harbor to the three fish hatcheries we were scheduled to visit. Within minutes of being airborne we were able to see the huge fingers of oil spreading southerly from the area where the tanker was still impaled on the reef. Thirty minutes later our plane landed in the bay at the first hatchery, Esther.

After demonstrating the use of the test kit to the hatchery manager, two samples were obtained from the water near the fish pens. These samples were analyzed with the test kit, and the indications using the color chart results for gasoline as a guide were 0.2 ppm and 1.5 ppm. These results were unexpected, as no visible oil was apparent from the air as our plane flew in to the hatchery.

The next hatchery visited was the Main Bay Hatchery. A test kit was also left there following demonstration of its usage. One sample was taken near the fish pens, which indicated a concentration of 0.5 ppm aromatics.

The third landing was made in the water of the Port San Juan hatchery. Two samples were taken, indicating concentrations of 0.5 and 0.6 ppm.

The following day a return to Houston was made in order to prepare a comprehensive series of standards from 125 ppb to 20 ppm of the Prudhoe Bay crude in seawater. It was necessary for this work to be performed at the Houston laboratory because a large assortment of glassware and appropriate reagents were required to simultaneously prepare the 11 different standards that were utilized in the study.

The procedure for the 11 concentrations employed called for first preparing a solution of the Prudhoe Bay crude in hexane (5:100), then making a 100:1 dilution of the hexane stock in acetone. This resulted in a 500 ppm stock, which was then used to prepare 500 mL standards of: Blk, 125, 250, 500, 750, 1000, 2000, 3000, 4000, 5000, 10000, and 20000 ppb. When the 500 mL standards were prepared (in Galveston Bay saltwater), each was extracted according to the test kit method with 5 mL extractant reagent for two minutes. After all extractions had been performed and 3 mL amounts of the extractant had been collected in 16×100 mL test tubes, the color development catalyst was added and the tubes were shaken for two minutes in a darkened room. Upon completion, each tube was placed in a rack previously prepared and labeled, then the rack containing the 12 tubes was taken into a sunlit room for the photographs (f16 at 125th sec). This whole procedure was repeated twice more, as a quality control measure.

A remarkable difference in hue is observed as the concentration of the crude oil in the water increases. At approximately 1 ppm the blue colors of the polynuclear aromatics begin to neutralize the more orange colors of the single ring aromatics. This effect is particularly noticeable in the extractant (liquid) phase of the test tube, so that the liquid actually appears colorless above the gray color of the catalyst. In the photographs taken with the liquid phase masked, an evenly progressive increase in intensity of color or saturation is evidenced.

Enlarged copies of these photographs were sent to the various entities utilizing the Field Test Kit, including the Alaska Department of Environmental Conservation, the Department of Fish and Wildlife, and eight of the fish hatcheries themselves. Due to the extent of the spread of the oil and its contamination of the surrounding shoreline it must be assumed that the partitioning of these aromatic components into this prolific marine area will continue for quite a long period.

UV/VIS SPECTROPHOTOMETER STUDIES

Determinations of principal wavelengths and reflectance data were made in correspondence with aromatic compounds depicted on the color chart. These investigations were conducted by preparing a range of concentrations of selected aromatic compounds, performing the Hanby extraction/colorimetric procedure and then immediately measuring the reflectance of the catalyst.

METHOD

Ten parts-per-million (vol/vol) solutions of benzene, toluene, o-xylene, special unleaded gasoline, naphthalene, and diesel were prepared by injecting 20 mL amounts of each compound into 2.0 L of deionized water at 20°C to 21°C and stirring for one hour. Dilutions from the stock solutions were prepared to 0.01, 0.02, 1.0, and 5.0 ppm. The extraction/colorimetric procedure employed with the Field Test Kit was modified to fit the requirements of the UV/VIS reflectance apparatus. Four microliters of the extraction reagent were used to extract the water samples for two minutes. The extraction solvent was then drained into a cuvette. Two grams of the catalyst material was added to the cuvette, which was covered with its Teflon® cap, and the mixture was shaken vigorously for three minutes. The cuvette was placed in the spectrophotometer and scanned over a range of 350 nm to 600 nm.

