

**FIELD SCREENING FOR BTEX IN SOILS,  
USING ULTRA-VIOLET DERIVATIVE SPECTROSCOPY\***

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**ABSTRACT**

A new instrument has been developed which screens a contaminated soil sample for benzene, toluene, ethylbenzene and xylenes (BTEX) in ten minutes. Using the technology of ultra-violet absorption derivative spectroscopy, the instrument analyzes the volatile organics purged from a heated, ten gram soil sample. The unique molecular absorption bands of each aromatic hydrocarbon are sensed, digitized and compared to calibration spectra in a laptop computer, which controls the instrument. The range of operation is 5 to 500 ppm by weight BTEX. Field results indicate excellent correlation with BTEX analysis using the EPA Purge and Trap gas chromatography procedure. The instrument is rugged and operates from a van or trailer using generator power.

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### I. INTRODUCTION TO THE PROBLEM

Benzene and the other aromatic hydrocarbons are the most hazardous to human health of the petroleum hydrocarbon constituents. For this reason, benzene, toluene, ethylbenzene and xylenes (BTEX) are monitored in soils around leaking underground storage tanks.

Many state environmental regulations require the amount of BTEX in soils to be less than some regulated value. In Texas, this value is 30 ppm by weight. Contaminated soil above this level must be removed or treated so that ground water contamination is avoided.

The most accurate soil analysis procedure is the EPA 8020 method using solvent extraction and purge and trap gas chromatography with photoionization detection. However, this procedure is costly and time consuming. On-site screening is helpful in knowing when contaminated soil is encountered or determining when clean soil has been reached during an excavation removal process. On-site screening techniques vary from smelling the soil sample to employing an on-site lab with gas chromatography/mass spectroscopy capability.

In order for an on-site screening method to be useful, it should meet the following criteria:

1. Total analysis time per sample must be short, i.e. less than 15 minutes
2. The extraction of volatile organics from the soil must be reasonably constant for different lithologic soils or correction factors must be known.
3. The detection principle must be specific to BTEX or, if there exists interferences from other components of hydrocarbon fuels, the interference must be constant and known.

Ultra-violet derivative spectroscopy and thermal soil desorption meet these objectives. Together they form a rapid, accurate means to screen soils for BTEX and even heavier aromatics, such as naphthalene.

## II. DERIVATIVE SPECTROSCOPY

### A. Absorption Spectroscopy

Most applications of derivative spectroscopy use the technique in the absorption mode. When radiation, either visible, infrared or ultra violet wavelengths, passes through an absorbing gas, the amount of light reaching a detector,  $I$ , is a function of the amount of light, before absorption,  $I_0$ , the absorption strength of the gas,  $K$ , the concentration,  $C$ , and the path length,  $L$ , the radiation traverses through the compound. In most applications, the relationship follows "Beer's Law".

$$I = I_0 e^{-KCL}$$

The absorption coefficient  $K$ , is a function of wavelength, being large at those wavelengths which greatly absorb and zero at wavelengths where the compound is transparent and does not absorb any of the incident light.

The absorption coefficient is a property, unique to each molecule. Thus a graph of absorption coefficient versus wavelength provides a unique pattern of highs and lows that can serve as a "fingerprint" of that specific molecule. Whenever radiation is passed through a cell containing that specific molecule and the light intensity reaching a detector is plotted against wavelength, the same pattern is produced. This radiation intensity plot versus wavelength is known as an "absorption spectrum" for that specific molecule. The first derivative with respect to wavelength of this intensity spectrum plots the "slope" of intensity versus wavelength. The second derivative of intensity with respect to wavelength plots "curvature" of intensity versus wavelength. The second derivative spectrum is very similar to the absorption coefficient plot versus wavelength, that is, the peaks occur where the coefficient,  $K$ , is large. It can be shown that the height of the second derivative peaks are linear with concentration, when absorption follows Beer's Law.

A derivative spectrometer can provide the first or second derivatives of intensity versus wavelength. Some instruments mathematically produce the derivatives; other produce the derivatives optically.

### B. History of Derivative Spectroscopy

The basic values of derivative spectroscopy were first noted in the literature in 1956, when Collier and Singleton published results of taking time derivatives of the output of a scanning infrared spectrometer. (1) The second derivative with respect to time was directly related to wavelength due to the constant scanning motion of the spectrometer. They discovered a means to see much more information hidden in the normal intensity versus

wavelength spectrum. Specifically, impurities in commercial cresol were dramatically detectable in the derivative spectrum yet invisible in the normal absorption. This quality of derivative spectroscopy was documented in detail twenty years later by O'Haver and Green, at the University of Maryland, in their numerical error analysis for the zeroth, first and second derivatives used for quantitative analysis of mixtures. (2)

In 1970, Williams and Hager published results of three years of research at the University of Florida into wavelength modulated derivative spectroscopy. (3) The technique resulted in a direct derivative output signal which greatly increased signal-to-noise ratio over electronic differentiation. By modulating the wavelength of radiation exiting a spectrometer, the detector output signal was processed to extract a close approximation of the true derivatives with respect to wavelength. Hager and Anderson published the theory of this form of derivative spectrometer (4) which was patented by Williams and the University of Florida.

