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Analysis of Smoke Samples from Oil Well fires in Kuwait

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# Report of Test on Analysis of Smoke Samples from Oil Well Fires in Kuwait

by

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## INTRODUCTION

This report describes results from a preliminary series of measurements concerning the smoke production from the Kuwait oil well fires. Detailed chemical analysis of the smoke is being carried out for determination of the fraction of ambient aerosol arising from the Kuwait oil well fires on a local, regional, and global scale. The overall goal is to characterize the amount of smoke particulate produced and its chemical makeup, as well as the amount of various gaseous species including  $\text{SO}_x$  and PAHs from individual well fires. This information will be used together with the burning rates of a large number of oil well fires to estimate the total production of smoke and gases from all the fires in Kuwait. The source term information is essential for risk assessment in regard to health effects, environmental/climate impact, and visibility.

Smoke samples were collected in the Al Maqwa oil field in Kuwait on May 15, 1991 from two locations illustrated on the map (Fig. 1). The first set was collected about 3 meters above ground at an "ambient" location; that is, the sampling was not from a plume but was from the oil field region. These samples are indicated as ambient oil field samples. The second set of samples, denoted as plume samples, was collected in the plume of a combination jet-pool fire at a height of about 1 meter. The ground level plume consisted of whitish smoke, while black smoke was emanating from the flames (See Figure 2). It was the whitish smoke that we were sampling.

The particulate was collected on quartz filters, polytetrafluoroethylene (PTFE) filters, on stages of a cascade impactor, and on carbon coated transmission electron microscopy (TEM) grids. Volatile polycyclic aromatic hydrocarbons (PAHs) were collected downstream on XAD-2 sorbent and CO and  $\text{CO}_2$  were collected in PTFE sampling bags. The sampling procedures are described in more detail below.

The smoke analysis included the determination of the mass of particulate on the filter, the relative amounts of organic and elemental carbon in the particulate, the PAH content of the particulate and gas, the chemical composition by laser microprobe mass spectroscopy (LMMS), and the particle size distribution by transmission electron microscopy and by cascade impactor. Gas chromatography was used to analyze the CO and  $\text{CO}_2$  concentration in the gas samples.

## SMOKE SAMPLING

Smoke samples were collected on 47 mm diameter quartz fiber filters for thermal-optical analysis of organic versus elemental carbon content. Standard precautions were taken to avoid sample contamination before sample collection by heating the filter for two hours at  $700^\circ\text{C}$  to remove organic contaminant and also heating the aluminum foil used to line the sample containers to  $500^\circ\text{C}$  for several hours. All filters and impactor substrates were weighed and sealed with Teflon tape in Petri dishes lined with aluminum foil. As a further precaution, sets of filters were placed in plastic bags partially filled with filtered air. After the samples were collected, they were resealed with teflon tape in Petri dishes and maintained at about  $5^\circ\text{C}$  to avoid evaporation of the organic fraction until they were analyzed. The sample flow was maintained at 67

cm<sup>3</sup>/s (4 L/min.) using a battery operated pump (Gillian<sup>1</sup>), which contains a flow controller element to maintain constant flow with increasing pressure drop across the filter. A calibrated flowmeter was used to adjust the pump flow before collecting the smoke. A small fraction of the exhaust from the diaphragm pump, about 2 cm<sup>3</sup>/s, was directed to a 5 L PTFE gas sampling bag for subsequent CO and CO<sub>2</sub> analysis.

The PAH sampling train was operated at a flow rate of 50 cm<sup>3</sup>/s (3 L/min) and contained a 37 mm filter holder followed by a 8 mm OD by 110 mm long sorbent tube filled with two sections of XAD-2. Analysis of the second section allows detection of PAH vapor breaking through the first section. The entire sampling train including disposable filter holders, sorbent tubes, connectors, and PTFE filters were obtained from one vendor, SKC. The sorbent tubes were covered with aluminum foil to minimize exposure of the PAH collected on the XAD-2 to sunlight. After collecting the samples, they were sealed and kept at about 5°C.

A six stage cascade impactor (Marple Personal Cascade Impactor), which provides size segregated samples, was used at a flow of 33 cm<sup>3</sup>/s (2 L/min). The ambient sample collected by this method was too small for gravimetric analysis, but the size segregated samples were useful for single particle analysis by LMMS. Samples were also collected directly on carbon coated TEM grids (3-mm diameter, 0.13 mm thick, and 200 mesh copper). Two grids were attached to the metal sampling housing with double stick tape in the case of the plume sample and to the side of the Van just below the roof in the case of the ambient sample.

## PARTICLE AND GAS ANALYSIS

### Smoke Concentration and Yield

The mass concentration of smoke was determined from the total volume of air sampled and the mass of smoke collected. The plume samples were collected for about 20 minutes and about 1 mg of smoke particulate was collected. This is a convenient sample size for gravimetric analysis with a 0.01 mg sensitivity microbalance. The Kuwait ambient sample was collected for thirty minutes resulting in the collection of about 0.05 mg of particulate matter. The time averaged mass concentrations (See Table 1) for the two plume samples are  $21 \pm 1$  mg/m<sup>3</sup> and  $15 \pm 1$  mg/m<sup>3</sup> and  $0.05 \pm 0.03$  mg/m<sup>3</sup> for the Kuwait ambient sample.

