



## Characterization of acid tars

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### ABSTRACT

Acid tars from the processing of petroleum and petrochemicals using sulfuric acid were characterized by gas chromatography/mass spectrometry (GC/MS), inductively coupled plasma/optical emission spectrometry (ICP/OES), differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectrometry, and scanning electron microscopy/energy dispersive X-ray (SEM/EDX) micro-analysis. Leaching of contaminants from the acid tars in 48 h batch tests with distilled water at a liquid-to-solid ratio 10:1 was also studied. GC/MS results show that the samples contained aliphatic hydrocarbons, cyclic hydrocarbons, up to 12 of the 16 USEPA priority polycyclic aromatic hydrocarbons (PAHs), and numerous other organic groups, including organic acids (sulfonic acids, carboxylic acids and aromatic acids), phenyl, nitrile, amide, furans, thiophenes, pyrroles, and phthalates, many of which are toxic. Metals analysis shows that Pb was present in significant concentration. DSC results show different transition peaks in the studied samples, demonstrating their complexity and variability. FTIR analysis further confirmed the presence of the organic groups detected by GC/MS. The SEM/EDX micro-analysis results provided insight on the surface characteristics of the samples and show that contaminants distribution was heterogeneous. The results provide useful data on the composition, complexity, and variability of acid tars; information which hitherto have been scarce in public domain.

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## 1. Introduction

### 1.1. Acid tars

Acid tars are wastes generated during the processing of coal, petroleum, and petrochemicals, which are considered hazardous in most jurisdictions (e.g. [1]). Kolmakov et al. [2] described acid tars as a non-utilizable solid waste with resinous and viscous characteristics and varying flowability. Three processes lead to the generation of acid tars: (i) oil re-refining—the removal of metal impurities from spent lubrication oils using concentrated sulfuric acid; (ii) benzole refining—production of purified fractions of benzene, toluene and xylene (BTX) from crude benzole, a by-product of coal carbonization; and (iii) petroleum fractions refining—the use of concentrated sulfuric acid to remove unsaturated hydrocarbons and sulfur compounds from heavy lubricant fractions to produce white oil used for medicinal, cosmetic and specialized lubrication purposes [3–5]. The initial materials and treatment processes leading to the generation of acid tars are not exactly alike; hence the nature and composition of acid tars differ from process to process. However, the common denominator among these processes

is the use of concentrated sulfuric acid in the cleansing of organic substances [3,6].

Historically, acid tars have been disposed with or without prior treatment in worked out quarries, clay or gravel pits, or landfills, normally referred to as acid tar lagoons [3,7–9]. There are many such disposal sites in the UK and others have been reported in the United States, Canada, Australia, and other European countries including The Netherlands and Russia [10]. This dumping is not environmentally sustainable because of the potential risk posed by the components of acid tars to human and ecological receptors.

Although the quantity of acid tars generated has been greatly reduced due to the development of efficient catalytic processes by the petroleum industry [2,3,11], an effective treatment method is needed for existing acid tar lagoons and for the quantities that are still being generated. Kolmakov et al. [12] reviewed various methods for the processing of acid tars into other products but concluded that none of the approaches are satisfactory; thus the fundamental need for an effective remediation method still remains. Attempted remediation technologies include monitored natural attenuation and excavation and disposal into landfills [13], cement-based stabilization/solidification (S/S) [14], containment using construction materials such as clay/cement/plastic membrane materials [15], incineration in a cement plant/utilization as a fuel substitute [3,12,13], and fluidized bed incineration [16]. However, these technologies have not been well researched and their feasibility and effectiveness remains questionable due to poor tech-

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nical reliability (e.g. natural attenuation), difficulties in materials handling due to the sticky consistence of acid tars and their corrosive nature (e.g. excavation, S/S, and incineration), and the potential for undesirable emissions (incineration).

### 1.2. Composition of acid tars

One hindrance to developing an effective remediation method for acid tars is the lack of detailed data about their composition. According to Kolmakov et al. [17], the composition of acid tars has not been well studied; available data only report general properties, measuring the percentage of organic compounds, water, and acid. More detailed compositional data is also important in determining the toxicity and potential risk that acid tars could pose to human, animal and environmental receptors given a plausible pathway.

Acid tars contain a broad range of toxic substances including sulfuric acid, organic compounds and heavy metals. Frolov et al. [18] reported that fresh acid tars contains between 25% and 65% sulfuric acid, a variable organic content of 34–94% resin/oil/asphaltene substances, 5–60% sulfonic acids, and 1–6% carboxylic acids, and alkali metals originating from caustic waste co-disposed with the acid tars. Puring et al. [19] carried out a study on the components of dumped acid tars. They reported variable depth-dependent percentages of sulfuric acid, sulfonic acid, carboxylic acids, and unsulfonated organic matter. In another work [20], it was reported that fresh acid tars contains mainly sulfuric and sulfonic acid, while acid tars that have been dumped for several years contained predominantly weak carboxylic acids. A group analysis of acid tars [17] using various stages of solvent extraction and column chromatography also revealed that the studied sample contained considerable amounts of asphaltenes, carbenes, carboids, and hydrocarbons, and low amounts of resins and other impurities. The hydrocarbon fraction was further separated into alkylbenzene, PAHs, and naphtheno-aromatic hydrocarbons; however, the individual compounds in these fractions were not characterized.

All reported studies stopped at the group analysis of acid tars; no literature was found on the detailed analysis of individual organic compounds or metal elements present in acid tars. There are no specific techniques recommended for acid tar analysis; however, it might be possible to adapt techniques recommended for other materials with adequate consideration given to the compounds of interest. For example, Nesbit et al. [21] stated that gas chromatography by simulated fractional distillation, class separation by thin layer chromatography/flame ionisation detection, and thermogravimetric analysis could be adapted to characterize the organic fractions of tarry waste. Also, methods for bitumen, crude oil, and heavy petroleum fraction characterization such as asphaltene precipitation using n-alkane solvents (e.g. [22–27]) could be adapted for acid tars. Liu et al. [28] used a saturates, aromatic, resin, and asphaltene (SARA) separation technique [29] to analyse coal tar from the pyrolysis of coal asphaltenes. Saturates and aromatics from this separation were further separated into individual organic compounds using gas chromatography. Similarly, Philip et al. [30] used gel-permeation chromatography, vacuum distillation, SARA separation, elemental analysis, nuclear magnetic resonance spectroscopy, and gas chromatography/mass spectrometry (GC/MS) to study the components of heavy fuel oils. Other possible analytical techniques include inductively coupled plasma/atomic emission or mass spectrometry (ICP/AES or ICP/MS), which could be used for the qualitative or quantitative analysis of metals following extraction by acid digestion; differential scanning calorimetry (DSC), which is useful in the quantitative and qualitative determination of the various phase transitions occurring in a material subjected to temperature variation, thus providing data on the physical and chemical nature of the components of the material; Fourier transform infrared (FTIR) spectrometry, useful in the qualitative and

semi-quantitative determination of the organic functional groups present in a material, and to complement results from GC/MS analysis; and scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDX), which can provide data on the morphology and mineralogy characteristics of a material, and can also be used to qualitatively and semi-quantitatively determine the elemental components of the material, at the microscale, and to complement results from ICP/AES or ICP/MS. A batch leaching procedure, such as BS EN 12457, can be used to assess the solubility and/or affinity of contaminants for the aqueous phase, which contributes significantly to the environmental risk posed by waste materials.