Under a licensing agreement with the University of Florida, Spectrometrics of Florida and then Lear Siegler, Inc. developed and sold a variety of instruments to measure trace gases in complex mixtures. (5) This quality of derivative spectroscopy to extract a very low information signal from a noisy radiation detector output was investigated by O'Haver and Begley and published in 1981. (6) They found the derivative signals, in general, to achieve much greater signal-to-noise ratios than the zeroth order (direct intensity) signal and that noise decreased with higher order derivatives. However, for most applications, the signal also decreases with higher order derivatives and, in most cases, the second derivative offers the maximum signal-to-noise ratio.

Applications of derivative spectroscopy accelerated during the 1970s. Lear Siegler provided an EPA approved sulfur dioxide analyzer for measuring ambient air and marketed an in-stack analyzer world-wide for the continuous measurement of sulfur dioxide and nitric oxide in stack emissions. (7) Jones, with Gulf Research and Development Corporation, reported on the use of derivative spectroscopy to monitor drilling mud continuously, at the well-site. Trace benzene and toluene were detected to indicate the proximity to an oil producing zone. (8) A Lear Siegler SM400 laboratory gas analyzer was purchased by Oak Ridge National Laboratory and modified to provide real-time vapor monitoring of benzene, cresol, phenol, naphthalene and toluene in a coal-conversion process to sub part-per-million concentrations. (9) Houpt and Baalhuis, in the Netherlands, reported on the use of a second derivative spectrometer as a gas chromatograph detector, detecting benzene to five nanograms in a seven milliliter optical cell cuvette. (10)

### III. THE B-TEX 9000

#### A. General Description

The B-TEX 9000 Analyzer utilizes the technology patented by the University of Florida and was developed and is manufactured under an exclusive licensing agreement with the University of Florida, by Exploration Technologies, Inc.

A ten gram soil sample is placed in a glass vial and heated for five minutes at a temperature of 250 degrees centigrade. Evolved gases are then swept into the instrument for analysis.

Ultra-violet radiation from a deuterium lamp is dispersed by a monochromator and the dispersed radiation passes through the volatilized gases within the 900 cc sample cell and impinge upon a photomultiplier tube. The electrical signal from the photomultiplier is processed to provide a voltage proportional to the second derivative of intensity with respect to wavelength. This second derivative signal is a function of the absorbing gases in the cell and their concentrations.

The wavelength of radiation passing through the sample cell is controlled by a stepper motor that positions the monochromator grating. Furthermore, the wavelength is modulated about this center wavelength by oscillating the entrance slit of the monochromator. Wavelength modulation allows for the extraction of the second derivative from the detector. The second derivative voltage is digitized and sent to a microcomputer. Here, the signal is recorded and stored in the form of a spectrum or a digitized plot of measurement versus wavelength.

During operation, the computer controls the stepper motor and thus the wavelength. Through a computer program, a selected range of ultra-violet wavelengths is scanned while the computer stores the measurement data. After the scan, that spectrum is analyzed by the computer and compared with similar spectra of specific compounds at known concentrations. These calculated values are displayed in parts per million, by weight, in a ten gram soil sample. Figure 1 is a photograph of the B-TEX 9000 system, including optics, electronics and computer. Figure 2 is a photograph of the thermal desorber and a sample vial of soil.

#### B. Derivative Spectra of BTEX

The aromatic hydrocarbons exhibit unique absorption spectra in the ultra-violet from 240 to 290 nanometers (nm). The sharp, strong absorption bands are due to the molecular state changes of the benzene ring structure, common to all aromatics as they absorb ultra-violet radiation of discrete wavelengths.

Figure 3 shows the second derivative spectra of benzene, toluene, a xylene mix and naphthalene. Each spectrum is unique, with the absorption bands shifting to longer wavelength for the heavier molecules.

Figure 4 shows four spectra from soil containing four benzene concentrations of benzene at 4, 8, 16 and 24 ppm by weight. The peak heights grow linearly with increasing concentration of benzene.

The computer contains similar calibration spectra for each aromatic analyzed. When an unknown mixture of BTEX is introduced into the sample cell and a spectrum recorded, the computer does a least squares fit of the calibration spectra to best reproduce the unknown spectrum. The computer then displays the calculated concentrations of benzene, toluene plus ethylbenzene, xylenes and naphthalene in under five seconds.

