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A METHOD FOR DETECTION OF DIESEL SOOT AND COAL IN DUST SAMPLES

Regional Program Report: PR 95-04

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Project No. 4-03-830

This work was supported by the
Federal Panel on Energy R&D (PERD)

January 1994

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ACKNOWLEDGEMENTS

The development of this analytical method has been sponsored jointly by Environment Canada, Energy, Mines and Resources Canada, and B.C. Ministry of Environment. In addition, guidance, technical support and samples have been provided by the Greater Vancouver Regional District, Neptune Terminals Limited, Westshore Terminals Limited, and Ridley Terminals Limited.

Special thanks are given to Dr. David Poon, Project Officer, Environment Canada, Mr. Barid Manna, B.C. Ministry of Environment, Dr. Randy Mikula and Dr. David Fung of Energy, Mines and Resources Canada, Mr. Ken Stubbs, Greater Vancouver Regional District, Mr. David Crook, Westshore Terminals Limited, and Mr. Frid Lederer, Neptune Terminals Limited.

1

INTRODUCTION

This method describes a technique for determining coal and diesel soot in a dust sample. These contaminates are extracted in an organic solvent, before and after external pyrolysis, cleaned-up using column chromatography and then analyzed for polycyclic aromatic hydrocarbons (PAHs) using high pressure liquid chromatography with an ultra-violet detector (HPLC-UV). The PAH content of the room temperature extract, without external pyrolysis, corresponds to the diesel soot. Room temperature extraction of the sample after pyrolysis gives the PAH content derived from the diesel soot and coal dust in the dust sample. The difference between the two values is equivalent to the coal content in the sample.

2 SUMMARY

2.1 Room Temperature Extraction Without External Pyrolysis

A portion of the dust sample is weighed into a small test tube. Dichloromethane is added and the sample is extracted for 10 minutes using an ultrasonic sound bath containing water. After sonification the sample is centrifuged and the supernatant liquid is removed with a Pasteur pipette. The supernatant liquid is retained and the residue is re-extracted with a further aliquot of dichloromethane for 10 minutes in the ultrasonic sound bath.

After extraction, the combined supernatants are poured into a glass syringe and forced through a Millipore filter. The filtrate is collected in a test tube and blown to dryness under a jet of nitrogen. The residue is then dissolved in benzene and transferred to a chromatographic preparation column filled with alumina for clean-up (Section 2.3).

2.2 Room Temperature Extraction With External Pyrolysis

Another portion of the same dust sample as described in Section 2.1 is weighed into a thick-walled glass tube previously flame-sealed at one end. The tube, with contents, is clamped in an upright position, evacuated with a vacuum pump and flame sealed under vacuum.

The sealed evacuated tube containing the sample is then heated in a muffle furnace at conditions optimized in earlier work (10 minutes at 400°C). After cooling, the tube is cut open and tetrahydrofuran, an efficient coal solvent, is added to the tube. The residue is then extracted by placing the tube and contents in an ultrasonic bath for 60 minutes. The tube and contents are centrifuged and the supernatant liquid is removed with a Pasteur pipette and retained. The residue is re-extracted with an additional aliquot of tetrahydrofuran in the ultrasonic bath for 30 minutes, centrifuged and the supernatant liquid is combined with the previous extract. The combined extracts are then poured into a glass syringe and forced through a Millipore filter. The filtrate is collected in a test tube and blown to dryness under a jet of nitrogen. The residue is then dissolved in benzene and transferred to a chromatographic preparation column filled with alumina for clean-up (Section 2.3).

2.3 Column Chromatography Clean-Up of Room Temperature Extracts With and Without External Pyrolysis

Chromatographic peaks for the polycyclic aromatic hydrocarbons (PAHs) of interest in the identification of coal and diesel soot in dust samples are superimposed on an envelope of interfering compounds. This envelope can be reduced by clean-up of the extract prior to HPLC-UV analysis by using column adsorption chromatography. In this method neutral alumina is heated overnight (600°C) and after cooling a weighed amount is poured into a glass chromatography column containing benzene. After eluting the benzene, the extract is added to the top of the alumina column with several washes of benzene, and is then washed through the column with excess benzene. This extract is the room temperature extract, with or without pyrolysis, prepared as described in Section 2.1 and 2.2. The PAHs are eluted with the benzene and polar compounds such as phenols are retained by the alumina.

The benzene wash containing the PAHs is collected in a flask and then most of the benzene is removed by distillation under a vacuum with a Buchi REIII Rotavapor. The remaining volume (~2 mL) is removed by blowing to dryness under a jet of nitrogen. Toluene can be used instead of benzene in the above procedure, however its higher boiling point results in a greater loss of PAHs in the preparation of the final extract. The residue (PAHs) in the flask is then transferred to a sample vial with hexane, blown to dryness in the vial with a jet of nitrogen and then made up to a known volume with solvent (acetonitrile + dichloromethane) for subsequent analysis with the HPLC-UV chromatograph.

2.4 Determination of PAHs Using a High Pressure Liquid Chromatograph and Ultra-Violet Detector

The optimum instrument conditions for the HPLC-UV chromatograph, and the automatic sampler, are established using the polycyclic aromatic hydrocarbon standard containing 16 PAHs as listed in Table 1. The chromatograph (Hewlett Packard 1084A) is fitted with a Supelco column LC-PAH and the mobile phase is water:acetonitrile. The chromatograph and automatic sampler programs established for this work are listed in Table 2 and a chromatogram for the polycyclic aromatic standard is shown in Figure 1. Peak heights obtained by analyses of unknown extracts are measured and adjusted to a constant weight of starting material (5 mg) and a common chromatographic attenuation factor. The peak heights for the room temperature extract without external pyrolysis (diesel) are then subtracted from equivalent peak heights for the room temperature extract with external pyrolysis (coal and diesel) to give values equivalent to the coal content.

These peak heights for the diesel and coal portions are then compared with known primary standards, processed in the same way as the unknown, for each peak identified in the chromatogram. The mean value for the results from all the compounds selected is then calculated to give the final diesel or coal concentration.

3 APPARATUS

3.1 HPLC system capable of constant flow such as the Hewlett Packard 1084A Chromatograph.

3.2 Chromatographic column such as a Supelco Column (150 mm x 4.6 mm ID) LC-PAH. Cat. No. 5-8318.

3.3 Ultraviolet detector, 254-nm with a noise specification of 2 x 10-4AU or better.

3.4 Chromatographic data system having sufficient parameters to accurately follow a sloping baseline such as the Hewlett Packard 79850A L.C. Terminal.