### 1.3. Aims and objectives

In preparation for a laboratory study of S/S treatment of acid tars, a series of laboratory experiments was conducted to thoroughly characterize two real acid tar samples obtained from the petroleum industry, and to investigate the leaching of organic and inorganic components from them. Adapted analytical techniques include GC/MS, ICP/AES, DSC, FTIR spectrometry, and SEM/EDX spectrometry. The result is expected to demonstrate the applicability of these techniques and provide useful decision-making information for risk assessment and treatment of acid tars.

## 2. Materials and methods

### 2.1. Acid tar samples

Two different samples of acid tars generated from petroleum processing were provided for study without further information by an anonymous source. Physical observation of the samples show that one of the samples (designated as D) is a very dark resinous oily material with a very strong offensive odour, while the other (designated as G) is a gray to dark grainy material with less oily content and a less offensive odour.

### 2.2. Physical characterization

The acid tar samples were characterized as follows, using separate grab samples for each measurement:

- Bulk density was estimated in triplicate by weighing compacted volumes in a measuring cylinder
- Moisture content was determined in triplicate by heating pre-weighed samples at 105 °C to constant weight.

### 2.3. Chemical characterization

Fig. 1 shows the flow chart for the chemical analysis of the acid tars. Grab samples of each acid tar were split and characterized using adaptations of two methods: the US Environment Protection Agency Test Methods for Evaluating Solid Waste (SW-846) Physical/Chemical Methods and SARA separation.

#### 2.3.1. USEPA test methods for evaluating solid waste [31]

A 2.5 g grab sample of each acid tar was subjected to soxhlet extraction (Method 3540C) using a 1:1 volume of acetone and dichloromethane. Although the method stipulated that 10 g of sample should be used, a smaller sample was used because initial extraction of 10 g of tar D showed that complete extraction was not achievable due to the high proportion of organic compounds. Copper filings were added to the samples for sulfur removal. The extracts were then separated into aliphatic, aromatic, and polar fractions using hexane, dichloromethane and methanol respectively by Method 3611B (alumina column cleanup and separation

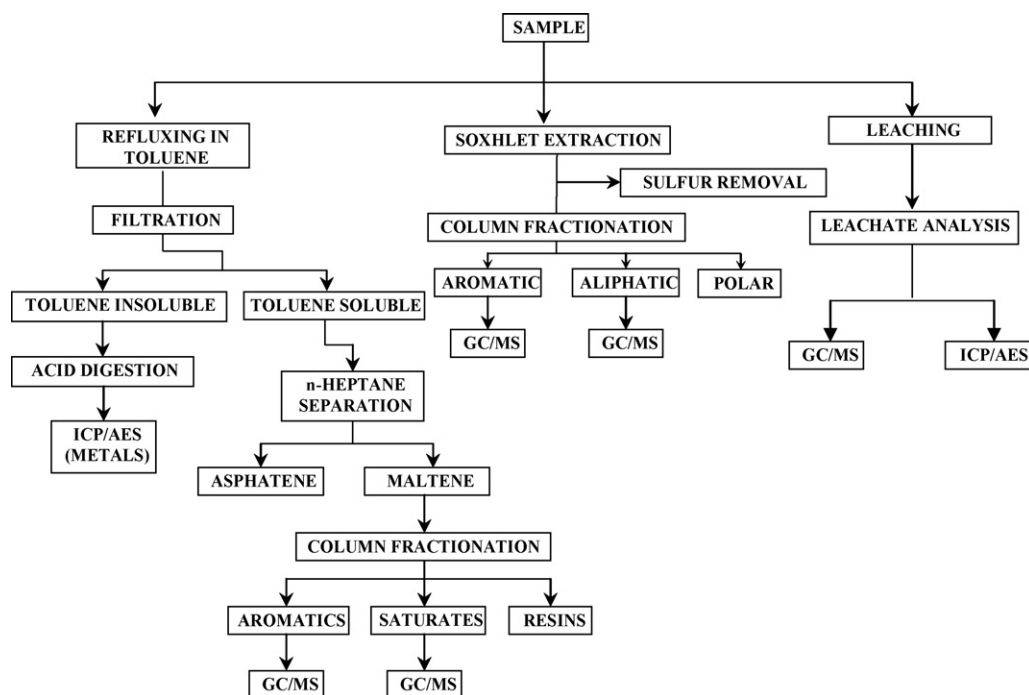


Fig. 1. Acid tars analysis protocol.

of petroleum wastes). Prior to analysis by GC/MS, solvent was removed from each fraction in a fume cupboard and the weight of each fraction was determined.

### 2.3.2. SARA separation [29]

A 4 g sample of each acid tar was separated into toluene soluble and insoluble fractions by refluxing in 300 mL of hot toluene for 16–24 h. After refluxing, the toluene soluble fraction was vacuum filtered using a 0.7  $\mu\text{m}$  Fisher-brand glass micro-fibre filter paper. The toluene insoluble filtration residue was dried in a fume cupboard and preserved for metal analysis while solvent was removed from the toluene soluble fraction using a rotary evaporator. The toluene soluble fraction was then separated into asphaltene and maltenes using *n*-heptane precipitation. The asphaltene fraction was dried in a fume cupboard and preserved for further analysis while the maltene fraction was separated into saturates, aromatics, and resin through silica gel packed column chromatography using *n*-hexane, 20% (v/v) dichloromethane/*n*-hexane, and 50% (v/v) dichloromethane/methanol respectively. Prior to analysis by GC/MS, solvent was removed from each fraction in a fume cupboard and the weight of each fraction was determined.

### 2.3.3. Aqueous pH and base neutralization characteristics (BNC)

The pH of aqueous extracts of the acid tar samples at liquid-to-solid (L/S) ratios of 5, 10, 20, and 40, was measured after a contact time of 48 h, without filtration, using a Jenway Model 4330 conductivity/pH meter equipped with a double junction Ag/AgCl reference glass electrode.

The base neutralization capacity of the acid tar samples was determined by mixing a constant weight of acid tars with increasing doses of hydrated lime, resulting in a dry mass of  $\text{Ca}(\text{OH})_2$ /dry mass of acid tar ranging from 0.25 to 4.0, at increments of 0.24, with a L/S ratio of 20. The samples were agitated end-over-end in a rotary extractor for 24 h and the pH of the supernatant was measured.

### 2.3.4. Metal analysis

The metal contents of the toluene insoluble fractions were determined in triplicate by acid digestion of 3 separate grab

samples of 0.5 g using nitric acid, hydrofluoric acid, and perchloric acid [32]. The concentrations of metals were determined by analysing the digestion filtrates using a JY Horiba Ultima 2 ICP/AES.

