

Measurement of Volatiles, Semi-volatiles and Heavy Metals in an Oil Burn Test

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I. Introduction

In-situ burning is one of the many countermeasures to combat oil spills. The primary advantage of burning is rapidity: in some favourable cases it can remove as much oil in one day as would be removed in one month by mechanical removal. Damage to shoreline and biota can thus be minimized. In addition it requires much less equipment and man-power resources. In remote areas where the logistics of cleanup equipment is insurmountable, in-situ burning may be the only practical means of oil removal.

On the other hand, burning produces large volume of smoke and, until there is a clear understanding of the constituents of the emitted smoke/soot and the remaining residue, in-situ burning is not likely to win public acceptance.

In view of this, a consortium of over 15 agencies in the US and Canada have joined forces to study burning and are actively planning to conduct large scale experiments. As part of this effort, a meso-scale burning exercise was carried out during April-June 1991 at Mobile, Alabama. Two preliminary and eleven burn tests, each with 2000-5000 gallons of crude oil, were conducted at the facilities of Fire and Safety Test Detachment at Sand Island situated at Upper Mobile Bay. A variety of parameters that might affect burning and smoke production were tested. During each burn, extensive samples were taken from the oil, residue and the smoke plume itself. In addition to ground station samplers, air-borne samplers were also employed. The analytical parameters include volatiles and semi-volatiles of environmental interest, and heavy metals typically contained in the starting crude oil.

In this paper, the detailed analytical work employed to analyze the burn samples is outlined and discussed. Real-time CO₂, SO₂ particulates and benzene/toluene/ethyl-benzene/xylene (BTEX) measurements were carried out by REAC, an EPA contract lab. The limited scope of this paper does not cover the results of those tests.

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1992.

II. Experimental

SAMPLING

A layout of the site with schematics of sampling equipment is shown in Figure 1. The burn was conducted in a specially-constructed open steel pan (51x51 ft) with an outer perimeter filled with water. In a typical burn, 2000-gallons of Louisiana crude was released on about 3 feet of water. The oil was ignited and the burn generally lasted about 15-20 min. Details of the major sampling apparatus are described below:

Polycyclic Aromatic Hydrocarbon (PAH):

AirCon air samplers (Gilian) were used at 50 feet upwind, 100 and 200 feet downwind from the burn pan. The pumps were operated at a nominal flow rate of 10 L/m. Air was draw through a 37-cm 2- μ m TFPE filter, followed by a 8x110 mm size XAD sorbent tube. Typical sample volume was 100 L.

Cumulative samples for PAH analysis were also taken at two downwind locations throughout the duration of the burn project. Sampling media was the same as standard PAH method. The cumulative sample volume was typically 1400 L.

Aliquots of fresh crude and burnt residue were taken before and after each burn. The water in the burn pan was also sampled before and after the burn for PAH and metal analyses.

Volatile Organic Compound (VOC):

Gilian HFS-513 personal samplers were employed at the same location: sampling media was a two-stage coconut charcoal tube (8x110 mm, 600 mg) at a nominal flow rate of 2 L/m. Typical sample size was 50 L. Again, cumulative samples were taken at two downwind locations; sample size was an average 500 L.

Metals:

Heavy metals in soot were collected using Gilian personal samplers on a 37-cm, 0.8- μ m membrane cellulose ester (MCE) filter again at the same locations. Operated at 2 L/m, the pump collected a typical sample volume of 40 L.

C2-C12 VOC:

Whole air/smoke samples were taken using 6 L evacuated stainless steel canisters (Summa canisters, Scientific Instrumentation, Moscow, Idaho) at the 100 ft downwind location.

Polychlorinated dibenzo-p-dioxin/furan (DX/DF):

High volume samplers (PS-1, General Metal Works) were employed to collect cumulative samples at upwind and downwind locations. Sampling media were 4 in. glass-fibre filter followed by a 2x3 in. polyurethane foam plug (PUF). Flow rate was nominally 200 L/m; the cumulative sample volume was an average 70 cubic meters.