3.5 Chromatographic autosampler such as the Hewlett Packard Series 1050 Autosampler.

3.6 Chromatographic glass columns (250 mm x 10 mm OD) with TFE-fluorocarbon stopcock and fitted with glass wool plugs.

3.7 Glass pyrolysis tubes (200 mm x 10 mm OD x 6 mm ID) flame sealed at one end with glass blowing torch.

3.8 Evaporative concentrator such as a Buchi REIII Rotavapor with water bath and temperature control (±2°C).

3.9 Glass syringe (5 mL) with detachable needle to fit a 0.45 µm Millipore filter.

3.10 Glass test tubes (10 mL) and test tube rack.

3.11 Nitrogen cylinder and reducing gauge with fine needle valve control.

4 REAGENTS AND MATERIALS

4.1 Purity of water - Deionized water must be used in this method.

4.2 Acetonitrile - OmniSolv Grade.

4.3 Tetrahydrofuran - OmniSolv Grade with no stabilizer.

4.4 Methylene Chloride - OmniSolve Grade.

4.5 Benzene or Toluene - OmniSolv Grade.

4.6 Hexane - OmniSolv Grade.

4.7 PAH Standards, analytical reference grade or highest purity available.

4.8 Reference Standards containing coal of choice (-200 mesh) and NBS Standard Reference Material 1650 - Diesel Particulate Matter.

4.9 Neutral alumina - Brockman Activity 1, 80-200 mesh heated overnight at 600°C and cooled in a desiccator before use.

4.10 Solvent washed (dichloromethane) glass wool.

4.11 Millex-HV 0.45 µm filter unit manufactured by Millipore - Cat. No. SLHVO25NB.

5 PROCEDURE

5.1 Preparation of Standard and Field Samples

5.1.1 Standard Samples

It is preferable to use the same coal in preparing primary standards as the coal, or mixtures of coals, suspected of causing the pollution problem. This is because different coals have varying amounts of PAHs depending upon their geographical and/or geological nature. The coal is air dried, crushed and sieved, through a 75 µm sieve (-200 mesh) before use.

The diesel soot used for the primary standards is obtained as a NBS Standard Reference Material 1650. If available locomotive diesel soot can also be used as there is not such a large variation in PAH content in diesel soots compared to coals from different sources.

These materials are weighed out accurately using a balance capable of weighing to 0.1 mg. Chromatographic grade sand, previously crushed, sieved through a 75 µm sieve and fired at 650°C in a muffle furnace, to remove any carbon, is used as the inert filler.

Other possible contaminates such as grain dust or sawdust have been added to primary standards at the 2% wt. level. However, these additives have been shown to have little or no effect on the separation of diesel soot and coal in dust samples and can be omitted in the preparation of the primary standards.

5.1.2 Field Samples

Field samples tested in this program have been derived from dust-fall or high volume collection systems.

The liquid + solids collected in dustfall samples are filtered through a Nuclepore Polycarbonate (PC) Membrane 47 mm 0.4 µm filter to separate the dust from rain water. The filter is then sonicated in a minimum amount of water in an ultrasonic sound bath to remove dust from the filter. The extract is then evaporated to dryness in a petri-dish to give a solid residue suitable for analysis in the procedures described in Section 5.2 and 5.3.

High volume dust samples are collected on a large filter paper. (Micro Filtration Systems - quartz fiber filter 8" x 10"). This filter paper is weighed before and after collection of the dust sample and these values are used to calculate the amount of filter paper that it is necessary to process to give 5-7 mg of dust. This method of determining the weight of filter paper required for processing as described in Section 5.2 and 5.3 assumes that the dust is evenly distributed over the total exposed area of the filter paper.

The high volume filter paper could also be sonicated in water and treated as described for the dust fall samples, however, this approach has not been tested to date.

5.2 Room Temperature Extraction of Dust Sample Without External Pyrolysis (Diesel Content)

5.2.1

Weigh the dust sample (5 mg to 7 mg) or filter paper (50 mg to 100 mg) from the high volume sample containing an equivalent amount of dust into a small test tube (10 mL).

5.2.2

Add dichloromethane (4 mL) to the sample and place test tube and contents in an ultrasonic sound bath and sonify for 10 minutes. Filter paper from high volume sample will require greater volume of dichloromethane (~8 mL).

5.2.3

After sonification, the sample is centrifuged (15 min) and the supernatant liquid is removed with a Pasteur pipette and retained in a test tube (10 mL).

5.2.4

The residue is re-extracted with a further aliquot of dichloromethane (2 mL) (high volume sample ~8 mL) for 10 minutes in the ultrasonic sound bath and then centrifuged (15 min).

5.2.5

The supernatant liquid is removed with a Pasteur pipette and combined with the supernatant from the first extract.

5.2.6

The combined extract is poured into a 5 mL glass syringe fitted with an 0.45 µm Millipore filter. The extract is forced through the filter with the syringe and the filtrate is collected in a test tube (10 mL).

5.2.7

This filtrate is then purged with a jet of nitrogen to remove the dichloromethane and give a residue containing PAHs. Care must be taken not to use excessive nitrogen blow down to ensure minimum loss of lower molecular weight PAHs.

5.2.8

The residue is then dissolved in benzene (2 mL) and transferred with several benzene washes (~3 x 2 mL) to a chromatographic preparation column filled with alumina for clean-up (Section 5.4).

5.3 Room Temperature Extraction of Dust Sample With External Pyrolysis (Diesel + Coal Content)

5.3.1

Weigh the dust sample (5 mg to 7 mg) or filter paper from high volume sample (50 mg to 100 mg) containing approximately 5 mg to 7 mg of dust into a glass tube. This tube is previously flame sealed at one end and is approximately 200 mm long by 10 mm O.D. and 6 mm I.D.

5.3.2

Clamp the tube containing the sample in an upright position, attach a vacuum line and evacuate the tube to less than 1 m bar. The tube is then flame sealed with a glass blowing torch under vacuum. This seal should be as far from the sample as possible so as not to heat the sample.

5.3.3

Heat the sealed evacuated tube containing the sample for 10 minutes at 400°C in a muffle furnace.

5.3.4

After cooling the tube is cut open and the residue is extracted in the tube, with 2 mL tetrahydrofuran (without stabilizer), by placing tube and contents in an ultrasonic bath for 60 minutes.

Extraction efficiency is improved, if a high volume sample is being analyzed, by cutting the tube open at both ends and washing the contents into a 50 mL beaker, with a minimum volume of tetrahydrofuran (~10 mL). The beaker and contents are then extracted in an ultrasonic bath as described above and in Sections 5.3.5 to 5.3.7 below.

5.3.5

After sonification the sample is centrifuged (15 min) and the supernatant liquid is removed with a Pasteur pipette and retained in a test tube (10 mL).

5.3.6

The residue is re-extracted with a further aliquot of tetrahydrofuran (2 mL) (high volume sample ~10 mL) for 30 minutes in the ultrasonic sound bath and then centrifuged (15 min).

5.3.7

The supernatant liquid is removed with a Pasteur pipette and combined with the supernatant from the first extract.

5.3.8

The combined extract is poured into a 5 mL glass syringe fitted with an 0.45 µm Millipore filter. The extract is forced through the filter with the syringe and the filtrate is collected in a test tube(10 mL).

5.3.9

This filtrate is then purged with a jet of nitrogen to remove the tetrahydrofuran and give a residue containing PAHs. Care must be taken not to use excessive nitrogen blow down to ensure minimum loss of lower molecular weight PAHs.