### 2.3.5. Leaching studies

A modified BS EN12457-2 batch leaching test for granular wastes was carried out on the acid tar samples. Duplicate experiments of 20 g dry mass of each of the acid tar samples was carried out at ambient temperature (21–25 °C) using 200 mL of deionised water to obtain a L/S ratio of 10. Granular samples of particle size between 1 and 4 mm were contained in a Teflon-sealed glass bottle and were agitated end-over-end in a rotary extractor for 48 h at a speed of 30 rpm. At the end of the experiment, the samples were vacuum filtered using a 0.7  $\mu\text{m}$  Fisher-brand glass micro-fibre filter paper. The filtrates were stored for a maximum of 7 days at a temperature below 4 °C prior to extraction of leached hydrocarbons using dichloromethane liquid–liquid extraction. A set of similar leaching experiments were conducted in duplicate at L/S ratio of 5, 10, 20, and 40 using plastic bottles; leachates from the L/S = 10 samples were analysed for leached metals by ICP/AES, while the L/S = 5, 10, 20, and 40 were analysed for leached sulfates using a Leco sulfur analyser.

### 2.3.6. GC/MS analysis

Duplicate GC/MS analyses of 1 mL solutions of the aliphatic and aromatic fractions from soxhlet extraction, SARA separation, and liquid–liquid extracts, spiked with internal standards were performed using a PerkinElmer Clarus 500 gas chromatograph coupled to a PerkinElmer Clarus 500 mass spectrometer equipped with split/splitless injection. Method 8270C (semi-volatile organic compounds by GC/MS) was adapted for the analyses. Prior to analysis of samples, blank GC/MS runs were performed to ensure that there were no interferences from the analytical system, glassware and reagents. Blank analyses were also performed in between extract analyses to ensure that there was no carryover between analyses. In order to obtain a consistently quantifiable chromatograph, the GC was operated in the splitless mode during the injection of sam-

ples and the split vent opened at a ratio 50:1 after 1 min, for the liquid–liquid extracts. For the analysis of the fractions from soxhlet extraction and SARA separation, the GC was operated in the split mode at a ratio of 50:1 at all times. Helium gas flowing at 30 cm/s was used as the carrier gas. The temperature of the 30 m by 0.25 mm capillary column was programmed at 40 °C for 6 min and then ramped to 320 °C at 10 °C/min, after which it was held at 320 °C for 6 min, for a total running time of 40 min. The mass spectrometer was operated in a the full scan mode [total ion current chromatograph (TIC)], scanning between 50 and 450 m/z with an inlet line temperature of 250 °C and source temperature of 200 °C and an electron ionisation (EI) mode of 70 eV. Calibration standards were also analysed using the same conditions as were used for the samples. The chromatograph of the calibration standard was used to determine the response factors for the analytes of interest. The concentrations of compounds of interest were then determined from the resultant chromatographs by comparing their responses with those for the internal standards. Attempts were made to identify unknown compounds using the TurboMass library software of the GC/MS by comparing unknown spectra with the library of known spectra.

## 2.4. Thermal analysis

### 2.4.1. Loss-on-ignition

To estimate the organic carbon content, loss-on-ignition was measured in triplicate by igniting the dried samples of acid tar in a furnace at 550 °C for 6 h; the residues remaining after 550 °C were further ignited at 950 °C for another 6 h to determine the inorganic carbon content.

### 2.4.2. Differential scanning calorimetry (DSC)

Changes in the acid tar samples as a function of increasing temperature were studied using a TA Instruments DSC Q100 calorimeter. Analyses were conducted on samples weighing between 10 and 20 mg packed and crimped in an aluminium pan and cover, at a heating rate of 10 °C/min under flowing nitrogen gas (30 mL/min) and temperature ramping from 35 °C to 550 °C. Powdered alumina was used as the reference sample.

## 2.5. Microstructural analysis

### 2.5.1. Fourier transform infrared (FTIR) spectrometry

FTIR analysis of as received acid tar samples and asphaltene fractions was performed using a Thermo Nicolet Nexus 670 FTIR spectrometer. Optically transparent discs were prepared by grinding and thoroughly mixing approximately 0.01 g of each of the acid tar samples with approximately 0.2 g of potassium bromide (KBr). About 0.02 g of the mixture was then compressed in a mini-press to form the transparent discs. Infrared spectra were obtained within the region of 4000 and 400 cm<sup>-1</sup> with a spectral resolution of 4 cm<sup>-1</sup> and aperture size of 100 μm. To ensure an acceptable signal-to-noise ratio, 128 scans were collected for each sample. Air was used as the background spectra.

### 2.5.2. Scanning electron microscopy/energy dispersive X-ray (SEM/EDX) micro-analysis

Micrographs and energy dispersive X-ray spectra were collected for each sample using a Hitachi S-4500 II cold field emission SEM instrument coupled to an EDAX energy dispersive X-ray micro-analyser equipped with a compact detector unit. SEM imaging was carried out at an operating voltage ranging between 10 and 20 kV and an emission current of 16 μA.

## 3. Results and discussion

### 3.1. Physical properties

The physical properties of the two acid tars are summarized in Table 1. The difference in the density between the two samples suggests that they have different compositions. The bulk density results are within the range reported in other works (e.g. [4,6,33]). The relatively high density of acid tar has been attributed in part to its sulfuric acid content (density 1.96 g/cm<sup>3</sup>) [13]. The moisture content of acid tars has been reported to be in the range of 2–40% depending on the type, with those originating from white oil production (petroleum refining) typically having moisture content between 3% and 10% [3], which is similar to the moisture contents of 7–10% obtained here.

### 3.2. Chemical characteristics

#### 3.2.1. Organic contents

The results of the group fractionation results obtained by the USEPA SW-846 test methods and SARA separation are summarized in Table 1. Acid tar D contains a high proportion of organic compounds, as shown by the loss-on-ignition, as well as the DCM/acetone extractable and toluene soluble fractions. Acid tar G contains a higher proportion of inorganic compounds. The organic carbon contents measured by loss-on-ignition exceed those determined by the two fractionation methods. It seems that the samples contain inorganic substances that were ignited below 550 °C but not extractable by organic solvents.

Figs. 2 and 3 show the chromatographs for the aromatic and aliphatic fractions obtained via the USEPA SW-846 test methods. D contains more detectable organic compounds compared to G. A combination of GC/MS library searches, comparison of retention times with those of standard samples, and comparison of detected spectra with those of the TurboMass NIST library and those from an online spectral database: spectral database of

**Table 1**  
Characteristics of acid tars.

Properties	D	G
Bulk density (g/cm <sup>3</sup> )	1.12 ± 0.1	1.42 ± 0.1
Moisture content (% wet mass)	9.30 ± 1.1	7.25 ± 1.0
pH		
L/S=5	0.84 ± 0.02	0.87 ± 0.07
L/S=10	1.03 ± 0.05	1.06 ± 0.04
L/S=20	1.18 ± 0.03	1.23 ± 0.01
L/S=40	1.42 ± 0.02	1.55 ± 0.03
Loss-on-ignition (% dry mass)		
Organic carbon	95.1 ± 0.6	40.5 ± 2.3
Inorganic carbon	0.7 ± 0.1	5.4 ± 0.2
Fractional composition		
USEPA SW-846 test methods		
DCM/Acetone extraction residue (% dry mass)	25.8 ± 0.3	82.4 ± 0.3
DCM/Acetone extractable (% dry mass)	74.2 ± 0.4	17.6 ± 0.3
Aliphatic compounds	6.4 ± 0.5	0.3 ± 0.1
Aromatic compounds	10.1 ± 0.4	0.5 ± 0.1
Polar compounds	3.9 ± 0.1	1.9 ± 0.1
% not eluted	53.8 ± 0.3	14.9 ± 0.3
SARA separation		
Toluene insoluble (TI) (% dry mass)	48.2 ± 0.5	94.6 ± 0.6
Toluene soluble (TS) (% dry mass)	51.8 ± 1.1	5.4 ± 0.5
Asphaltene	19.3 ± 0.6	2.3 ± 0.2
Maltene	32.5 ± 1.5	3.1 ± 0.3
Saturated compounds	14.5 ± 0.6	0.5 ± 0.1
Aromatic compounds	16 ± 1	0.3 ± 0.1
Resin	0.5 ± 0.02	1.8 ± 0.1
% not eluted	1.1 ± 0.03	0.5 ± 0.1