### C. Performance Characteristics

#### Detection Limits

The detection limits vary for different compounds, being primarily set by the strength of absorption and the shape of the absorption bands. The property sensed is the second derivative of intensity with respect to wavelength (the curvature of the intensity distribution).

A method of partial least squares is calculated by the computer to separate a complex, multiple compound spectrum into its fundamental components. This process then creates a similar complex spectrum made up of calculated concentrations of single compound library spectra. The variation or residual between the unknown complex spectrum and the computer derived spectrum is displayed as a "prediction error". A perfect match between a computer generated spectrum and the sample spectrum will give a zero prediction error but there is always some positive value due to noise. An indication of the accuracy of a complex determination is available through this prediction error value.

Detection limits at a signal to noise ratio of 2:1 are given below for selected aromatic hydrocarbons:

COMPOUND	PPM (WT)	COMPOUND	PPM(WT)
Benzene	1.0	Xylenes	2.0
Toluene	2.0	Naphthalene	0.5
Ethylbenzene	2.0		

## Accuracy and Precision

Accuracy depends upon calibration spectra that comprise the library. The aromatic hydrocarbons are calibrated by injecting small (microliter) quantities of the diluted compounds into a moist sand and then thermally desorbing using a standard procedure. The spectrum is then recorded. Accuracy of plus or minus 10% is readily achievable.

Precision of replicate spectra is better than 95% when concentration signals exceed instrument noise by 10:1. Precision decreases as the signal approaches the detection limit for a given compound.

Figure 5 is a plot of sixteen soil samples spiked with various amounts of total BTEX and then analyzed by the B-TEX 9000.

### D. Other Information

#### Weight of Sample Required

A soil sample of ten grams was selected to achieve a useful total BTEX concentration range of from 5 to 500 parts per million by weight. For more contaminated samples, the weight is reduced to one gram.

#### Instrument Physical Description

The BTEX Analyzer consists of four packages: The thermal desorption/injection unit, the optics package (which contains the sample cell) the electronics chassis and a computer.

The thermal desorption/injection unit has dimensions of 8" x 10" x 12" and weighs 10 pounds. The optics package weighs 30 pounds and has dimensions of 18" x 17" x 9". The computer can be a desk top type or a laptop with IBM-AT features.

The entire system has been ruggedized for field use and requires only 110 vac power which can be supplied by a generator.

#### Time Required for Analysis

The sample vial is heated for 5 minutes and headspace volatiles are purged for an additional 2 minutes. After sample introduction into the sample cell, a wavelength scan from 240 to 290 nanometers requires 2 1/2 minutes. The computer then requires 10 seconds to analyze that spectrum and display concentration data. Total analysis time is less than 10 minutes.

#### IV. FIELD STUDIES

Two B-TEX 9000 instruments were mounted in trailers and have been operating in the field for past six months, powered from portable generators. The primary application has been to determine the horizontal and vertical extent of soil contamination by analyzing soils from borings around leaking underground storage tanks. The instrument has proved very useful in measuring BTEX levels in soils during over-excavation after tanks have been removed.

Data obtained from field screening has been compared to laboratory results using EPA methods of analysis on duplicate samples. Predicted concentrations vary considerably more than with the laboratory prepared spiked soil samples, varying in some cases as much as  $\pm 100\%$ . The reason for this variation is due to the inhomogeneity of samples and losses of volatiles between sample taking and laboratory analysis. Samples are always stored on ice but losses can occur due to headspace collection and venting when sample jars are opened. Of even more significance, replicate samples on-site have been demonstrated to show large variations due to localized contamination or "nugget effects". Only real-time screening can properly handle the selection of appropriate samples in a real-world environment.

It is well known that benzene weathers more rapidly than xylenes. Such differences can be used in real-time screening to identify recent spills and leaks from older more weathered releases. The B-TEX 9000 spectral display is particularly useful in identifying such differences. Figure 6 shows spectra from a common site where samples were taken only one foot apart which clearly illustrates this difference. A fresh spill from a pipe rupture further contaminated soils which had been previously contaminated one year earlier. The fresh gasoline contamination primarily contained benzene and toluene while the old gasoline contamination had the benzene and toluene weathered away, leaving behind a residual xylenes signature. Naphthalene, which tends to migrate slowly and resist weathering, was also clearly identifiable in the older, more weathered sample.

Other field applications of the B-TEX 9000 include on-site analysis of soil gas. By taking a matrix of soil gas samples using rapid, hand driven probes, the horizontal extent of contamination can rapidly be determined. Then from this data, boring sites can be selected to determine the vertical extent of contamination. Thus, using the B-TEX 9000, a laptop computer and available graphics software packages, a complete three dimensional picture of BTEX contamination can be printed in real time, in the field.