INSTRUMENTAL PARAMETERS

For this study a Varian DMS 300 UV/VIS spectrophotometer was utilized. Instrument settings were: slit width 2 nm, tungsten source, scan rate 50 nm/min. All of the scans were corrected to 100% transmittance baseline using a blank sample which was scanned in reference to a barium sulphate reflectance disk. The sample compartment was fitted with a diffuse reflectance accessory which was modified by blocking out the top portion of the light path so that only the catalyst in the bottom half of the cuvette would be scanned.

DISCUSSION

Figures 9.1 through 9.3 show the spectrograms for each of the three substances scanned. The concentration for each of the plots is as follows (ppm by volume): A=0.1, B=0.2, C=1.0, D=5.0, E=10.0. These concentrations exhibit well defined differences in the traces of their reflectance curves for each of the substances.

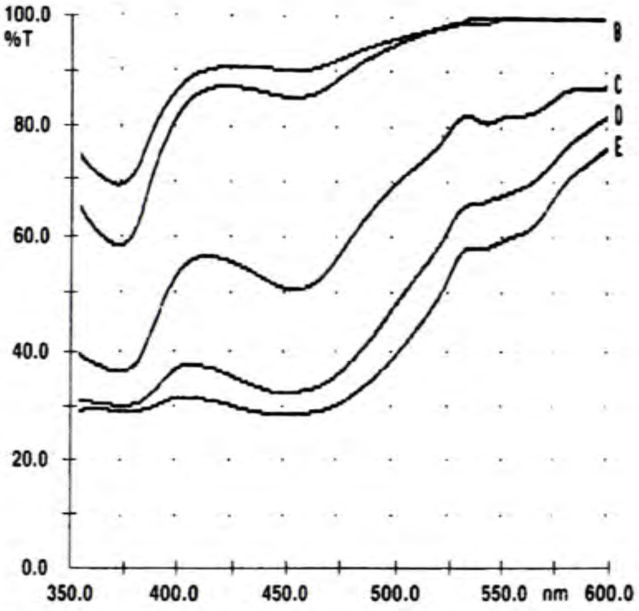

Figure 9.1. Spectrogram for benzene.

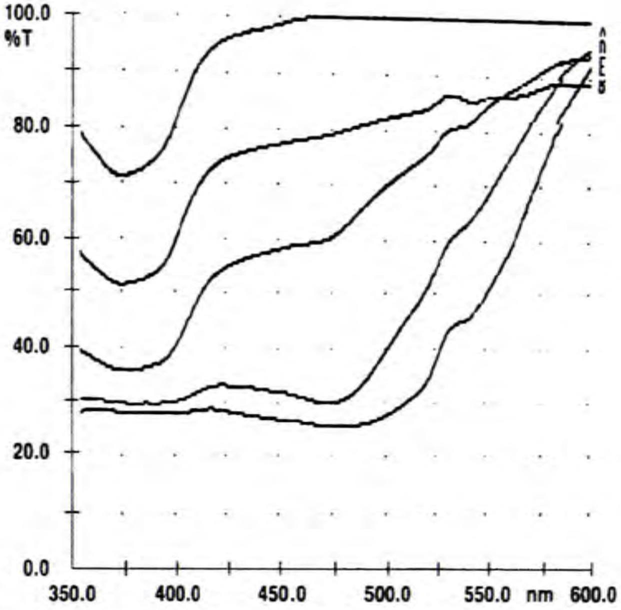

Figure 9.2. Spectrogram for toluene.

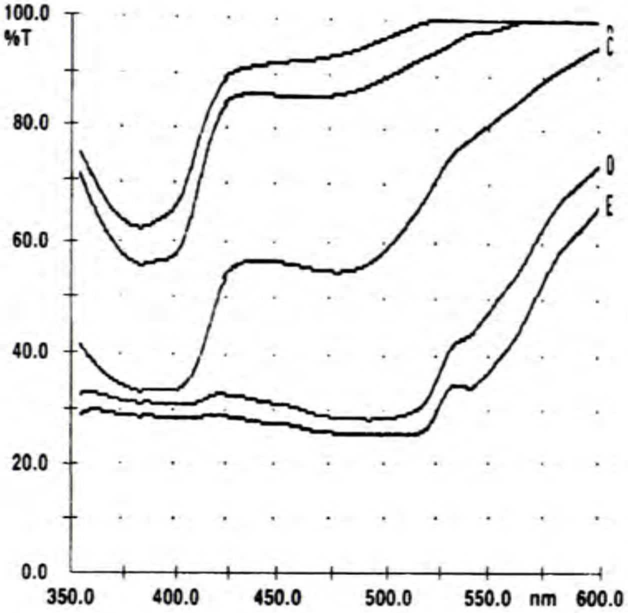

Figure 9.3. Spectrogram for o-xylene.