5.3.10

The residue is then dissolved in benzene (2 mL) and transferred with several benzene washes (~3 x 2 mL) to a chromatographic preparation column filled with alumina for clean-up (Section 5.4).

5.4 Column Chromatography Clean-Up of Room Temperature Extracts With and Without External Pyrolysis

5.4.1

Take neutral alumina (Brockman Activity 1, 80-200 mesh) and heat overnight at 600°C in a muffle furnace.

5.4.2

After cooling in a desiccator, 8 g of the alumina is poured into a 250 mm x 10 mm OD chromatography column containing a glass wool plug and 25 mL of benzene.

5.4.3

The column is consolidated with a vibrator and the benzene is allowed to elute from the system until the top surface of the column is just covered by a benzene layer. Benzene eluted at this stage is discarded.

5.4.4

The extract prepared as described in Section 5.2 or 5.3 is then added to the top of the alumina column with several washes of benzene (3 x 2 mL).

5.4.5

Benzene containing the PAHs is allowed to drain through the alumina column into a 250 mL flat bottomed round flask until the liquid level is just above the alumina. At this time, 100 mL of benzene is added to the column and this volume plus eluted PAHs compounds are allowed to drain into the flask.

5.4.6

The flask containing the benzene and eluted PAHs is connected to a Buchi REIII Rotavapor and the benzene is removed by distillation under vacuum.

5.4.7

The distillation is continued until about 2 mL of liquid remains in the flask. At this stage the flask is removed and the remaining volume is removed by blowing to dryness under a jet of nitrogen.

5.4.8

The residue (PAHs) in the flask is transferred with a Pasteur pipette to the autosampler vial with 3 x 2 mL hexane washes.

5.4.9

The autosampler vial containing the hexane and PAHs is then blown to dryness, made up to a volume of 250 µL with solvent (acetonitrile 90% volume + dichloromethane 10% volume) and capped.

5.4.10

The prepared sample can then be stored in a refrigerator for several days for subsequent analysis or analyzed immediately by HPLC-UV chromatography.

5.5 Determination of PAHs Using a High Pressure Liquid Chromatograph and Ultra-Violet Detector.

5.5.1

The optimum conditions for the HPLC-UV chromatograph and the autosampler as listed in Table 2 are entered into the chromatographic data system.

5.5.2

A standard PAH sample containing 16 known PAHs is injected to confirm column (Supelco LC-PAH) and chromatograph's efficiency (Table 1) (Figure 1).

5.5.3

The extracts prepared for unknown and primary standards containing diesel soot and coal are then injected onto the column with the autosampler.

5.5.4

Chromatograms obtained from extracts, with and without external pyrolysis are shown in Figure 3 (standard) and Figure 4 (unknown).

5.5.5

The clean-up procedure (Section 5.4) does not reduce the contaminating envelope entirely and the base line, from which peak heights are measured, is drawn in as shown in Figures 3 and 4.

5.5.6

Initial peaks with retention times of less than 14 minutes are not considered in the calculation as these lower molecular weight compounds are affected by the clean-up procedure. Excessive N_2 blow down during solvent removal can cause loss of more volatile compounds in the extract.

5.5.7

Peaks used in the calculation of diesel soot and coal in dust samples are in the region varying between retention times of 14 to 20 minutes - see Figure 2 for peak identification. These peaks have been identified by comparison of retention times with known standards, however other unknown PAHs may evolve at the same times.

5.6 Calculation of Results

5.6.1 Measurement of Selected Peaks and Calculation of Results

5.6.1.1

Peak heights (mm) for peaks at retention times shown in Figures 3 and 4 are measured and adjusted to a constant weight of starting material(5 mg) and a common chromatographic attenuation factor (Table 3).

5.6.1.2

The peak heights for the room temperature extract without external pyrolysis (diesel) are then subtracted from the peak heights for the room temperature extract with external pyrolysis (coal and diesel) to give values equivalent to the coal content (Table 3).

5.6.1.3

The peak heights for the coal and diesel portions are then compared with the primary standard, processed in the same way as the unknown, for each retention time(Table 4).

5.6.1.4

The mean value for the results at different retention times is then calculated to give the final coal and diesel concentration. An example of the calculation for a particular retention time and summary of the results for the unknown sample is given in Table 4.

5.6.2 Mathematical Method with Different Primary Standards

This mathematical approach was developed to try and account for the contribution made by coal to the diesel value when the mixture was extracted with dichloromethane at room temperature. Standards were prepared with a known weight % of diesel soot and no coal and conversely the same weight % of coal and no diesel soot. Values obtained for these standards were then incorporated as contribution factors in two simultaneous equations representing the response from room temperature extracts of a mixture containing coal and diesel soot, with and without external pyrolysis. The derivation of these equations and examples of their application are described in Sections 5.6.2.1 to 5.6.2.4 below.

5.6.2.1

Peak heights are measured and normalized as described in Section 5.6.1.1.

5.6.2.2

In addition to primary standards containing diesel soot and coal a further two standards are included in the calibration process. These latter standards contain either diesel soot or coal only and are used to calculate contribution factors.

5.6.2.3

This mathematical method is derived as follows:

- The response from a mixture containing coal and diesel soot at room temperature (Equation 1) and after external pyrolysis (Equation 2) are described as:

$$x\,C_1 + y\,D_1 = A_1 \tag{1}$$
$$x\,C_2 + y\,D_2 = A_2 \tag{2}$$

Where x = weight % of coal/100

y = weight % of diesel soot/100

A_1 = response of mixture at room temperature

A_2 = response of mixture after external pyrolysis

C_1 = response of coal with no diesel at room temperature

C_2 = response of coal with no diesel after external pyrolysis

D_1 = response of diesel with no coal at room temperature

D_2 = response of diesel with no coal after external pyrolysis

Solving equations (1) and (2) for x and y:

Multiply Equation (1) by:

$$C_2 / C_1 \rightarrow x\,C_1 \frac{C_2}{C_1} + yD_1 \frac{C_2}{C_1} = A_1 \frac{C_2}{C_1}$$

$$\therefore \quad x\,C_2 + y\,D_1 \frac{C_2}{C_1} = A_1 \frac{C_2}{C_1} \tag{3}$$

and subtracting Equations (2) - (3) $yD_2 - yD_1 \frac{C_2}{C_1} = A_2 - A_1 \frac{C_2}{C_1}$ (4)

$$\therefore \quad y(D_2 - D_1 \frac{C_2}{C_1}) = A_2 - A_1 \frac{C_2}{C_1} \tag{5}$$

$$\therefore \quad y\left(\frac{C_1D_2 - D_1C_2}{C_1}\right) = \frac{A_2C_1 - A_1C_2}{C_1} \tag{6}$$

$$\therefore \quad y = \frac{A_2C_1 - A_1C_2}{C_1D_2 - D_1C_2} \tag{7}$$

$$\text{and} \quad x = \frac{A_1 - yD_1}{C_1} \tag{8}$$

Values obtained from the chromatograms after normalization to a constant weight and attenuation are then substituted in Equations (7) and (8) to give the percent weight of diesel soot and coal.