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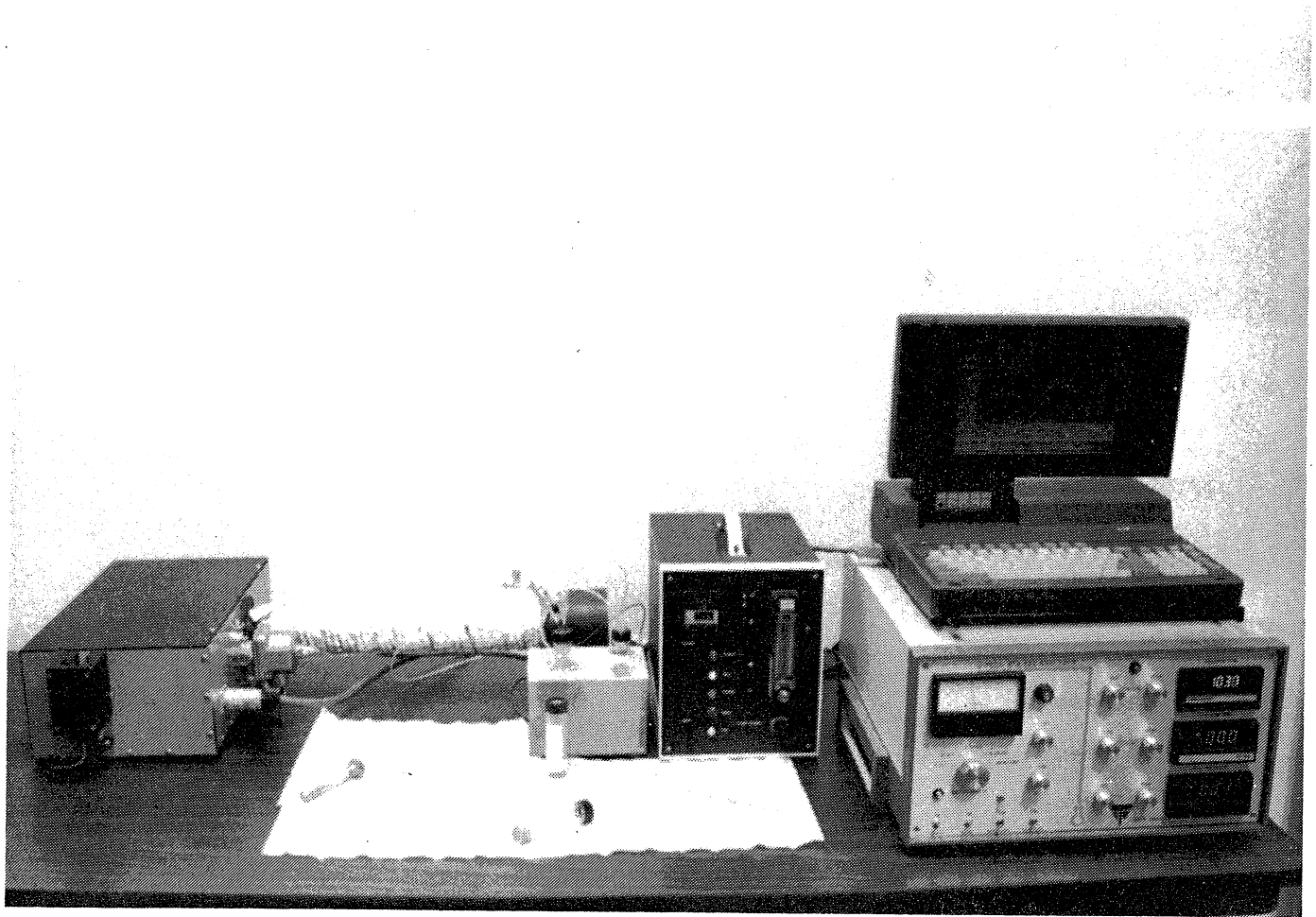