Figure 9.4 shows the reflectance trace for different concentrations of benzene. These concentrations are (ppm by volume): A=0.01, B=0.05, C=0.25, D=1.0. These runs were scanned on the spectrophotometer from 250 nm to 700 nm at different instrument settings: slit width=1.0 nm, scan rate=20 nm/min, smoothing constant=5 (sec). The different instrument parameters, plus the fact that a special cuvette was constructed to cover a larger area of the reflectance opening, contributed to the greatly enhanced differences in the traces at these, even lower, concentrations.

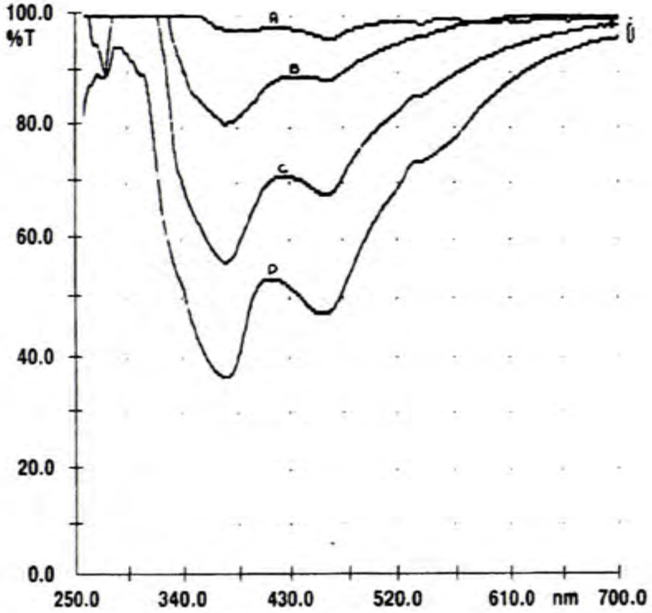

Figure 9.4. Reflectance trace for different concentrations of benzene.

Additional studies have been undertaken to determine the relationship of color intensity with concentration. These studies were performed using a hand-held colorimeter that measured the reflectance of the Field Test Kit color development reagent at 10 nanometer increments from 400 to 600 nm. The plot of these measurements (Figure 9.5) demonstrates the expected log relationship of concentration to reflectance—which can be closely correlated with transmittance. The regular test procedure employing 100 grams of soil was utilized. Gasoline (Exxon Plus Unleaded) was added to the soil to give concentrations as follows (mg/kg): 0, 10, 25, 50, 75, 100, 150, 200, and 400. The three plots in this figure are the reflectances measured at 430, 450 and 470 nm (1, 2, 3).

In conjunction with these analyses using the Field Test Kit, spiked soil samples were prepared for purge and trap GC/FID analyses. In this procedure approximately 10 g aliquots of clean soil were weighed into 40 mL VOC vials. Appropriate