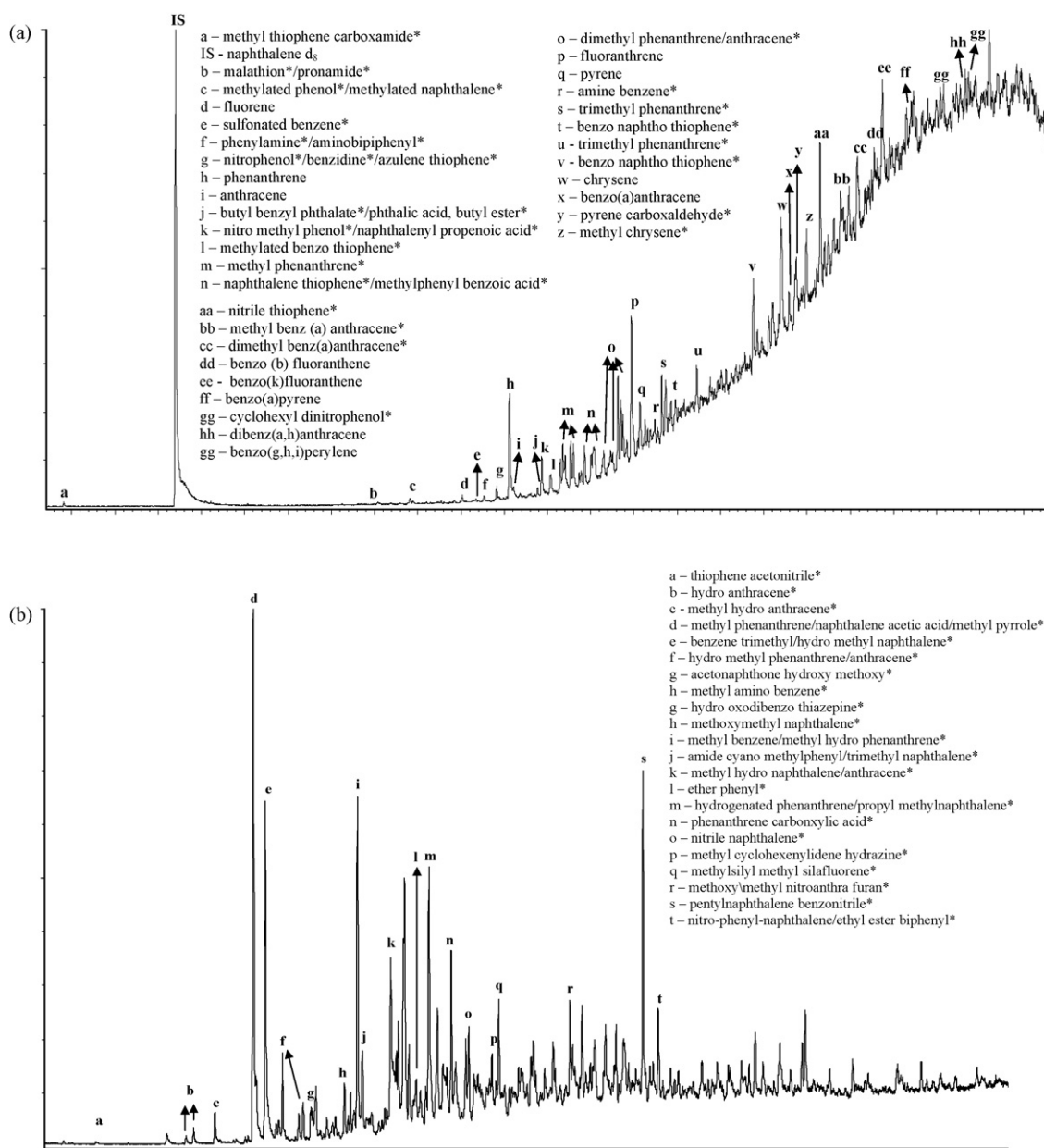


Fig. 2. (a) Chromatograph for aromatic fraction of acid tar D; \*tentative identification. (b) Chromatograph for aromatic fraction of acid tar G; \*tentative identification.

organic compounds (SDBS) [34] was used to identify and suggest probable functional groups for compounds detected in each fraction. Results suggested that the samples contain various saturated and unsaturated aliphatic hydrocarbons, cyclic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), organic acids (sulfonic acids, carboxylic acids, and aromatic acids), phenyl, nitrile, amide, furans, thiophenes, pyrroles and phthalates.

Analyses of the aromatic fractions showed that D contains twelve of the 16 USEPA's priority PAHs, though none of these was detected in G. Analysis of the aliphatic fractions revealed the presence of saturated hydrocarbons from C<sub>14</sub> to C<sub>36</sub> in both samples. Unsaturated and branched chained aliphatic hydrocarbons were also present in the aliphatic fractions.

Apart from the organic acids, other organic groups detected are similar to those reported to be present in similar materials such as ash coal tar, coal tar pitch, heavy oil residues, crude oil, and bitumen. For example, Herod and Kandiyoti [35] reported the presence of furans, PAHs, nitrile, and thiophenes in coal tar pitch. Similarly,

ATSDR [36] reported the presence of these organic groups in coal tar and coal tar pitch. Lazaro et al. [37] also reported the presence of phenyl, alkanes, methylated PAHs, furans, and thiophenes in tar obtained from co-pyrolysis of waste lubricating oil and coal. Alkanes, alkenes, and thiophenes have also been reported to be present in asphalt samples [38]. Similarly, Philip et al. [30] reported the presence of saturated hydrocarbons up to C<sub>32</sub> in heavy fuel oil; they also reported the presence of phenyls and PAHs in the aromatic fraction of this sample.