FIGURE 1. B-TEX 9000 SYSTEM WITH LAPTOP COMPUTER

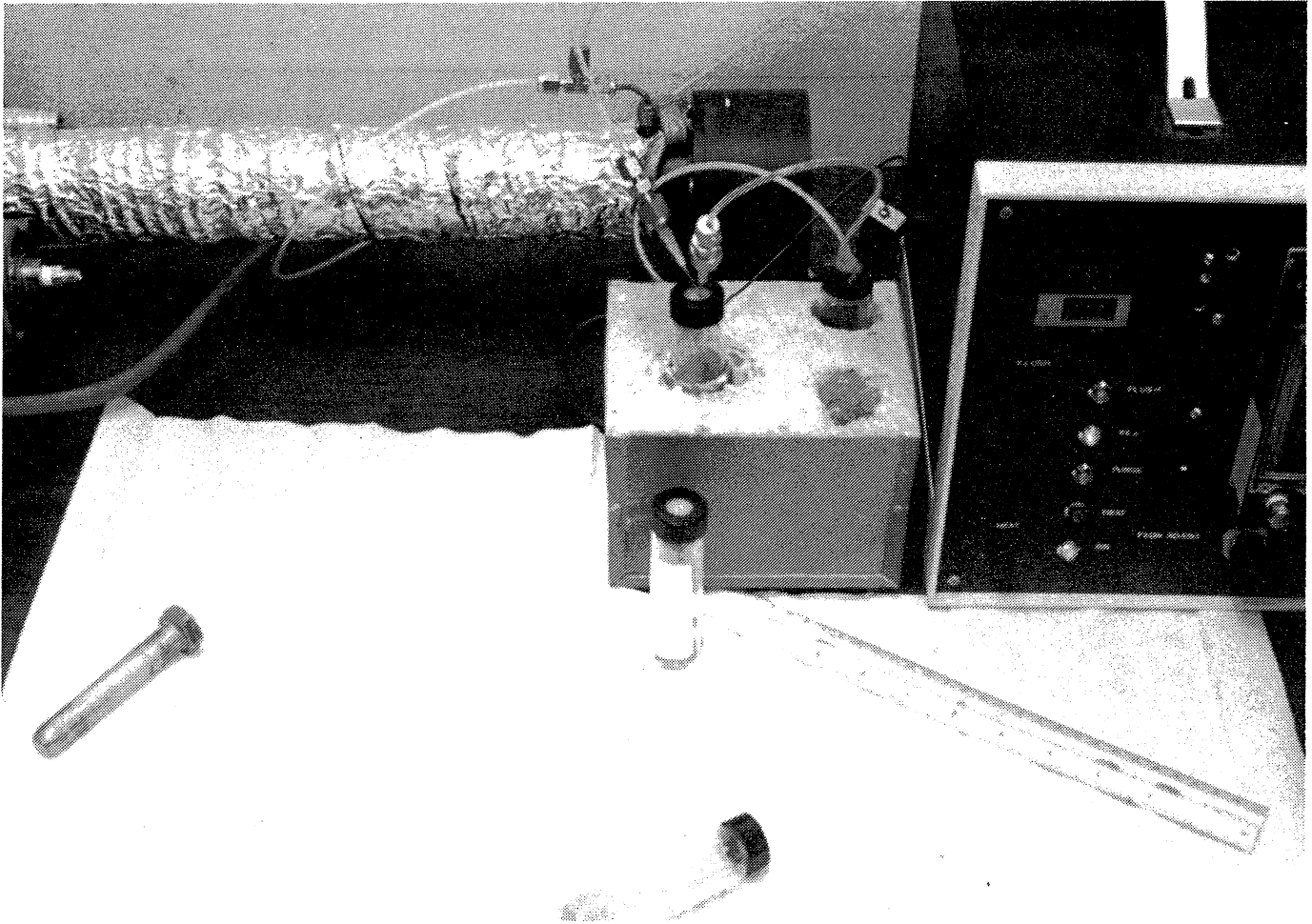


FIGURE 2. THERMAL DESORBING BLOCK WITH SAMPLE VIAL IN PLACE