An example of the application of this method is:

C_1 = 25 mm for a peak at room temperature for sample containing 100% coal and no diesel soot

C_2 = 185 mm for the same peak after external pyrolysis of sample containing 100% coal and no diesel soot

D_1 = 170 mm for same peak at room temperature for sample containing 100% diesel soot and no coal

D_2 = 170 mm for same peak after external pyrolysis of sample containing 100% diesel soot and no coal

and A_1 = 36.5 mm response for same peak in mixture of diesel soot and coal at room temperature

A_2 = 52.5 mm response for same peak in mixture of diesel soot and coal after external pyrolysis.

Then

$$y = \frac{A_2C_1 - A_1C_2}{C_1D_2 - D_1C_2} = \frac{(52.5 \, x \, 25) - (36.5 \, x \, 185)}{(25 \, x \, 170) - (170 \, x \, 185)} = 0.2$$

$$x = \frac{A_1 - yD_1}{C_1} = \frac{36.5 - (0.2 \, x \, 170)}{25} = 0.1$$

$\therefore$ Mixture contains 20% weight of diesel soot and 10% weight of coal.

5.6.2.4

Results shown in Table 5 and 6 are determined using either one prominent peak or the mean value of six prominent peaks displayed in the chromatogram. The primary standards considered are:

- diesel soot 10% wt. + coal 0% wt.
- diesel soot 0% wt. + coal 10% wt.
- diesel soot 10% wt. + coal 10% wt.

This results in the equations being modified to give:

$$y = \frac{(A_2C_1 - A_1C_2)0.1}{C_1D_2 - D_1C_2}$$

$$x = \frac{(A_1 \, x \, 0.1 - yD_1)}{C_1}$$

An example of the application of this method is as follows:

From Table 5 consider the Diesel:Coal mixture of:

2:10(wt.%) which is standardized against a Diesel:Coal mixture of 10:10(wt.%)

The standard mixture gives:

C_1 = 3.6 mm (Peak height mm 10% coal standard at 20°C)

D_1 = 14.0 mm (Peak height mm 10% diesel standard at 20°C)

C_2 = 19.6 mm (Peak height mm 10% coal standard at 400°C)

D_2 = 18.9 mm (Peak height mm 10% diesel standard at 400°C)

unknown gives A_1 = 6.9 mm (Peak height mm unknown at 20°C)

A_2 = 29.8 mm (Peak height mm unknown at 400°C)

Now %y (diesel)

$$= \frac{(A_2C_1 - A_1C_2)0.1}{C_1D_2 - D_1C_2}$$

$$= \frac{29.8 \, x \, 3.6 - 6.9 \, x \, 19.6(0.1)}{3.6 \, x \, 18.9 - 14.0 \, x \, 19.6}$$

$$= \frac{(107.28-135.24)0.1}{68.04-274.4}$$

$$= \frac{-2.796}{-206.36}$$

$$= 0.0135$$

$\therefore$ Percentage of Diesel $= 0.0135 \text{ x } 100 = 1.35$

Now %x (coal) $= \frac{(A_1 \; x \, 0.1 - yD_1)}{C_1}$

$$= \frac{6.9 \, x \, 0.1 - 0.0135 \, x \, 14.0}{3.6}$$

$$= \frac{0.69-0.189}{3.6}$$

$$= \frac{0.501}{3.6}$$

$$= 0.139$$

$\therefore$ Percentage of Coal $= 0.139 \text{ x } 100 = 13.9\%$

6 REPEATABILITY, ACCURACY AND LIMITS OF DETECTION

6.1

Repeatability of the method in terms of retention time, peak height and concentration is good both for consecutive determinations and for samples analyzed several months apart as shown in Tables 7 and 8.

6.2

The accuracy (within 10% to 20% of theoretical value) is acceptable at low concentrations (<20% wt.) for diesel and coal mixtures, but at higher concentrations the diesel content tended to be greater and the coal less than the theoretical value (Table 9). This is due to excessive extraction of PAHs from the coal at room temperature without pyrolysis. This problem can be resolved by preparing standards in a similar concentration range to the unknown. If possible, standards should also be prepared from the same coal as that present in the sample being analyzed.

Accuracy in the determination of low diesel in combination with high coal concentrations can also be improved by using the mathematical method described in Section 5.6.2 (Table 10). However, additional standards at say 8 wt. % and 15 wt. % diesel or coal are required to improve correlation as discussed in Section 6.4

6.3

The method is not capable of distinguishing between 2% wt. and 5% wt. diesel in high coal concentrations (>20% wt.) (Table 9) using a standard containing 5% wt. diesel soot and 25% wt. coal.

However, there is adequate peak height (i.e. 2 to 8 mm for 20 µL sample at an attenuation of 2^4) at the 2% weight concentration level and the HPLC attenuation could be increased to 2^2 without any sacrifice in instrument's stability. This would give peak heights of 8 to 32 mm, thus allowing much lower concentrations to be detected and measured providing primary standards in the same concentration range are available.

6.4

Regression analysis of results listed in Table 9 give the following expressions for diesel soot and Quintette coal in synthetic samples (19 data points).

Coal: $y = 0.98x + 0.96$ $r = 0.99$

where x = actual coal value

y = determined coal value

r = correlation coefficient*

Diesel: $y = 0.96x + 1.92$ $r = 0.93$

x = actual diesel soot value

y = determined diesel soot value

r = correlation coefficient*

*Closer this value is to 1.0 the better is correlation between x and y.

In the determination of these values for coal and diesel soot, using comparison of specific peaks (Tables 4 and 9), several standards were used. These standards were in the most appropriate range to the unknowns and resulted in good correlations for coal (r = 0.99) and diesel soot (r = 0.93).

Results obtained with the mathematical method are listed in Table 10 and regression analysis give:

Coal: $y = 1.17x - 1.47$ $r = 0.96$

where x = actual coal value

y = determined coal value

r = correlation coefficient*

Diesel: $y = 0.88x + 1.53$ $r = 0.74$

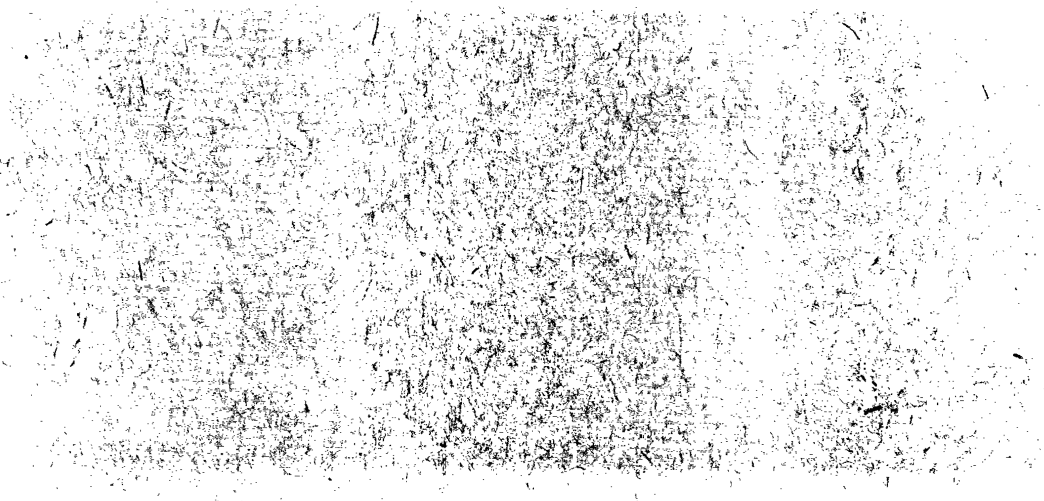
x = actual diesel soot value

y = determined diesel soot value

r = correlation coefficient*

*Closer this value is to 1.0 the better is correlation between x and y.