It is possible that some of the compounds detected in the samples are products of chemical reactions occurring between the various components of acid tars. For example, sulfonic acids could be formed when aromatic compounds react with sources of sulfur trioxide, e.g. concentrated sulfuric acid. Likewise, heterocyclic aromatic compounds such as furans, thiophenes, and pyrroles could be formed by the replacement of one of the ring carbons in an aromatic compound with oxygen, sulfur, and nitrogen respectively [39]. Condensation reactions are also possible, Frolov et al. [20] reported

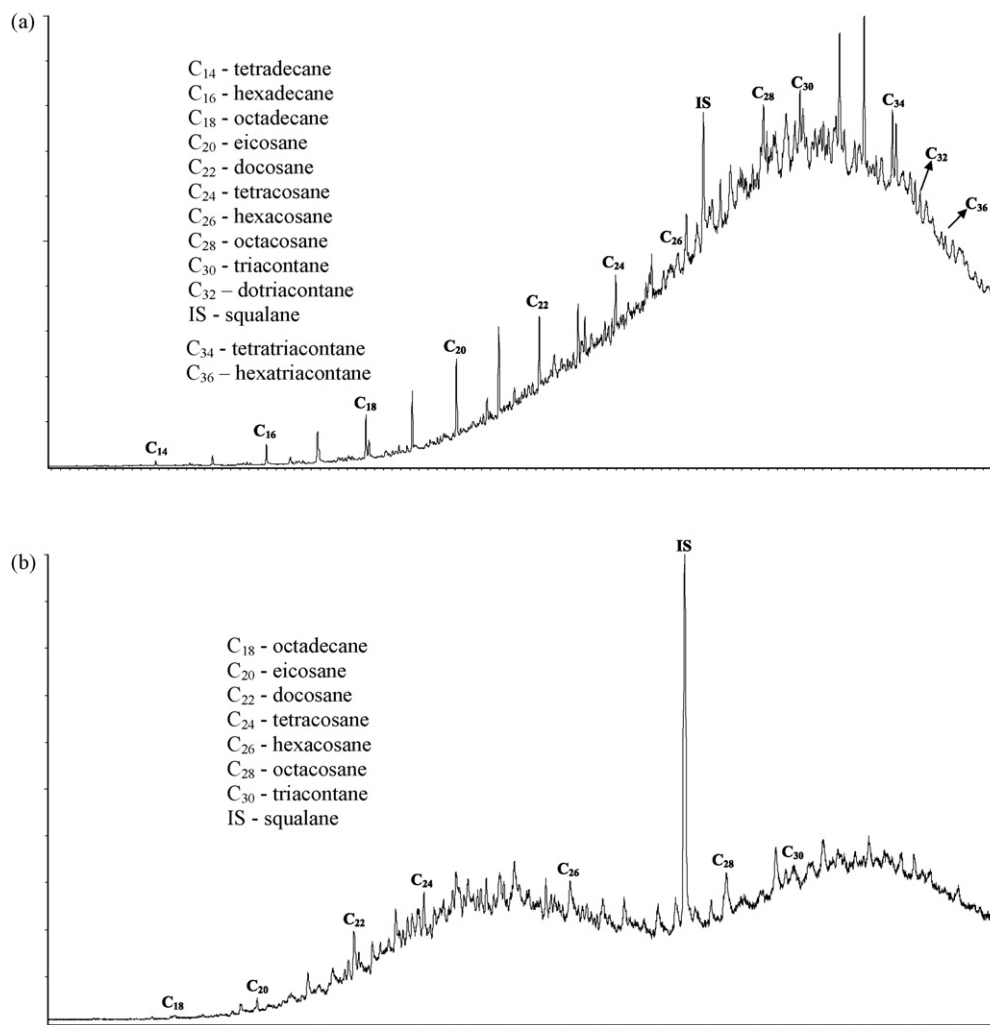


Fig. 3. (a) Chromatograph for aliphatic fraction of acid tar D. (b) Chromatograph for aliphatic fraction of acid tar G.

on the possibility of acid hydrolysis and dehydrogenative oxidation of disulfonic acids in fresh acid tars, leading to condensation of monosulfonic acids to disulfonic acids.

The quantification results for the detected aliphatic hydrocarbons and PAHs in the samples from USEPA SW-846 test methods are presented in Table 2. D contains considerably higher concentrations of aliphatic and aromatic hydrocarbons when compared to G. Although G does not contain any of the USEPA's priority PAHs, it contains several other aromatic hydrocarbons which could not be quantified due to lack of standard solutions for these compounds. The low concentrations of organic compounds in G are consistent with the loss-on-ignition result, which shows that G contains predominantly inorganic compounds. Silicate organic compounds were detected in the aromatic fractions of G suggesting the possibility of G being an acid tar contaminated soil, rather than a pure acid tar.

### 3.2.2. pH and base neutralization capacity

The pH values for distilled water extracts of the acid tars show that the two samples are highly acidic with values less than 1 at L/S ratio of 5; pH values at higher L/S ratios are suggestive of dilution of a strong acid, without buffering. This low pH indicates that the acid tars were from white oil production [4,13]. Fig. 4a shows a plot of pH against meq of OH<sup>-</sup>/g of acid tar in the BNC experiment; addition of less than 6.6 meq of OH<sup>-</sup>/g acid tar completely neutralized the acid present in the tar, in a strongly exothermic reaction. Results for

titration of NaOH against leachate from acid tars [40] show several plateaus at different doses of NaOH (Fig. 4b); it was suggested that this is an indication of a complex buffering system likely due to large range of acid species [13]. The increments of base addition in Fig. 4a were too large to reveal similar details.

### 3.2.3. Metal contents

Table 2 summarizes the quantification results for the metals detected in the two samples. The results show that lead and iron were the dominant metals. D shows a relatively higher concentration of lead, while Fe was dominant in G. The concentration of metals in any given acid tar is depended on the process leading to its generation. Acid tars from spent lubricant re-refining tend to have higher metal concentrations due to wear and tear from metallic parts during lubrication.

### 3.2.4. Leaching studies

Hydrocarbon and metal leaching results are also summarized in Table 2, which shows that some organic compounds present in the samples were not measurably leached out. Only 4 of the 12 priority PAHs present in D were leached out. Aliphatic hydrocarbons from C<sub>18</sub> to C<sub>28</sub> leached out of both samples while leaching was not detected for higher molecular weight hydrocarbons. It has been reported that the solubility of aliphatic hydrocarbons is related to their molecular mass [41]. Generally, hydrocarbons with higher molecular mass are less soluble, possibly due to a