Together with the field samples, reagent blanks (unopened tubes) and trip blanks (opened tubes exposed to the atmosphere for the same duration as the samples) were also sent and analyzed with the samples.

III. Sample workup

PAH:

PAH samples from AirCons were initially extracted ultrasonically in toluene/acetone (95/5 %) in accordance with NIOSH method 5510 (ref 1). The front-half and back-half of the XAD tubes were extracted separately to determine the distribution of collected PAH. From the preliminary runs, it was discovered the soot loading was very small and the PAH was below detection. The tube was then extracted whole to lessen the work load and to improve the detectability of low levels of PAH.

Soxhlet extraction was later used when it was found out the ultrasonic extraction did not recover all the PAH from the sampling media. The filter/XAD was placed in a cellulose thimble and spiked with a mixture of four deuterated PAH compounds and extracted by toluene/acetone in a Soxhlet overnight. The raw extract was dried over anhydrous sodium sulphate and roto-evaporated and concentrated to 1 mL. A d12-terphenyl internal standard was added prior to GC/MSD analysis.

Crude and residue sample was first dissolved in cyclohexane to precipitate asphaltenes. An aliquot equivalent to about 50 mg of oil was spiked and subjected to silica column cleanup. The saturates were first eluted with hexane; the aromatic (PAH) fraction was eluted using benzene. This fraction was concentrated and the column cleanup was repeated to remove the residual oil. An internal standard of terphenyl was added prior to injection. Water samples were spiked and extracted 3 times by dichloromethane (DCM). The extracts were dried, combined and concentrated to 1 mL before instrumental analysis.

VOC:

The method was based on NIOSH methods 1003, 1500 and 1501 for

the analysis of VOC having boiling points below 200°C in air samples (ref 1). The charcoal tubes were extracted ultrasonically with carbon disulphide (CS₂), a mixture of 5 internal standards were added and the extracts analyzed by GC/MSD, using a mixture of 45 native VOC and 5 internal standards for calibration.

Metals:

Samples preparation and analyses were performed by Lab Services Division, Food Production Branch, Agriculture Canada, Ottawa. The MCE filter was first spiked with an internal standard of Be and Y at 2 ppm. It was then wet-ashed by a 10-mL mixture of concentrated nitric and perchloric acid (4:1) and the digested sample was taken up with 10 mL concentrated hydrochloric acid. Final volume was typically 50 mL.

Analysis and Quantitation

PAH analysis was carried out on a Hewlett Packard (HP) HP5890GC/5971A Mass Selective Detector (MSD). A 30 m DB-5 fused silica column (0.25 mm, 0.25- μ m film) was used to separate the PAH mixture. It was coupled directly to the MSD operated in Selected Ion Monitoring (SIM) mode. Oven temperature was 90°C/min, ramped to 180°C at the rate 20°C/min and to a final temperature of 285°C and held for 10 min at the rate of 7.5°C/min. A 1- μ L aliquot of sample was injected splitless on the GC using a HP 7673 autosampler. A minimum of two ions of each PAH was monitored with a dwell time of 50 ms on a PC-based data station using HP1034B software.

Initially, a Supelco 610M PAH mixture containing 16 PAH compounds was used as calibration standard. Later on, an expanded list of PAH was furnished by using a standard reference material SRM-1491 which has 24 compounds covering the methylnaphthalenes and methylphenanthrenes, which are important constituents of crude oils. Area response of the quantitation ion was corrected by that of the terphenyl internal standard; recoveries of the four surrogate PAH spiked onto samples were monitored to ascertain the integrity of sample during sample workup.

VOC analysis was performed also on the GC/MSD, using a Restek RTX-5 column (crossbonded SE-54 phase, 30-m x 0.32-mm, 0.5- μ m film) for separation of the 45 VOC compounds on the target list. Oven temperature was 30°C/3-min, to 150°C @ 4°C/min and to 220°C/1min @ 8°C/min. The MSD was operated in scan mode from 35-360 amu with a scan rate of 1 scan/sec. Characteristic ions were extracted from each analyte peak from an appropriate time window and the area response was corrected with the 5 internal standards co-injected with the sample.