Results calculated with the mathematical method are based on a 10% wt. level of diesel soot and coal. This concentration level seems adequate for the determination of coal between concentrations of 2% wt. and 70% wt. (correlation coefficient = 0.96). However, the results for diesel soot are not satisfactory (correlation coefficient = 0.74) and it would seem that a range of primary standards, covering low and high concentrations of diesel soot, is probably required to improve correlation between determined and actual values.



TABLES

Table 1 Polyaromatic Standard for HPLC-UV Chromatograph

Peak Number	Compound	Retention Time (Minutes)	Concentration (mg/L)
1	Naphthalene	10.71	20
2	Acenaphthylene	11.80	40
3	Acenaphthene	13.20	20
4	Fluorene	13.49	4
5	Phenanthrene	14.31	2
6	Anthracene	15.01	2
7	Fluoranthene	15.95	4
8	Pyrene	16.54	2
9	Benzo(a)Anthracene	18.45	2
10	Chrysene	18.71	2
11	Benzo(b)Fluoranthene	20.37	4
12	Benzo(k)Fluoranthene	20.97	2
13	Benzo(a)Pyrene	21.67	2
14	Dibenzo(a,h)Anthracene	22.80	4
15	Benzo(g,h,i)Perylene	23.50	4
16	Indeno(1,2,3-cd)Pyrene	23.78	2

Table 2 Optimum Program for the HPLC-UV Chromatograph and Automatic Sampler

HPLC-UV Chromatograph		
Flow		0.75 mL/Minute
Percent Solvent B	B(Acetonitrile)	35.0%
Maximum Pressure		300 BAR
Minimum Pressure		0 BAR
Solvent Temperature	A(Water)	40°C
Solvent Temperature	B(Acetonitrile)	40°C
Oven Temperature		40°C
VW Signal		-
Wave Length		254:430 nm
Chart Speed		0.50
Zero		10.0
Attenuation		2↑5
Area Rejection		100
Slope Sensitivity		0.20
Sample Volume		20 µL
Time 2 Minutes	Percent B	35.0%
Time 5 Minutes	Integ.	2
Time 22 Minutes	Percent B	99.0%
Time 28 Minutes	Percent B	99.0%
Time 32 Minutes	Percent B	35.0%
Time 34 Minutes		Stop
Automatic Sampler		
Injection Volume		20 µL
Draw Speed		1000 µL/Minute
Stop Time		34.0 Minute
Post Time		5.0 Minute

Table 3 Re-Arrangement of Data from Room Temperature Extracts With and Without Pyrolysis to Give Peak Heights Equivalent to Coal and Diesel Content

Sample	Retention Time (Minutes)	Peak Heights (mm) Normalized for 5 mg Starting Material and A Peak Attenuation of 2^4		
		A* (Diesel & Coal)	B** (Diesel)	A-B (Coal)
Primary Standard***	14.51	49.0	16.5	32.5
	16.14	68.6	28.9	39.7
	16.66	62.4	25.6	36.8
	17.76	39.2	18.2	21.0
	18.08	38.3	18.2	20.1
	18.46	21.4	8.3	13.1
	18.93	24.1	12.4	11.7
Unknown	14.51	22.0	15.5	6.5
	16.13	35.3	24.7	10.6
	16.66	29.8	21.2	8.6
	17.75	22.0	15.5	6.5
	18.08	20.3	15.5	4.9
	18.46	8.6	6.3	2.3
	18.96	14.1	9.9	4.2

A = Room temperature extraction with external pyrolysis.*
*B** = Room temperature extraction without pyrolysis.*
*Primary Standard*** = 10% wt. coal (Quintette) + 10% wt. Diesel (1650).*

Table 4 Calculation of Coal and Diesel Content in an Unknown Sample

From results shown in Table 3:

Primary standard (10% weight coal + 10% weight diesel soot) at a retention time of 14.51 minutes has:

Peak Height Coal = 32.5 mm
and
Peak Height Diesel = 16.5 mm

Unknown at a retention time of 14.51 minutes has:

Peak Height Coal = 6.5 mm
and
Peak Height Diesel = 15.5 mm

Concentration of Coal in Unknown = $\frac{10}{32.5} \times 6.5 = 2.0$ Weight %

and

Concentration of Diesel in Unknown = $\frac{10}{16.5} \times 15.5 = 9.4$ Weight %

This procedure is carried out with each retention time using results in Table 3 to give the following results:

Retention Time (Minutes)	Coal Concentration (Weight %)	Diesel Concentration (Weight %)
14.51	2.0	9.4
16.13	2.7	8.5
16.66	2.3	8.3
17.75	3.1	8.5
18.08	2.4	8.5
18.46	1.8	7.6
18.96	3.6	8.0
	Mean = 2.6	Mean = 8.4

Unknown mixture contains 3% weight coal and 8% weight diesel.

Table 5 Mathematical Method of Calculation Using One Peak (17.7 min)

Peak Height (mm)		Factor	Determined Values Required for Calculation							
10% Coal + 0% Diesel Standard	20°C	C_1	3.6	3.6	3.6	3.6	3.6	3.6	3.2	3.2
10% Diesel + 0% Coal Standard	20°C	D_1	14.0	14.0	14.0	14.0	14.0	14.0	12.6	12.6
10% Coal + 0% Diesel Standard	400°C	C_2	19.6	19.6	19.6	19.6	19.6	19.6	18.1	18.1
10% Diesel + 0% Coal Standard	400°C	D_2	18.9	18.9	18.9	18.9	18.9	18.9	17.4	17.4

Calculation of Coal and Diesel In Sample

Peak Height (mm)		Factor	Determined Values Required for Calculation							
Unknown Mixture	20°C	A_1	14.0	1.2	3.6	6.9	12.7	13.9	15.8	20.8
Unknown Mixture	400°C	A_2	18.9	6.0	19.6	29.8	63.1	62.9	35.5	81.6

Results

Determined Diesel:Coal (wt. %)	10:0	0:3	0:10	1:14	1:31	2:30	10:10	7:39
Actual Diesel:Coal (wt. %)	10:0	0:2	0:10	2:10	0:30	2:30	10:10	10:30