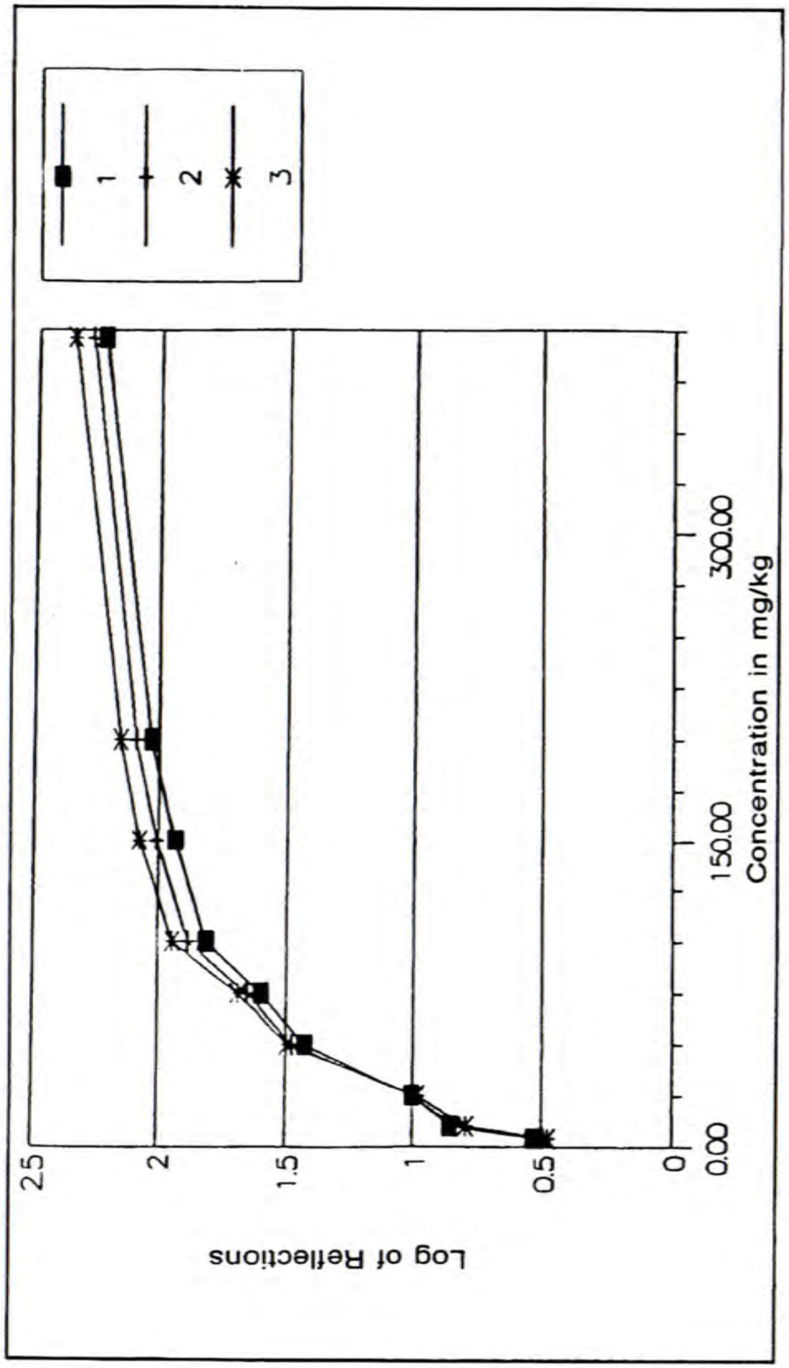

Figure 9.5. Reflectance of the Field Test Kit color development reagent.

additions of gasoline-spiked water was added to the vials to give the same concentrations as used in the Field Test Kit study. Figure 9.6 shows the results of the plot of spiked concentrations vs the recovered concentrations with the P&T/GC/FID analyses. In this instance, again, we see an exponential decline; however, here we are seeing a phenomenon of detector saturation as opposed to the $\log_{10}P_o/P$ (P_o=incident radiant energy, P=transmitted energy) plot of the test kit method.