**Table 2**  
Total and leached concentrations of hydrocarbons and metals.

Element/compound	Concentration in samples (mg/kg of acid tar)		Concentration leached (mg/kg of acid tar) (leachate pH = 1.1–1.3)	
	D	G	D	G
<b>Aliphatics hydrocarbon</b>				
Decane C <sub>10</sub>	nd	nd	nd	nd
Dodecane C <sub>12</sub>	nd	nd	nd	nd
Tetradecane C <sub>14</sub>	1.0–1.4	nd	nd	nd
Hexadecane C <sub>16</sub>	4.6–5.7	nd	0.004–0.008	nd
Octadecane C <sub>18</sub>	9.9–10.7	0.03–0.05	0.046–0.052	0.001–0.003
Eicosane C <sub>20</sub>	18.0–19.1	0.80–0.88	0.071–0.081	0.020–0.026
Docosane C <sub>22</sub>	15.8–16.8	0.42–0.44	0.070–0.078	0.018–0.022
Tetracosane C <sub>24</sub>	13.0–13.8	0.28–0.30	0.054–0.060	0.014–0.020
Hexacosane C <sub>26</sub>	16.9–17.5	0.79–0.83	0.058–0.064	0.016–0.022
Octacosane C <sub>28</sub>	5.8–6.2	0.18–0.22	0.044–0.050	0.008–0.012
Triacontane C <sub>30</sub>	12.2–13.6	0.37–0.43	nd	nd
Dotriacontane C <sub>32</sub>	5.8–6.8	0.01–0.02	nd	nd
Tetracontane C <sub>34</sub>	11.0–12.2	nd	nd	nd
Hexatriacontane C <sub>36</sub>	1.8–2.2	nd	nd	nd
<b>PAHs</b>				
Naphthalene	nd	nd	nd	nd
Acenaphthylene	nd	nd	nd	nd
Acenaphthene	nd	nd	nd	nd
Fluorene	0.11–0.15	nd	nd	nd
Phenanthrene	3.70–4.90	nd	0.010–0.016	nd
Anthracene	0.08–0.2	nd	0.001–0.003	nd
Fluoranthene	4.4–6.6	nd	0.006–0.010	nd
Pyrene	0.29–0.41	nd	0.001–0.005	nd
Chrysene	0.06–0.08	nd	nd	nd
Benzo (a) anthracene	1.6–2.0	nd	nd	nd
Benzo (b) fluoranthene	0.7–1.1	nd	nd	nd
Benzo (k) fluoranthene	nd	nd	nd	nd
Benzo (a) pyrene	0.19–0.33	nd	nd	nd
Indeno (1,2,3,cd) pyrene	0.18–0.26	nd	nd	nd
Dibenz (a, h) anthracene	0.07–0.09	nd	nd	nd
Benzo (g,h,i) perylene	0.17–0.23	nd	nd	nd
<b>Metals</b>				
Arsenic (As)	nd	nd	nd	nd
Boron (B)	10.7 ± 0.5 <sup>a</sup>	17.2 ± 2 <sup>a</sup>	2.7–3.1	1.7–1.9
Cadmium (Cd)	0.5 ± 0.2 <sup>a</sup>	20.4 ± 0.2 <sup>a</sup>	nd	0.23–0.27
Chromium (Cr)	5.0 ± 0.1 <sup>a</sup>	nd	0.32–0.38	nd
Iron (Fe)	1200 ± 15 <sup>a</sup>	6200 ± 90 <sup>a</sup>	31.2–31.8	80.0–86.1
Manganese (Mn)	9.5 ± 0.7 <sup>a</sup>	75 ± 15 <sup>a</sup>	0.18–0.28	0.9–2.3
Lead (Pb)	2420 ± 2 <sup>a</sup>	190 ± 22 <sup>a</sup>	31.0–33.0	6.2–6.8
Vanadium (V)	nd	nd	nd	nd
Zinc (Zn)	63 ± 8 <sup>a</sup>	nd	1.2–2.0	nd

nd: not detected.

<sup>a</sup> Standard deviation.

reduction in polarity with increased molecular mass [42]; hence reducing their tendency to leach out of the solid phase. Lassen et al. [43] related solubility to leaching of aromatic hydrocarbons and reported greater leaching for aromatic hydrocarbons with higher solubility. A comparison between the two samples show that although D had higher concentrations, the amount of leached hydrocarbons was higher for G. Based on the fractional composition and LOI results of the two samples, D contains mainly hydrocarbons and other organic carbon, while G has a high proportion of inorganic materials, suspected to be soils. Aliphatic hydrocarbons and PAHs will have a higher affinity for organic than inorganic materials, resulting in less leaching from D than G.

All metals detected in the samples were leached at measurable concentrations. Given the extremely low leachate pH of 1, it is remarkable that the leached amounts of metals are only a small fraction of the total amounts obtained by full digestion of the sample. This could be due to inadequate contact between the metal content of the samples and water, as a result of aggregation and oil coating of the waste particles.

Fig. 5 shows the concentrations of leached sulfates at the different L/S ratios. It indicates that sulfate leaching is governed by dilution as the total amounts leached were similar when con-

verted to mg/kg, and this can be attributed to the high solubility of sulfates.

The concentrations of leached hydrocarbons and metals are consistent with listing of acid tars as hazardous wastes [1,44]. PAHs, including the USEPA priority ones have been reported to be carcinogenic, mutagenic, and teratogenic [45]; furthermore, aliphatic hydrocarbons have been reported as eyes, skin and respiratory tract irritants and could potentially disrupt the central nervous system [46].

### 3.3. Thermal analysis

The DSC results are presented in Fig. 6, which shows heat flow curves as a function of temperature for acid tars D and G. Features of the curves indicate physical or chemical transitions in response to heating. The scans further support conclusions regarding the difference in the composition of the two acid tar samples based on the loss-on-ignition and chemical extraction results. While D shows eight different transition regions (a, b, d, e, f, h, i, j and k), G shows only three regions (c, d, and g). It can be concluded that G is a less complex material than D. Shishkin [47] reported that the different hydrocarbon constituents of a crude oil or residue occupy definite

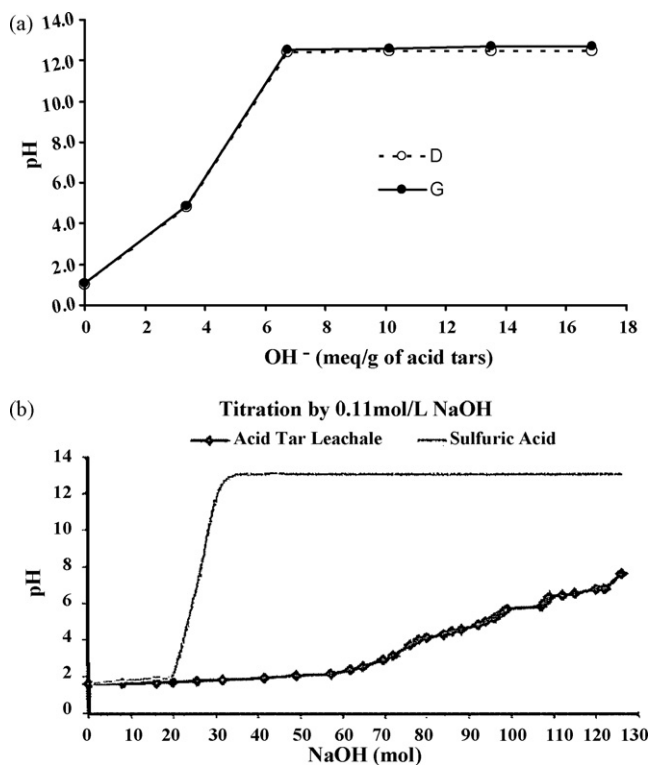


Fig. 4. (a) Base neutralization capacity of acid tar. (b) Titration of NaOH against acid tar leachate [13].

regions on a DSC scan and can be used to identify the components. Karacan and Kok [48], in their work on the DSC analysis of crude oil, also reported that the pyrolysis mechanism for the various components is dependent on the chemical nature of such components and follows its own reaction pathway independent of the presence of other components. Kok and Iscan [49] and Verkocy and Kamal [50] have reported that DSC scans of crude oil show at least three regions of chemical reactions. Results obtained by Shishkin [47] and Kok and Karacan [51] shows that transition regions at lower temperatures correspond to volatilization of the lighter crude oil fractions while those at higher temperature corresponds to the thermal breakdown of heavier fractions such as resins and asphaltene. Hence, it follows that G contains no or very low concentrations of high molecular weight constituents as no transition phase was