Table 6 Mathematical Method of Calculation Using Mean of Six Peaks

Peak Height (mm)		Factor	Determined Values Required for Calculation							
10% Coal + 0% Diesel Standard	20°C	C_1	22.1	22.1	22.1	22.1	22.1	22.1	20.5	20.5
10% Diesel + 0% Coal Standard	20°C	D_1	73.7	73.7	73.7	73.7	73.7	73.7	68.5	68.5
10% Coal + 0% Diesel Standard	400°C	C_2	99.3	99.3	99.3	99.3	99.3	99.3	104.1	104.1
10% Diesel + 0% Coal Standard	400°C	D_2	119.1	119.1	119.1	119.1	119.1	119.1	124.8	124.8

Calculation of Coal and Diesel In Sample

Peak Height (mm)		Factor	Determined Values Required for Calculation							
Unknown Mixture	20°C	A_1	73.7	12.8	22.1	38.4	74.9	79.7	89.0	118.6
Unknown Mixture	400°C	A_2	119.1	38.0	99.3	191.4	309.2	308.0	228.9	439.6

Results

Determined Diesel:Coal (wt. %)	10:0	1:3	0:10	-1:20	1:30	2:28	10:10	7:34
Actual Diesel:Coal (wt. %)	10:0	0:2	0:10	2:10	0:30	2:30	10:10	10:30

Table 7 Repeatability Results for Bullmoose Coal

	Retention Time (min)				Peak Height (mm)*			Mean Peak Heights
Compound	**1**	**2**	**3**	**Mean**	**1**	**2**	**3**	**(Limits)**
Extract with External Pyrolysis (400° C)								
Phenanthrene	14.19	14.17	14.18	14.18	67.2	65.8	63.8	65.6 (±2mm)
Fluoranthene	15.87	15.86	15.87	15.87	121.1	117.3	120.6	119.7 (±2mm)
Pyrene	16.27	16.26	16.27	16.27	90.1	91.1	93.1	91.4 (±2mm)
1-Methyl Pyrene	18.01	18.00	18.00	18.00	63.6	61.8	63.8	63.1 (±2mm)
Chrysene	18.58	18.57	18.56	18.56	33.5	37.2	35.5	35.4 (±2mm)
Extract without External Pyrolysis (20° C)								
Phenanthrene	14.26	14.19	15.21	14.55	7.0	5.1	4.1	5.4 (±2mm)
Fluoranthene	15.97	16.30	16.90	16.39	19.2	15.3	10.4	15.0 (±5mm)
Pyrene	16.38	16.80	17.52	16.90	14.0	11.2	9.3	11.3 (±3mm)
1-Methyl Pyrene	18.11	18.04	19.05	18.40	12.2	11.2	11.4	11.6 (±2mm)
Chrysene	18.92	18.89	20.08	19.30	7.0	10.2	4.1	7.1(±3mm)

Peaks normalized for 5 mg material and 100% carbon.

Table 8 Repeatability Results for Diesel/Coal Mixtures with Time

	Actual Concentration Wt. %		Determined Concentration Wt. %					
Sample Number	**Diesel**	**Coal**	**Diesel**	**Coal**	**Diesel**	**Coal**	**Diesel**	**Coal**
			13/10/92		21/9/92		26/1/92	
8	2	10	4	14	6	11	6	9
11	2	30	9	24	7	24	5	29

Table 9 Results for Trial Using Unknown Samples (Comparison Peak Height Method)

# Standard Used to Calculate Unknown	Concentration (wt. %)		Actual Concentration (wt. %)	
	Diesel	Coal	Diesel	Coal
13	15	8	15	7
12	16	67	10	70
12	12	47	7	45
12	6	29	5	25
12	5	29	2	30
13	10	10	10	10
13	6	9	2	10
13	9	3	10	2
4	5	31	5	30
4	5	24	2	25
4	9	25	10	20
4	4	21	5	20
4	4	19	2	20
4	5	18	5	15
4	4	14	2	15
1	7	4	5	5
1	23	7	20	5
13	11	14	10	15
1	17	9	15	10

Standard #1 = 7% wt. coal (Quintette) + 15% wt. Diesel (1650)
Standard #4 = 25% wt. coal (Quintette) + 5% wt. Diesel (1650)
Standard #12 = 30% wt. coal (Quintette) + 10% wt. Diesel (1650)
Standard #13 = 10% wt. coal (Quintette) + 10% wt. Diesel (1650)

Table 10 Results for Trial Using Unknown Samples (Mathematical Method)

Concentration wt. % (Calculated using mean of 6 peaks with standards listed below)*		Actual Concentration wt. %	
Diesel	**Coal**	**Diesel**	**Coal**
21	0	15	7
0	83	10	70
6	48	7	45
0	36	5	25
3	27	2	30
13	6	10	10
4	10	2	10
14	0	10	2
3	35	5	30
7	23	2	25
12	27	10	20
2	27	5	20
4	18	2	20
10	15	5	15
9	8	2	15
4	7	5	5
18	14	20	5
8	15	10	15
16	15	15	10

**Standard #12 = 30% wt. coal (Quintette) + 10% wt. Diesel (1650)*
Standard #13 = 10% wt. coal (Quintette) +10% wt. Diesel (1650)
Standard #3 = 0% wt. coal (Quintette) + 10% wt. Diesel (1650)
Standard #7 = 10% wt. coal (Quintette) + 0% wt. Diesel (1650)