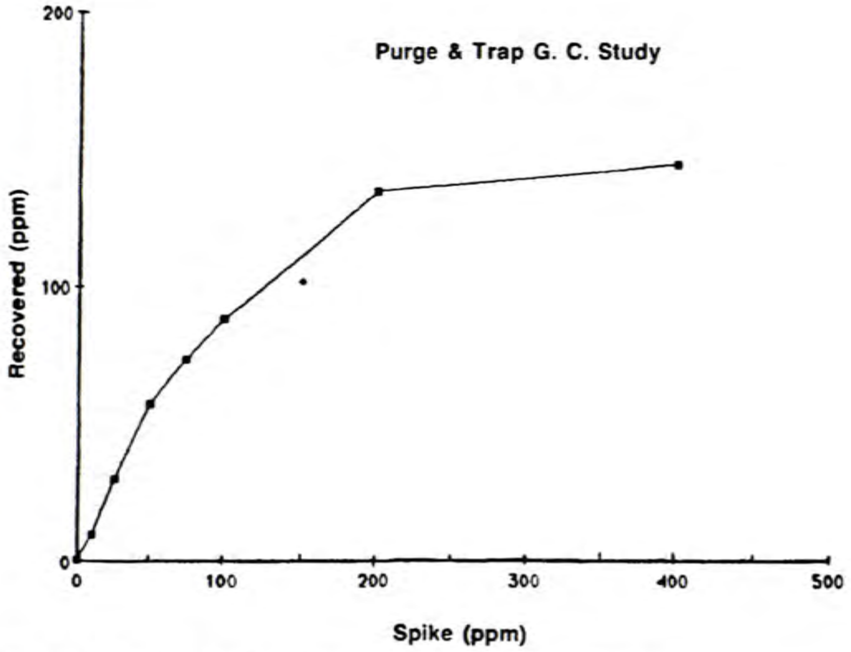

Figure 9.6. Plot of spiked concentrations vs recovered concentrations.

APPLICATIONS OF THE METHOD

In the two years since the introduction of the kit it has seen a wide variety of applications. Most prominently, perhaps, has been the utilization of this method in testing soil at underground storage tank removal and remediation sites. The ability to perform accurate, onsite evaluations of the level of fuel contamination in soil has provided contractors a low-cost and reliable means of exhaustively checking a large number of samples to ensure that soil removal operations have proceeded to a point well below maximum allowable levels.

Prior to the advent of this extraction/colorimetric technique, onsite soil analyses had been almost exclusively vapor or headspace methods. Several factors intrinsic to these methods can be seen as playing a fairly large role in their accuracy.

Probably most important among them are: the age of contamination, fuel type, and soil type. All three of these factors relate to the volatility of the analyte. Old gasoline spills, for instance, generally show a loss of the more volatile components. The range of volatility from gasolines through kerosene, diesel, and the heavier fuel oils; e.g., #5, #6, is very wide and the different soil types from loose, dry sands to moist, compact clays have, of course, an extremely deterministic effect on analyses that depend on vapor permeation.

Two approaches to soil analyses have been developed for the test kit. The first is a direct extraction method in which, typically, a 10 g soil sample is washed in a 20 mL amount of the alkyl halide extractant solvent. Essentially quantitative extraction of petroleum hydrocarbons in soil is achieved in three or four minutes of washing the sample. An aliquot (4.2 mL) of this extractant is then transferred to a test tube for catalyst addition and color development. This procedure takes about 10 minutes and has proved to be very effective for old fuel spills in which the more volatile components have essentially disappeared. This method has also been shown to be extremely sensitive in heavier fuel oil situations because of the presence of significant amounts of PNAs in these fuel types.

The second approach to soil analysis employed with the test kit is an analog to the EP toxicity or TCLP procedures in that an aqueous wash is first utilized to partition the petroleum hydrocarbon from the soil, simulating groundwater seepage effects. In this method, typically, a 100 g sample is washed in 500 mL of water containing 65 g of an inorganic salt flocculant mixture. The washing is carried out intermittently over a 30 minute period, then the wash water is extracted in the separatory funnel in the same fashion as the previously discussed water method. This method is appropriate for fresh solvent and gasoline situations, particularly where groundwater contamination is a dominant concern, but its applicability lessens considerably in instances where a less water-soluble fuel type is concerned or, again, with aged contamination sites.

CONCLUSIONS

The development of a field method for the analysis of organic contaminants at sub-part-per-million levels in water has proved to be a valuable tool in the establishment and the sampling of groundwater monitoring wells. The accuracy of the method has proved to far exceed that of direct injection gas chromatography. A rapid soil-wash method has also been developed employing the Hanby Field Test Kit technique which has proved to be effective on top and deep soils over a range of 5 mg/kg to 10,000 mg/kg gasoline in soil. Development of instrumental spectrophotometric techniques will allow even greater sensitivity and qualitative analysis of aromatic contaminants in soil and groundwater.

A variation of the procedure involving the extraction of a sample with an aromatic solvent and then addition of the Lewis acid catalyst allows for the determination of the presence of alkyl halides; e.g., trichloroethylene. In this

version of the test, a reflectance adapter for the spectrophotometer is not necessary since the color is not concentrated in the catalyst but is developed in the extractant solvent.

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