The CO<sub>2</sub> concentration in the plume corresponding to the 21 mg/m<sup>3</sup> smoke concentration is  $650 \pm 20$  ppm by volume and the concentration in the Kuwait ambient sample was  $380 \pm 20$  ppm as measured by gas chromatography (GC) equipped with a thermal conductivity detector operated at 200°C. The calibration of the GC was performed using NIST Standard Reference Material 2634, 789 ppm of CO<sub>2</sub> in nitrogen with an accuracy of  $\pm 8$  ppm. These values are to be compared with a reference ambient level of about 350 ppm in a pristine environment [1]. The CO concentration was below the detectable limit for the instrument (60 ppm).

From the measurement of the smoke collected on the filter and the CO<sub>2</sub> concentration, the smoke yield of whitish smoke in terms of grams of smoke per gram of fuel can be computed using the following equation [2]:

$$e = Y_c F_c \quad (1)$$

where  $F_c$  is the mass fraction of carbon in the crude oil and  $Y_s$  is the mass of smoke particulate divided by the mass of carbon in the combustion products including smoke and CO<sub>2</sub>. We estimate  $F_c$  as 0.86 based on elemental analysis for Arabian light crude and obtain  $Y_c$  of 0.13 based on the smoke mass on the filter, the CO<sub>2</sub> concentration minus the background concentration, and the volume of gas sampled. Using Eq.(1), we obtain a smoke yield of 0.11 g smoke per gram of fuel consumed. This number is an upper bound, since the mass of carbon in the form of volatile hydrocarbons is not included.

<sup>1</sup> Certain materials and equipment are identified in this report in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology.

### Organic/Elemental Fraction

The organic/elemental carbon fractions were determined by Sunset Laboratory<sup>1</sup> using a method-defined analysis similar to that described by Johnson *et al.* [3]. The organic carbon was determined by measuring the carbon content of the vapors produced by heating the sample in a helium environment, and the elemental carbon fraction was determined by heating the residue in a mixture of 2% oxygen in helium. As indicated in Table 1, the organic content of the plume sample was found to be  $92 \pm 3$  % and for the ambient sample was  $72 \pm 5$  %.

### PAH Analysis

Three PTFE filters (2 samples and 1 blank) and three XAD-2 cartridges (2 samples and 1 blank) were analyzed for polycyclic aromatic hydrocarbons (PAHs). The samples were fortified with perdeuterated derivatives of PAHs, which served as internal standards for the subsequent extractions and analyses. The samples were extracted with ultrasonic agitation in dichloromethane and the PAHs in the extract were measured using gas chromatography with mass spectrometric detection (GC-MS). Thirteen PAHs were measured in one of the PTFE filter samples (0.99 mg particulate loading, plume sample) whereas the other filter sample (approximately 0.05 mg particulate loading in the ambient sample) did not have detectable levels of the PAHs above the filter blank. Six PAHs were measured in extracts of XAD-2 cartridges collected downstream of a Teflon filter. Detectable levels of four of the six PAHs were observed on the downstream segment of one of the XAD-2 samples (each XAD-2 cartridge has two separate segments of the sorbent), suggesting that breakthrough occurred for those compounds on that cartridge. The details of the experimental procedure are described in the appendix.

Results of the PAH determinations of the filter and XAD-2 samples are shown in Tables 2 and 3, respectively. Except for a small phenanthrene contamination of 2.3 ng observed in the Teflon filter blank, the filter and XAD-2 blanks were free of PAHs. Significant concentrations of PAHs were observed in Filter 11 (plume sample) which was loaded with 0.99 mg of particulate matter (see Table 2). Detectable levels of PAHs were not observed in Filter 12 (ambient sample), which was composed of about 0.05 mg of collected particulate matter. A larger sample size would be needed to determine the PAH distribution in the Kuwait ambient. Results from the analysis of NIST SRM 1649, used in this study for analytical quality assurance (see Table 2), were in good agreement with concentrations listed in the SRM's Certificate.

Detectable levels of PAHs were observed in both the upstream and downstream XAD-2 segments of XAD-2 sample 11 (see Table 2). The PAHs measured on the downstream segment of XAD-2 sample 11 experienced breakthrough during sampling and may not have been collected quantitatively. Three PAHs were detected on the upstream segment of XAD-2 sample 12, with none detected on the downstream segment, suggesting that the PAHs were collected conservatively on the upstream XAD-2 segment.

As indicated in Table 4, the whitish plume smoke is more than a factor of five higher in the amount of benzo[a]pyrene, which is often used as an indicator of the health impact of PAHs, per gram of sample than either Alberta sweet crude oil or the urban dust standard; on the other hand, it is about a factor 10 lower than the black sooty smoke collected during the burning of Alberta sweet crude in the laboratory. This source information is one of the elements of a health effects analysis, which would also include the concentration of particulate to which individuals are exposed.