FIGURES

Figure 1 HPLC-UV Chromatogram for Polyaromatic Standard

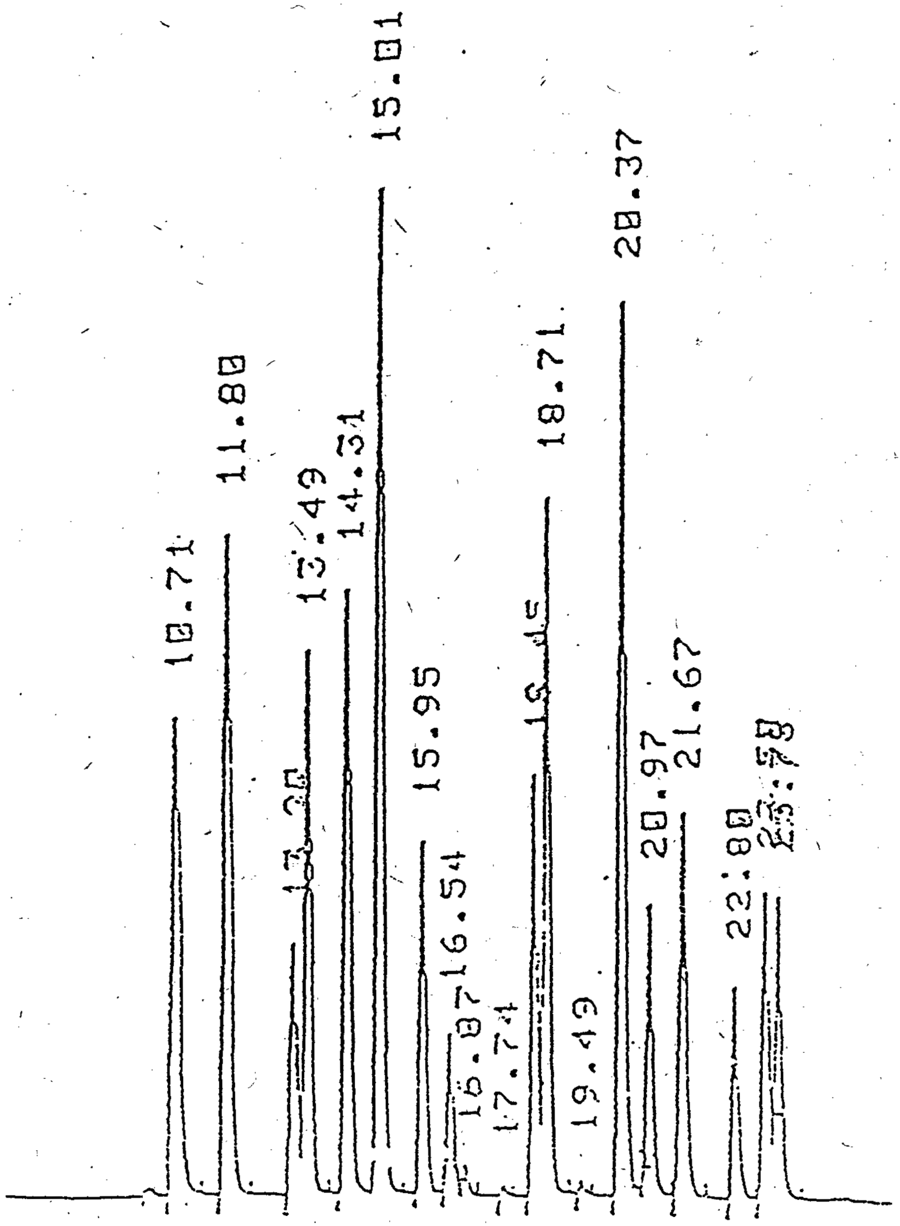
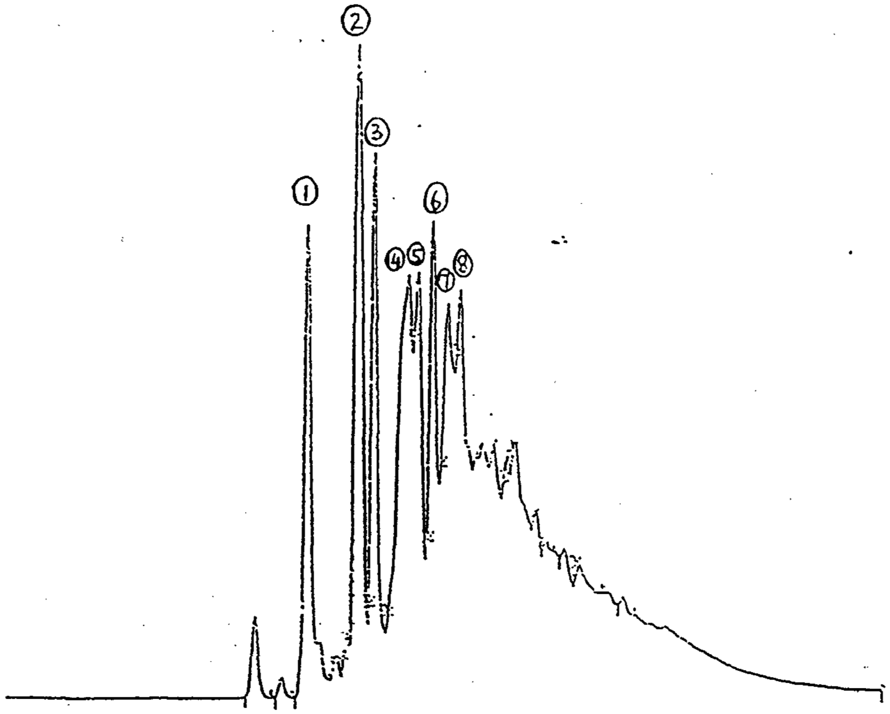
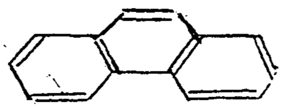


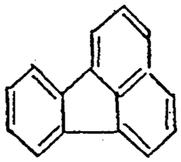
Figure 2 Probable Identification of Peaks Used to Measure Diesel Soot and Coal in Dust Samples



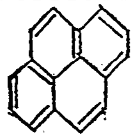
1.) Phenanthrene



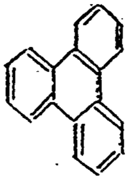
2.) Fluoranthene



3.) Pyrene



4.) Triphenylene



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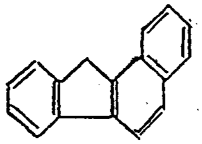
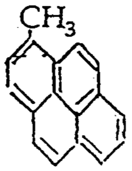
Benzo (a) Fluorene