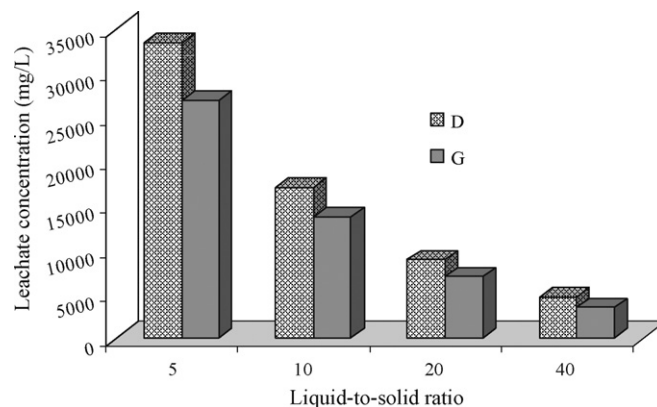


Fig. 5. Concentration of sulfate in leachate at different L/S ratios.

observed at higher temperature. D shows three peaks above 300 °C, indicating the presence of high molecular weight hydrocarbons, as well as five peaks at lower temperatures (<250) indicating the presence of different types of lighter hydrocarbon constituents. These results accord with the results obtained by SARA separation and GC/MS analysis.

### 3.4. Microstructural analysis

#### 3.4.1. Fourier transform infrared (FTIR) spectrometry

FTIR analysis was conducted on the two samples of acid tars and the asphaltene fraction from SARA separation of D. The results (Fig. 7) also confirm the differences between the two samples. Three differences observed between D and G include the spectrum band between 1100 and 1000 cm<sup>-1</sup> (spectrum n) in G which was not observed in D, the broad spectrum between 3700 and 2600 cm<sup>-1</sup> (between a and c) observed in G but less broad in D, and the absence of the expected characteristic carbon-hydrogen (CH) absorption band of hydrocarbons between 3100 and 2800 cm<sup>-1</sup> (spectrum b) in G. The 1100 and 1000 cm<sup>-1</sup> band, which also overlaps with the spectrum around 1190 cm<sup>-1</sup>, indicates the presence of silicates [52] in G, further buttressing the theory that G is an acid tar contaminated soil. The broad spectrum at 3700 and 2650 cm<sup>-1</sup> indicates the presence of heterocyclic compounds such as pyrroles, furans and thiophenes, and oxygen-containing compounds such as phenol and alcohol [53]. The broadness of the spectrum in G possibly indicates the relative higher concentrations and presence of these groups of compounds in G, supporting the GC/MS results for the aromatic

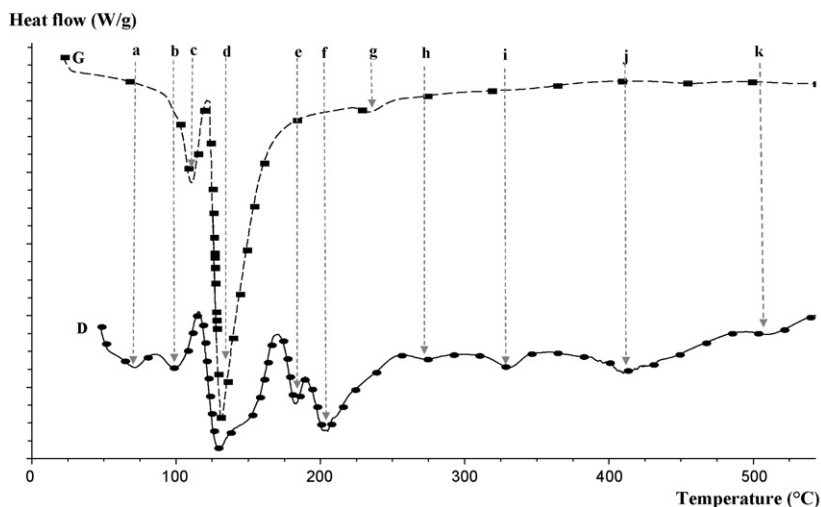


Fig. 6. DSC results for D and G.



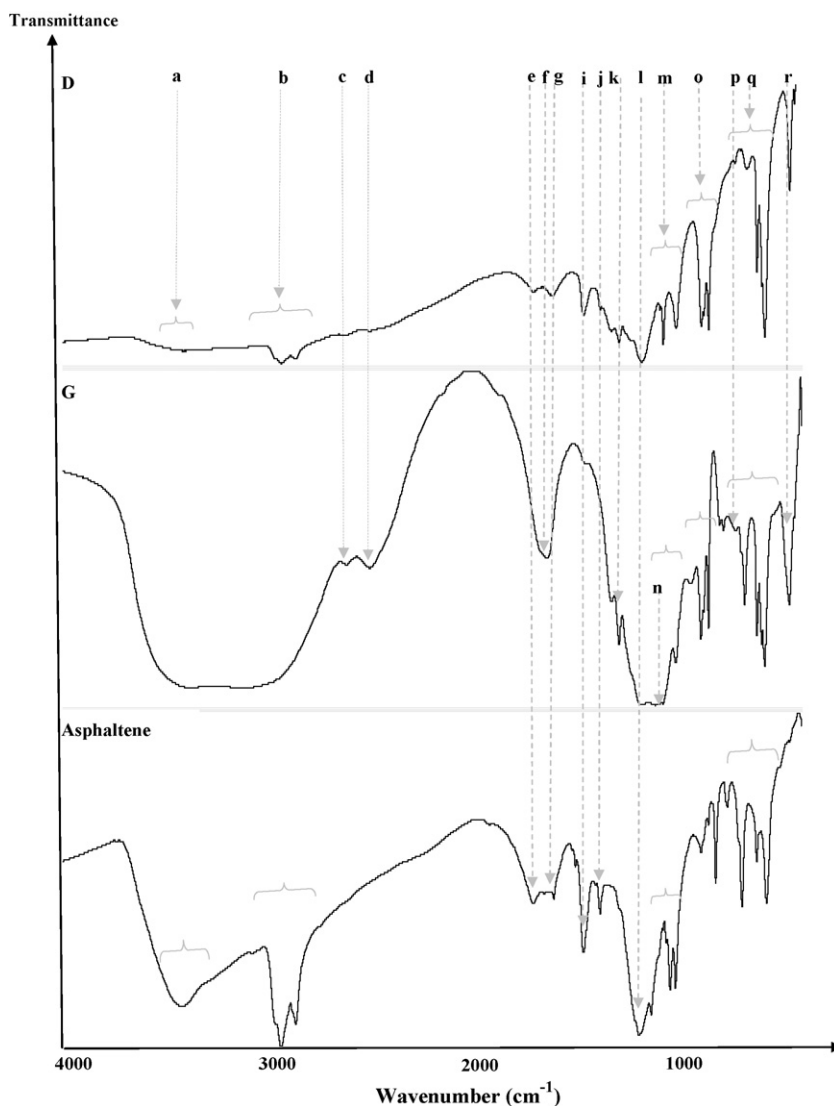


Fig. 7. FTIR spectra for D, G and asphaltene fraction.

fraction from G. The absence of the expected characteristic CH absorption band between  $3100$  and  $2800\text{ cm}^{-1}$  in G is unusual for any hydrocarbon-containing material; the presence of hydrocarbons in G has already been confirmed by GC/MS. It follows that this absence is not real and could be due to interference/overlapping from the dominant broad band from the heterocyclic and oxygen-containing compounds.