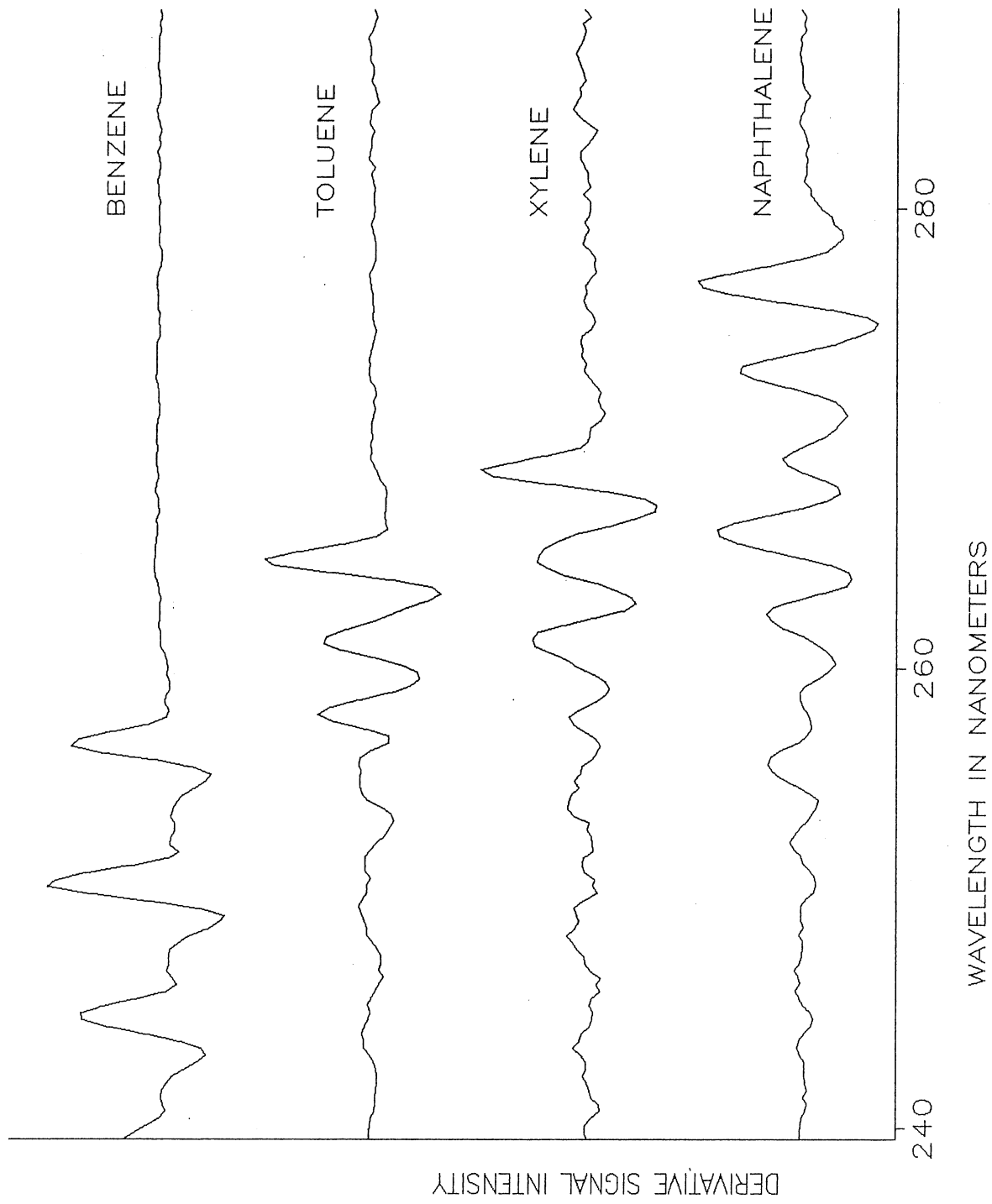


Figure 3. Aromatic Hydrocarbon Signatures

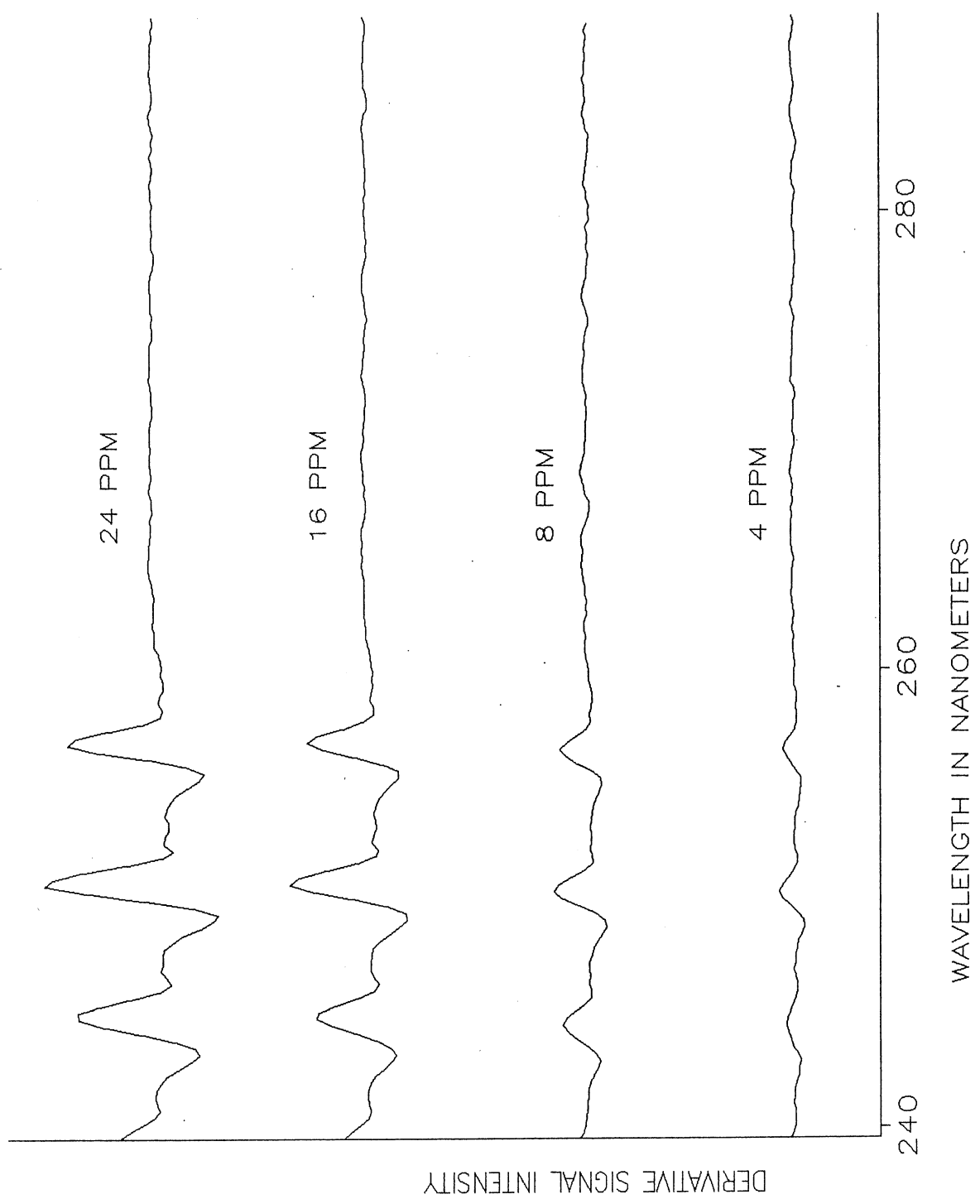