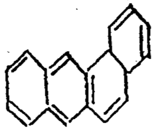


5.) Benzo (b) Fluorene

6.) 1-Methyl Pyrene



7.) Benzo (a) Anthracene



8.)Chrysene

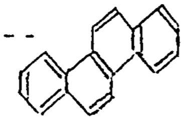
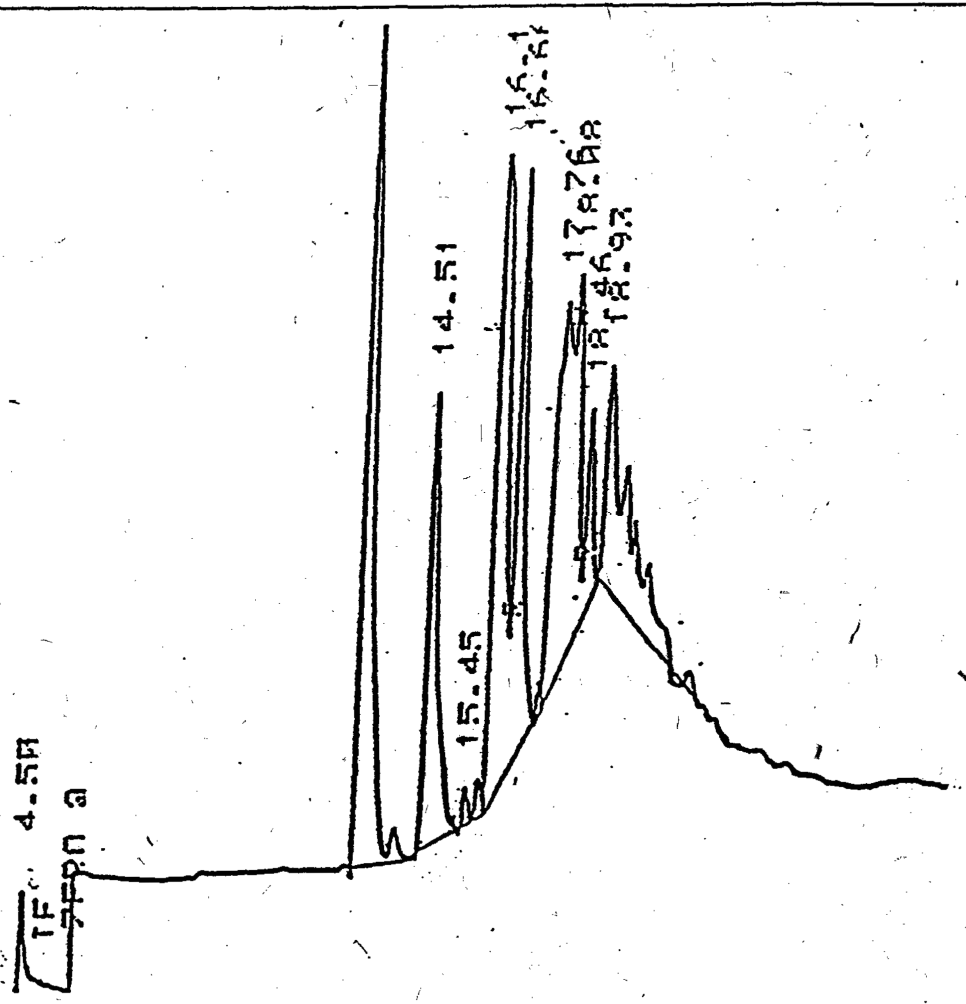
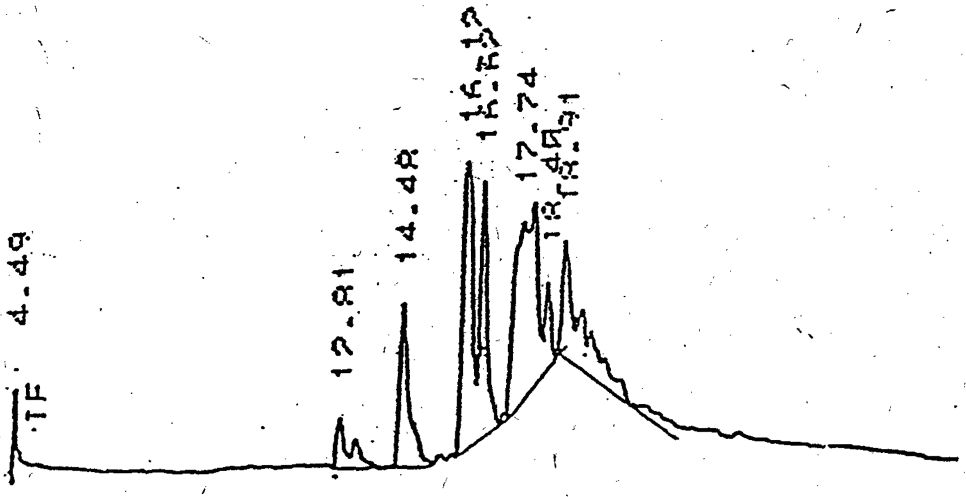


Figure 3 Primary Standard Chromatograms

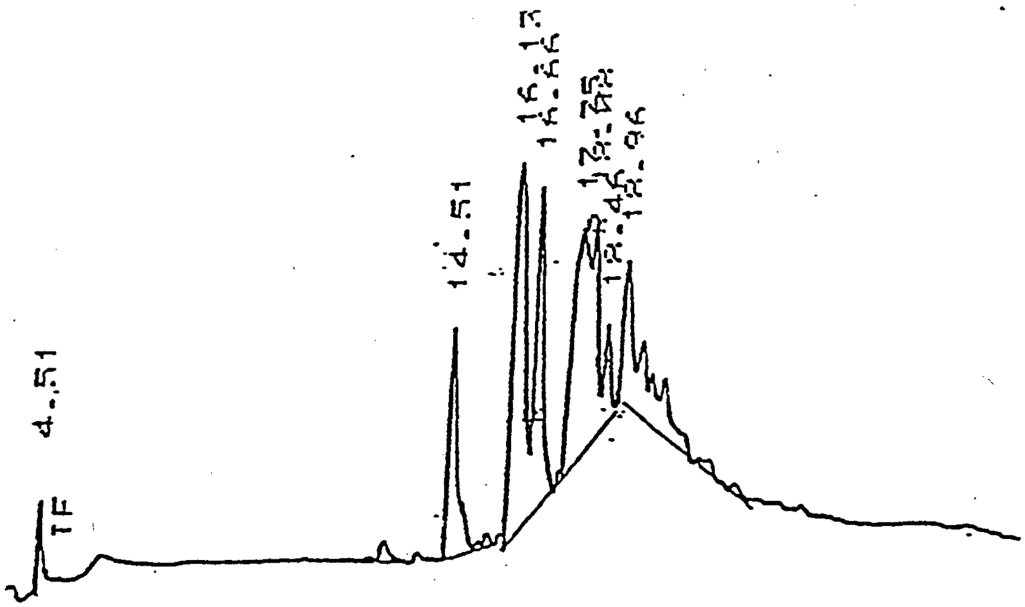


ROOM TEMPERATURE EXTRACT WITH PYROLYSIS (COAL + DIESEL)

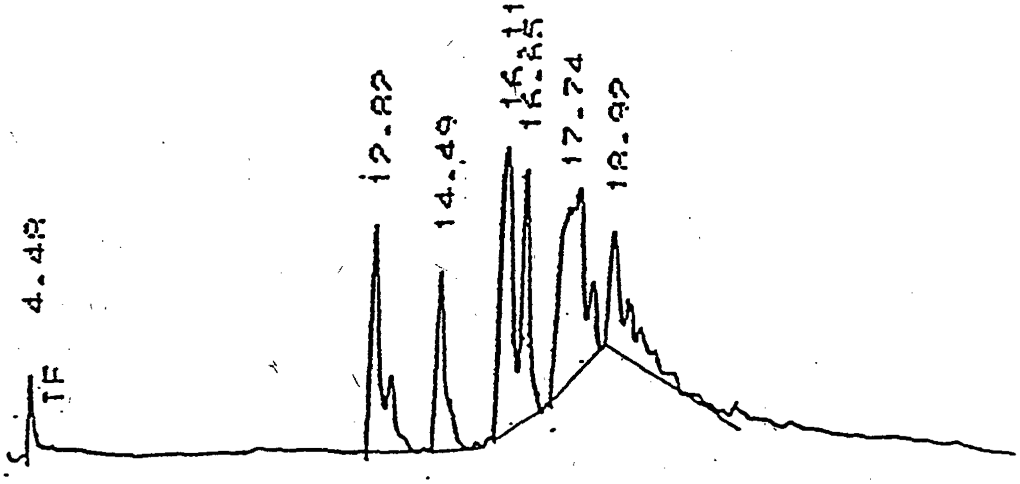


ROOM TEMPERATURE EXTRACT WITHOUT PYROLYSIS (DIESEL)

Figure 4 Unknown Sample Chromatograms



ROOM TEMPERATURE EXTRACT WITH PYROLYSIS (COAL + DIESEL)



ROOM TEMPERATURE EXTRACT WITHOUT PYROLYSIS (DIESEL)