An ARL 3510 ICP (Inductively Plasma Spectroscopy) was used to perform metal analysis. Calibration standard range was from 0-10 ppm.

C2-C12 VOC analysis was performed by Pollution Measurement Division, River Road Environmental Technology Centre, Ottawa. Approximately 1.2 L of sample air was pre-concentrated on a trap using liquid oxygen, at a sample flow of 40 mL/min for 30 min. The trap was heated up to 100°C, the VOC was backflushed into a GC/MSD. Peak identification was based on retention time as well as spectral matching against a NBS 49000-spectra library (Ref. 2).

Dioxin/furan cumulative samples were spiked with a mixture of ³⁷Cl-labelled DX/DF and soxhlet-extracted in toluene. The raw extract was cleaned using an acid/base-modified silica column, followed by fractionation on a basic alumina column. The DX/DF fraction was recovered using 25% DCM/toluene. Analysis was carried out on a medium/high resolution VG-70S sector GC/MS system, operated at a resolution of 6000 (Ref. 3).

IV. Results and Discussions

PAH in Air/Smoke Samples:

One of the primary objective of the burn study was to investigate the amount of environmentally significant pollutants generated, and could therefore provide basic input parameters necessary to assess the impact to the environment. PAH is known to be present in all combustion processes, and thus is a prime candidate for examination on any incineration process.

Upon reviewing the PAH data for ground samples, it became obvious that none of the filter/XAD samples had any PAH. The reason could be due to inadequate sensitivity of the method or insufficient sampling. Under the described experimental condition, the GC/MSD had a detection limit of 0.05-0.1 ng/ μ L (higher molecular weight PAH had poorer response due to discrimination by the splitless injector). This translated to a 0.1 μ g minimum detectable quantity of PAH per sample, assuming a final extract volume of 1-mL. A typical range of air/smoke sample volume in this burn study was 100-200 L. The overall method detection limit thus became 0.5-1 μ g/cubic meter (CM).

This would seem to be adequate for a typical smoke concentration of 20-330 μ g/CM, assuming a starting PAH concentration of 6000 ppm in the crude oil and a soot yield of 10%; concentration being dependent on the distance from the source (Ref.4). Examination of the exposed filter/sorbent tubes revealed that there was usually very little soot collected. The only plausible explanation for low PAH levels would be

errors in the sampling process. It turned out the location of the ground samplers were not ideal: the smoke plume did not always follow a trajectory that ran close to and parallel to the ground. In fact, for relatively calm days, the smoke plume was observed to angle upwards at a 20-40 degree angle, with the result that the smoke samples collected were not representative of the plume.

The airborne samplers, suspended in the smoke plume by blimps operated by NIST were at a better position. The blimps were manoeuvred in position and tethered to the ground at 100/200 feet locations. However, because of difficulty in manoeuvring the blimp once the burn commenced, coupled with the fact that the payload only allowed the use of low volume personal samplers, only a limited number of PAH runs were made. For those runs, the sampling duration was too short to provide a sufficient sample volume. To illustrate, in the preliminary burns conducted on April 16 and 17, one blimp sample was analyzed to have 4 $\mu\text{g}/\text{CM}$ of phenanthrene. This was barely above the method detection of 2.5 $\mu\text{g}/\text{cu m}$ because the sample volume was only 21 L! In the second run, the sample volume was even less at 12 L, but phenanthrene was detected at 12 $\mu\text{g}/\text{cu m}$, sufficiently above the detection limit of 4 $\mu\text{g}/\text{CM}$. These runs were collected approximately 100 ft downwind of the fire. The concentration, however, was still much lower than anticipated.