Figure 4. Signal Variation with Benzene Concentration

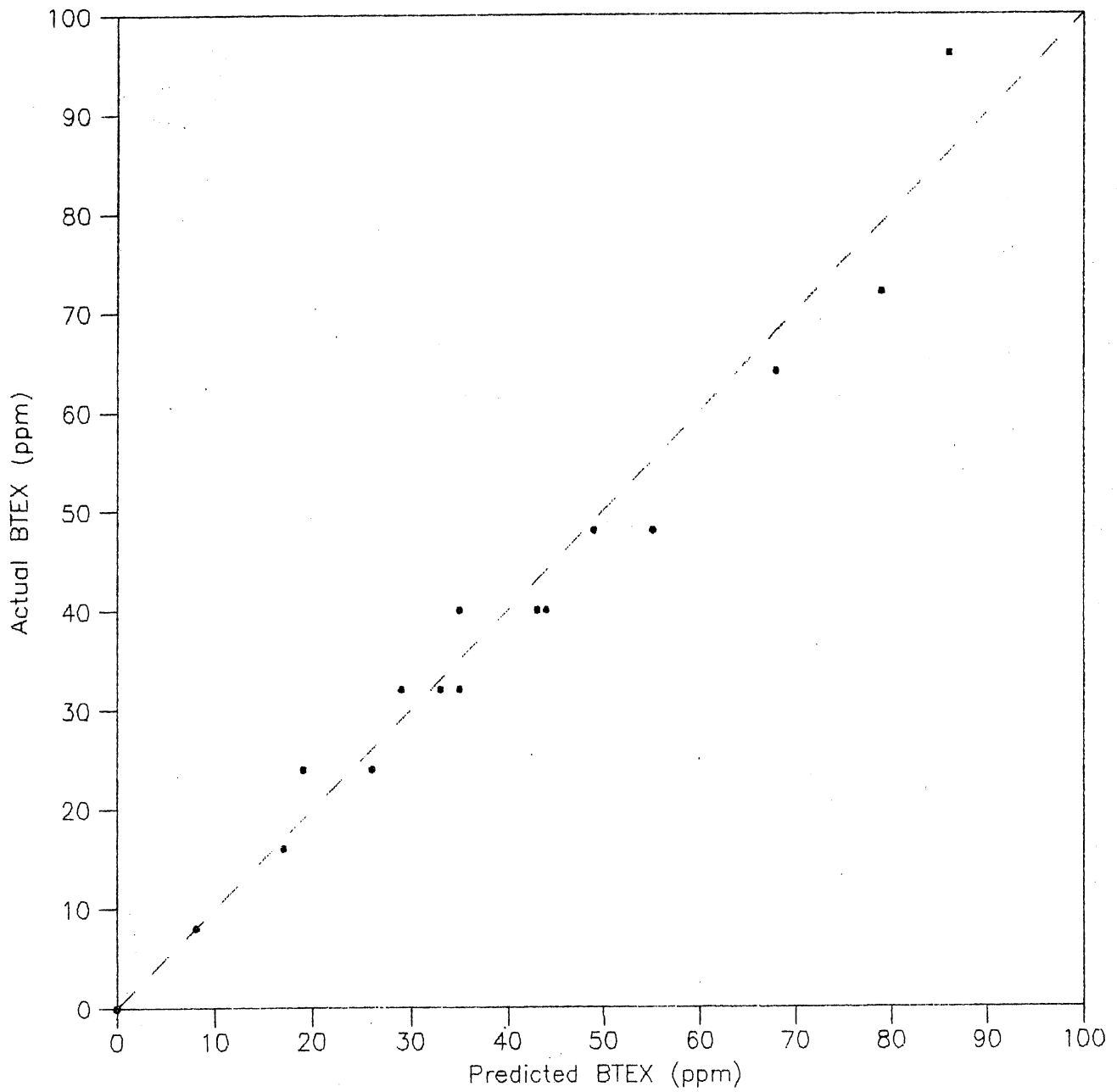


FIGURE 5. B-TEX 9000 