All other spectral bands were similar for G and D. The spectra observed around  $2600$  and  $2500\text{ cm}^{-1}$  (c and d) are characteristic spectra for thiols (S-H stretch: functional groups with sulfur and hydrogen) [52]. This spectrum is more intense in G, indicating the possibility of G containing more of this functional group. The spectrum observed around  $1650$ – $1600\text{ cm}^{-1}$  (spectrum f) suggests the possibility of nitrogen-containing functional groups such as nitrile, amines, and organic nitrates [52,53], it is however difficult to assign this spectrum as there are spectra for other functional groups in this region [52]. Overlapping could be observed in the spectrum for D, where two spectra (e and g) were present in this region.

The characteristic bands for long linear aliphatic hydrocarbons around  $1470$  and  $720\text{ cm}^{-1}$  (spectra i and p [52]) were present in both samples. These spectra were more intense in D, supporting the GC/MS and DSC results, which show that D contains more long chain aliphatic hydrocarbons than G. The bands observed between  $1000$  and  $500\text{ cm}^{-1}$ , showing several strong absorption spectra (o,

p, q and, r), can be assigned to C–H out of plane bending on an aromatic ring [52–54]. It must however be noted that it is difficult to use these bands as diagnostic for aromatics, as other functional groups such as aliphatic hydrocarbons could have absorption around these regions.

Infrared spectra of the asphaltene fraction show some differences compared to the raw samples. A narrower band was observed around  $3700\text{ cm}^{-1}$  and  $2600\text{ cm}^{-1}$  instead of the broader band observed in the raw samples. Furthermore, the asphaltene fraction shows a more intense spectrum of the characteristic CH absorption band of hydrocarbons between region  $3100$  and  $2800\text{ cm}^{-1}$ . Notably, the spectrum i, which indicates the presence of long chain hydrocarbon, were more pronounced in the asphaltene fraction, as were the spectra in the region from  $1000$  to  $500\text{ cm}^{-1}$ , indicating increased aromaticity. The changes observed in the asphaltene fraction demonstrate that the aliphatic and aromatic fractions in the samples have been extracted leaving only high molecular weight and heterocyclic compounds.

#### 3.4.2. Scanning electron microscopy/energy dispersive X-ray (SEM/EDX) micro-analysis

SEM micrographs of D and G are presented in Fig. 8. D had a smooth surface while G revealed the presence of grains. The smooth surface of D is similar to that reported for crude oil vacuum

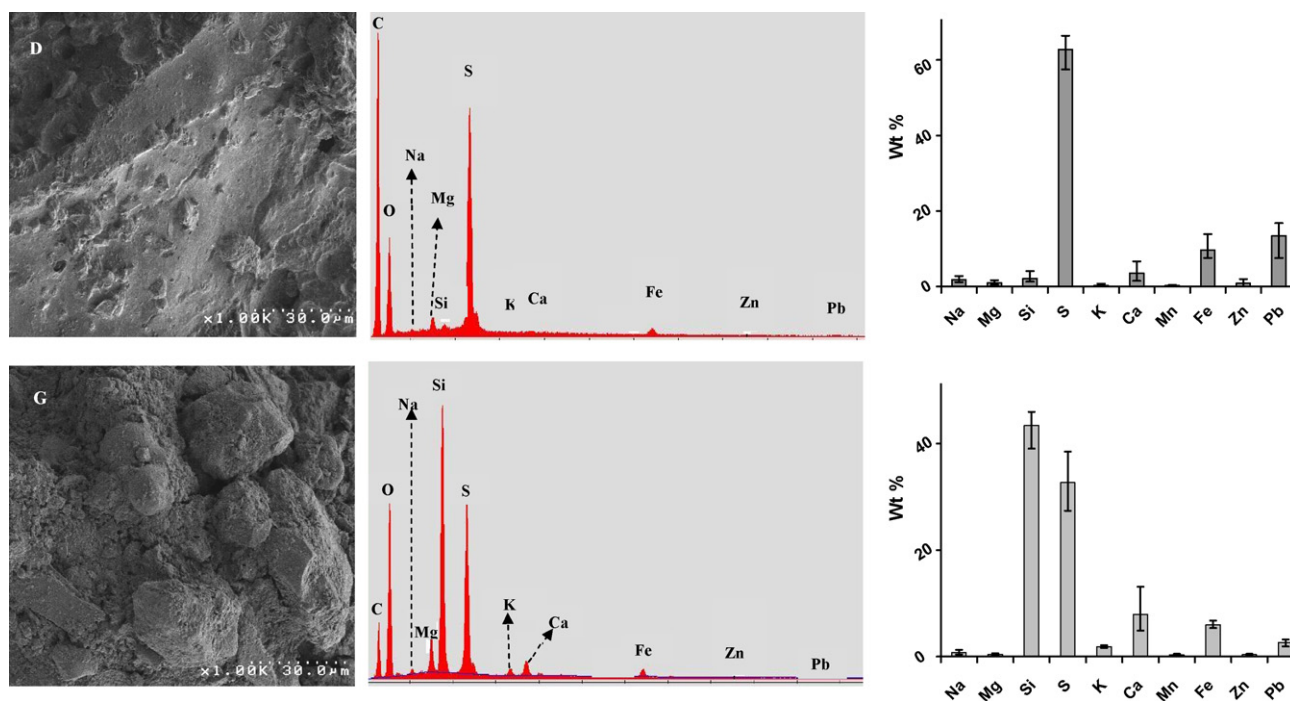


Fig. 8. SEM/EDX micrographs, spectra, and elemental analysis for D and G.

residue [55]. EDX spectra show the presence of a much stronger carbon peak in D than G. Both samples show a strong sulfur peak as expected. G shows a much stronger silicon peak than G, providing further evidence that G is an acid tars contaminated soil. The bar chart shows the average percentages of selected elements in the samples taken from three different points on the sample. Pb and Fe are seen to be present in significant concentrations; differences between these results and the ICP/AES determinations, may be attributable to the fact that EDX analysis is only semi-quantitative and because acid tars components are not evenly distributed within the samples at the microscale.

#### 4. Summary

The physical, chemical, thermal, microstructural characteristics of two anonymously provided acid tar samples were studied using different analytical techniques. The results revealed differences in composition between the two samples. The two samples show the presence of numerous organic compounds and heavy metals including saturated and unsaturated aliphatic and cyclic hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), organic acids (sulfonic acids, carboxylic acids, and aromatic acids), phenyl, nitrile, amide, furans, thiophenes, pyrroles, phthalates, lead, iron, zinc, boron, manganese and cadmium. One of the acid tar samples was found to contain 12 of the 16 USEPA priority polycyclic aromatic hydrocarbons. Many of these contaminants were found to leach at significant concentrations. The results obtained from this work demonstrated the applicability and complementarity of a range of analytical techniques for this purpose as well as revealing the complexity of acid tars and providing useful compositional information needed in planning an effective management method for acid tars.

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