PAH in Crude and Residue Samples:

The double silica column cleanup coupled with GC/MSD analysis enabled detection of PAH in crude/residue samples down to 1 μg PAH/g. The chromatogram was almost free from oil background. Resolution of the anthracene/phenanthrene, benzo(a)anthracene/chrysene pair was maintained at 5% and 8% respectively, well within the EPA method 500 series chromatographic criteria (Fig.2). By far the most abundant PAH in the crude oil were the naphthalene and methylated naphthalenes, followed by methylphenanthrenes (Fig.3). The parent PAH were only minor constituents of the total PAH found.

Analyses of various aliquots of the crude taken on different days showed total PAH to be remarkably constant at around 5000 $\mu\text{g}/\text{g}$, with over 90% PAH made up of three rings or less. Residue samples also showed consistent PAH levels but at much lower concentration at about 500 $\mu\text{g}/\text{g}$, despite the different burn conditions and sampling conditions (Fig.4). The chromatograms of the before and after burn had more or less the same profile but depletion of lighter PAH was noticeable. The marked difference was the make-up of PAH: the three rings or less PAH now only constituted about 50% of total. This was consistent with earlier work, demonstrating that there was a shift towards higher-molecular-weight PAH in the residue in soot. The enrichment factor,

however, was only about 2 to 5 instead of 10-20 from bench-scale burn experiments (Ref.5) .

VOC:

Most of the charcoal samples showed appreciable VOC composed mainly of straight-chain hydrocarbons and BTEX. Total VOC ranged from a low of 100 to a high of 4000 $\mu\text{g}/\text{CM}$, with most of them in the 1000-2000 $\mu\text{g}/\text{CM}$. In some runs the 200 feet downwind station collected more VOC than the 100 feet one. This was undoubtedly due to the meandering path of the smoke plume. On one day there was even more VOC in the 50 feet upwind than downwind ones, which was believed to be due to ground turbulence or shift in wind direction.

VOC samples were not analyzed until a few months later after the burn (the recommended holding period is 2 weeks). Analyses of duplicate sample sets showed agreement to be about 25%. In a subsequent QA exercise, comparison with an EPA contract lab showed the range of VOC was largely comparable. Some samples arrived from the field with the protective caps loose, raising concern about the integrity of the samples.

Metals in Filters:

Of the 11 elements measured (Zn, Cd, Pb, Co, Ni, Hg, Mn, Fe, Cr, Mg and V), none were found to be much higher than the detection limit of 1-100 $\mu\text{g}/\text{CM}$. Comparison of the crude/residue oil metals results showed for some metals that there was a slight enrichment of metals in the residue by a factor of 2 to 4. QA studies conducted in-house using the digested samples between Agriculture Canada showed excellent agreement, generally within 10-20%.

Dioxin/furan:

The DX/DF level in the cumulative samples was very low: with about 1 pg/CM of DX and 0.1 pg/CM of DF. The only detectable DX isomer was the higher chlorinated hepta- and octa- species. The concentration and isomer distribution was typical of an urban atmosphere level.

C2-C12 VOC:

The summa canister samples revealed concentration and pattern of VOC consistent with open evaporation of oil products. There was no evidence of formation of new combustion products.

Novel Sampling technique:

This burn study marked the first successful deployment of remote-control (RC) helicopter for air sampling. The helicopter was based on a hobby RC 60-size helicopter extensively modified by incorporating a remote start Gilian pump and strobe light to signal proper operation of

the sampler. With a gross weight of 15 lbs, including a full tank of gas, the flight duration was 15-20 min and an operating range of about 500-1000 ft.

In this particular burn, a flight path was adopted to enter the plume at about 700 feet from the fire so as not to interfere with the blimp operation. As that point, the smoke density was significantly reduced and the recovered sample had just trace levels of PAH in it. Nevertheless, presence of methyl-naphthalenes were detected, proving that the lighter PAHs were vaporised and carried sufficiently far downwind from the burn site. The blades were covered with soot at the end of the flight and were recovered using hexane-soaked swab. The swab was analyzed and had a PAH profile similar to that of the residue and, remarkably, relatively free from the anticipated background interference. This pointed to the interesting possibility of a passive sampling device in future work.