ANALYSIS OF LAB-PREPARED CONTAMINATED SOILS

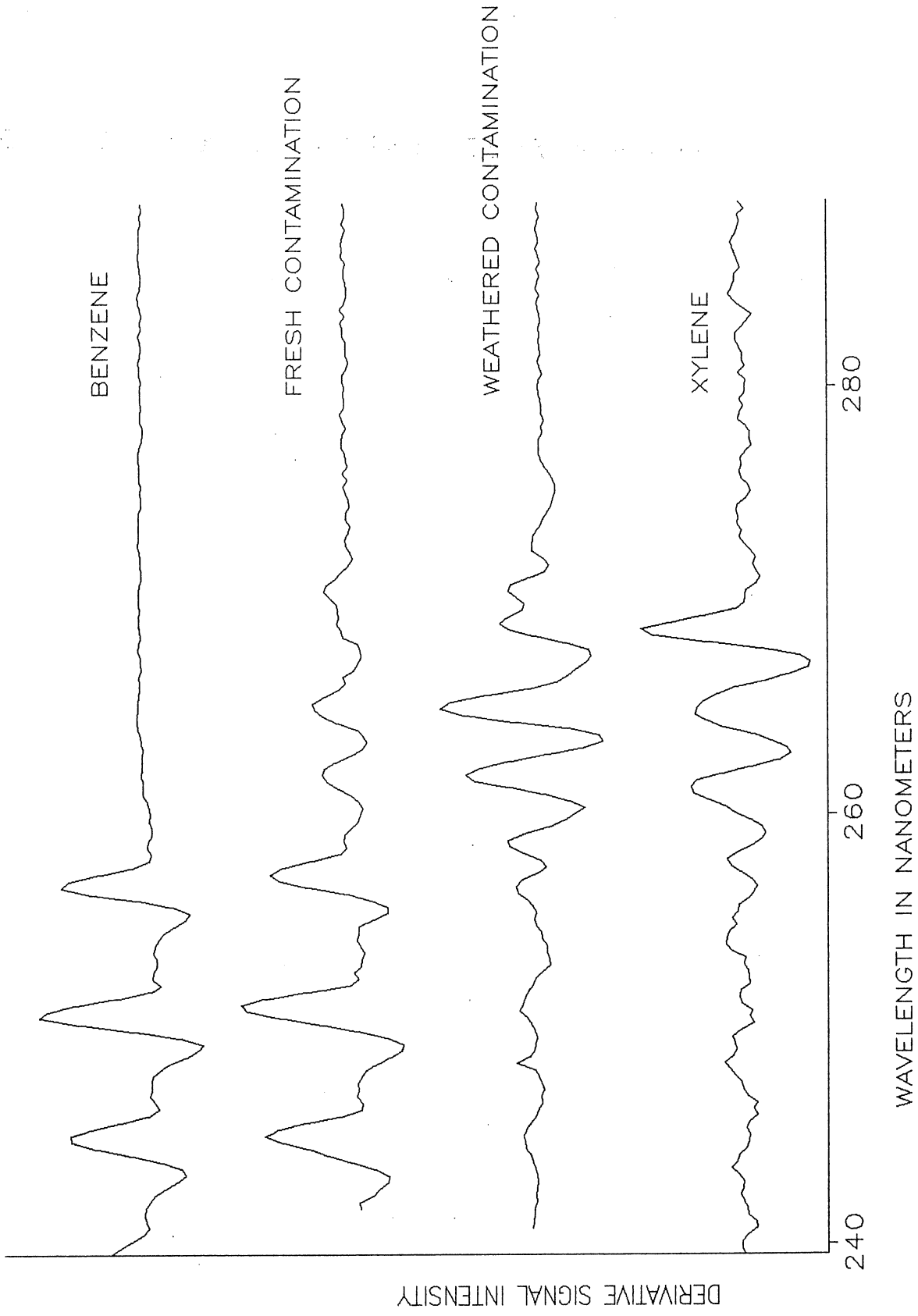


Figure 6. Weathering Effects in Contaminated Soils