V. Conclusion

An extensive sampling exercise was carried out to sample the pollutants in the smoke plume from a meso-scale in-situ burn experiment. Because the smoke plume did not always impinge on the samplers, the ground samplers did not collect sufficient samples for a definitive analysis. Crude/residue analyses showed the burn resulted in a significant reduction of PAH in the original oil, most of the reduction was thought to be simply evaporation or destruction from combustion. The residue did not have the degree of enrichment of the higher-molecular-weight PAHs as was the case in bench-scale burn experiments.

VOC, C_2 - C_{12} VOC and dioxin/furan measurement likewise did not show high levels of contamination from the burn itself for the same reason mentioned above. Most of the elevated levels of contaminants could probably be due to evaporation of the oil itself. Insufficient sampling was conducted to investigate the background levels from the weathering process.

A novel means of sampling using a RC helicopter was tried out. Although not typical of the scenario the helicopter was envisaged to perform, the exercise was deemed successful and valuable field experience was obtained.

Acknowledgements:

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FIGURE 1

MESOSCALE BURN SAMPLING

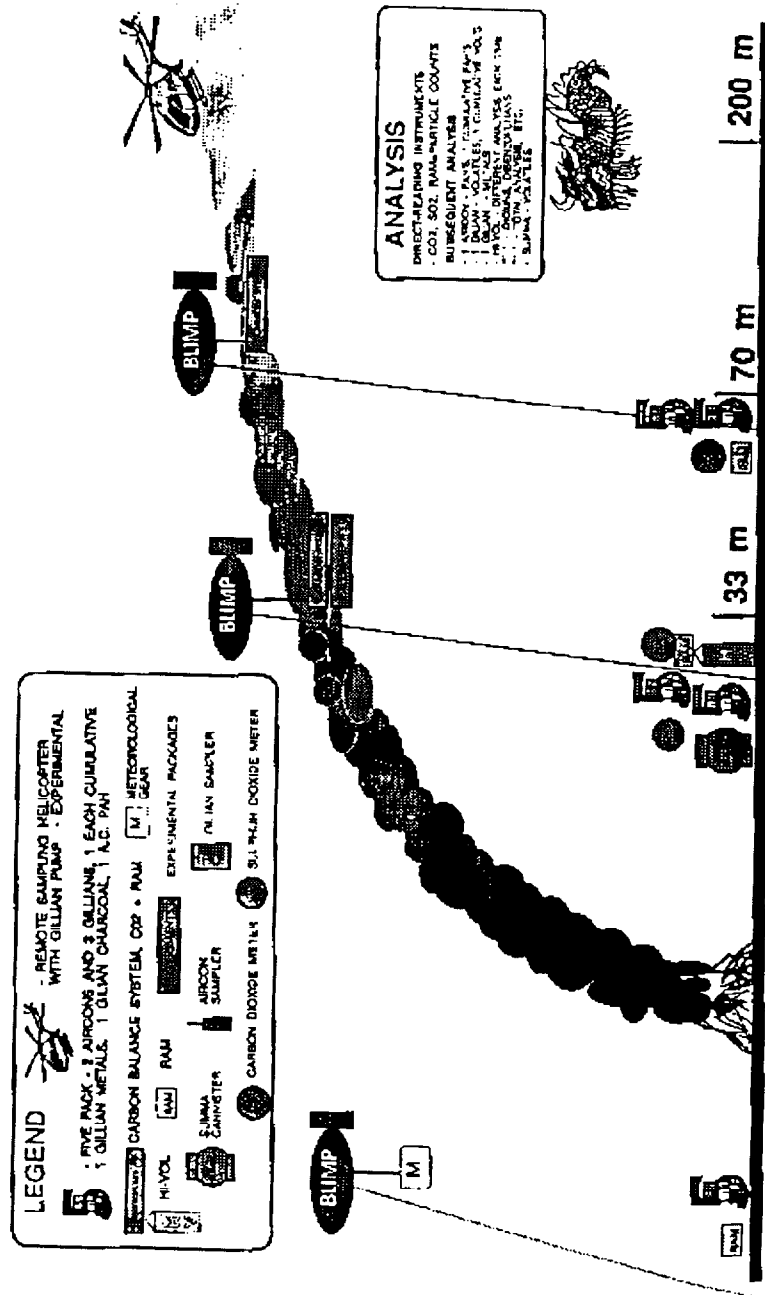


FIGURE 2

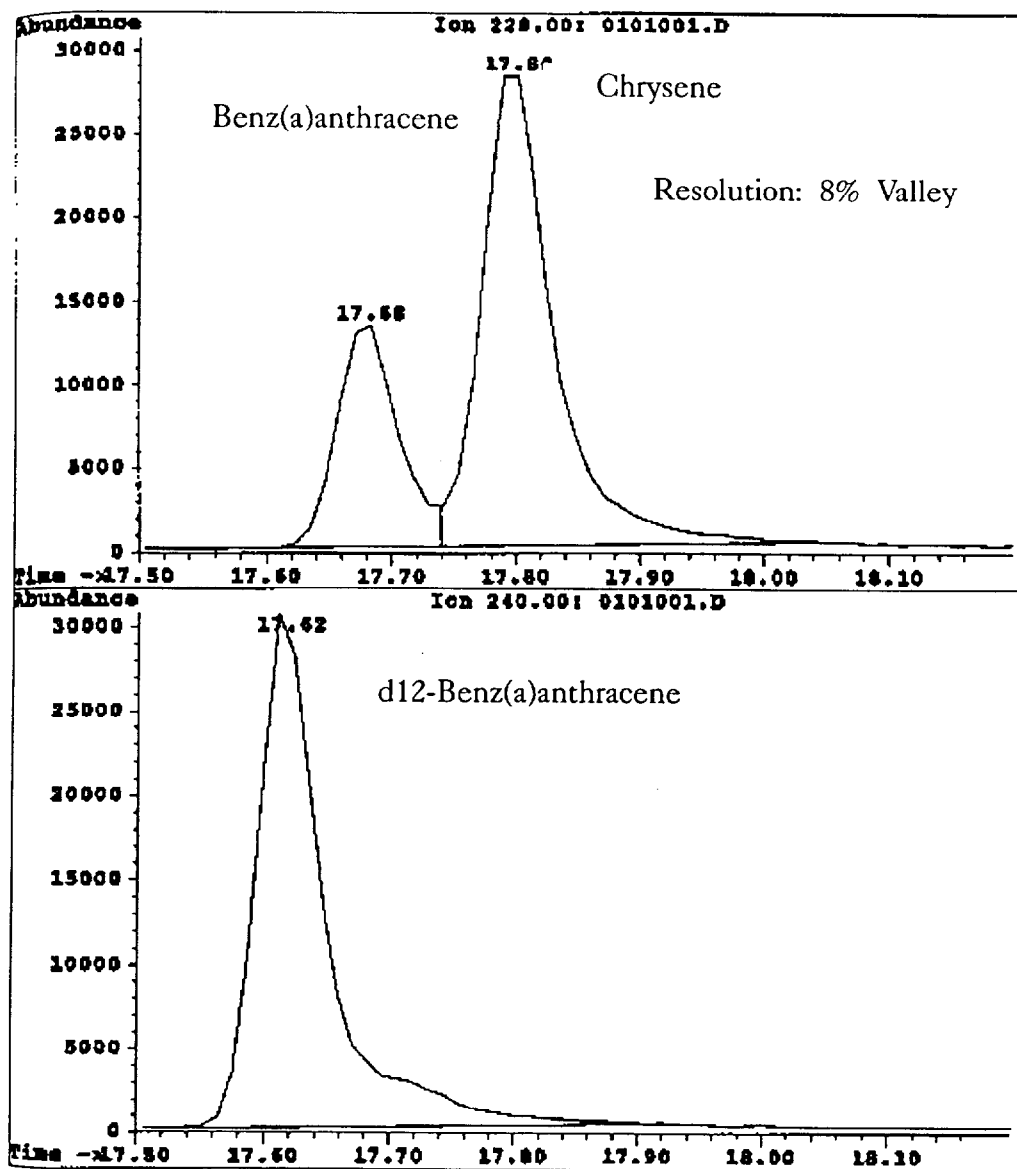


FIGURE 3

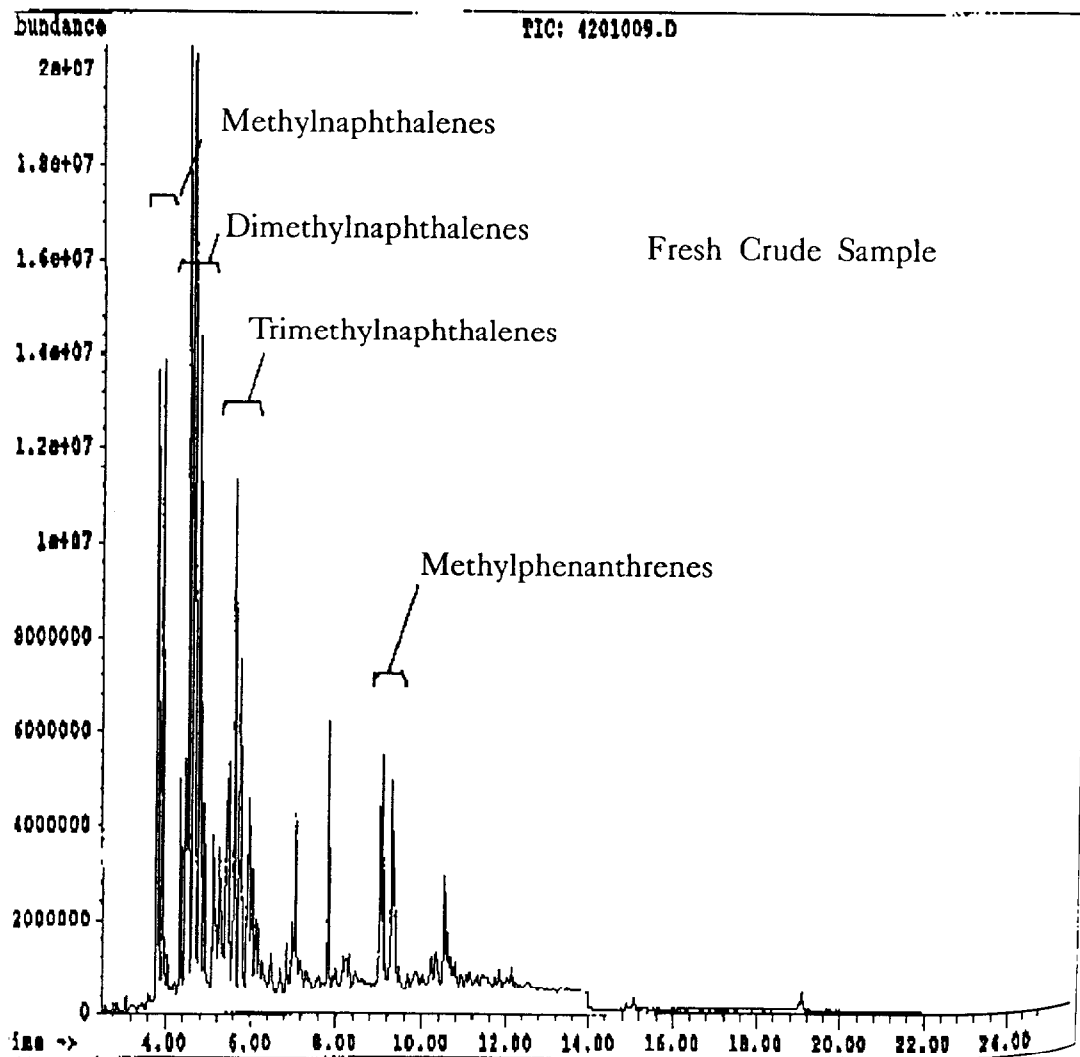


FIGURE 4