### Laser Microprobe Mass Spectroscopy

The laser microprobe (LAMMA 500) is a time of flight mass spectrometer that utilizes a Nd:Yag pulsed laser as the ablation and ionization source [4]. LMMS has been used in a previous study on carbonaceous particles in regard to source identification of atmospheric soot [5]. Particulate was analyzed from quartz fiber filters and from the particulate deposited on the 2  $\mu$ m cutoff size (sixth stage) of the impactor transferred to a quartz cover slip for the microprobe analysis. The negative ion spectra of the smoke particle is shown in Figure 3. The carbon clusters ranging in size from  $C_2$  to  $C_{10}$  is typical of all carbonaceous



material. The peaks at 16 ( $O^-$ ), 32, and 35 ( $Cl^-$ ) may be characteristic of the smoke, but they also may arise from the fine ambient dust. LMMS analysis for possible PAHs was conducted by operating the laser at low power to gently desorb material from the smoke. The positive ion spectra (Figure 4) suggests the likely presence of PAH compounds. Peaks at  $m/z=252$  could be the 5 ring benzo[a]pyrene, 276 and 302 could be six ring PAHs, and 326 could be a 7 ring PAH. There are peaks not shown on this plot extending out to  $m/z=450$ . Compared to the positive ion spectra for ambient samples collected in urban areas and to soot from the burning of acetylene, it appears that the Kuwait smoke results in larger PAH type structures. Such information may be useful in source apportionment though additional analytical measurements may be needed on remote samples to distinguish the crude oil smoke from other combustion sources such as wood burning.

After examining the impactor sample by LMMS, the 2  $\mu m$  sample was low temperature ashed in an oxygen plasma to remove carbon. The sample, viewed under light microscopy at 320X, revealed small dust or sand like particles. The laser microprobe analysis demonstrated that the particles are composed mostly of Si and have some Ba. Sand-like materials may be a significant portion of the aerosol.

#### Transmission Electron Microscopy

A TEM grid exposed to ambient smoke was analyzed with a JEOL 200 CX transmission electron microscope. Two smoke agglomerates were detected and their micrographs are shown on Figure 5. The larger agglomerate has an overall length of about 10  $\mu m$  with primary particle diameters ranging from 0.05  $\mu m$  to 0.2  $\mu m$ . The smaller agglomerate has a length of about 1.5  $\mu m$  with primary particle diameters ranging from 0.15 to 0.3  $\mu m$ . Compared to soot observed in laboratory scale burns, the two smoke agglomerates collected in Kuwait seem to have larger, less well defined primary spherules.

#### **PRELIMINARY CONCLUSIONS/RECOMMENDATIONS**

Limited data was obtained from one ambient site and one plume so that the conclusions we draw must be considered suggestive rather than definitive. Perhaps the greatest benefit of the measurements is to sharpen the focus of future studies in terms of the types of samples to be collected and the chemical analysis to be performed to allow quantitative characterization of the smoke source term for use in risk assessment.

1. The combination jet-pool fires produce a whitish ground level smoke that is primarily made up of organic carbon and a sooty plume emanating from the flames. Based on this observation and the high organic level of the ambient sample, we hypothesize that the whitish ground level smoke is the main component of the ambient aerosol in the local region (the country of Kuwait). To test this hypothesis, we recommend that a range of chemical measurements including organic/elemental carbon fraction be made in the whitish plume, in the sooty plume, and at several monitoring locations in Kuwait.
2. The carbon balance method indicates an upper bound of the white smoke yield as 0.11 g smoke per gram of fuel consumed. There is a need to include measurement of organic volatiles to obtain a more accurate estimate of the yield. Smoke yield measurements of both the black and white smoke need to be combined with burning rate information, wind velocity, and concentration for estimating the smoke emission from individual fires.
3. The benzo[a]pyrene in the whitish plume smoke for the one sample collected is mid range between that of soot from a laboratory crude oil burn and that of crude oil itself. It is recommended that the PAH analysis be made of the Kuwait crude oil, the whitish smoke, the black smoke, and of the ambient aerosol.
4. The LMMS spectra show potential for providing tracer information on a particle by particle basis for Kuwait smoke. It is recommended that smoke samples be collected from several wells together with samples of the crude oil. Single particle methods including LMMS, analytical electron microscopy, and Raman scattering should be applied to determine their applicability for source identification.

5. Transmission electron microscopy results, while very limited, suggest that the primary size of the smoke agglomerates is larger than is observed for laboratory scale burns. It is recommended that both electron microscopy and cascade impactors be used to quantify the size distribution and structure of the smoke from various well fires. The cascade impactor should also be used for collecting particulate smaller than 2.5  $\mu\text{m}$  aerodynamic diameter for chemical analysis. Particles in this size range can penetrate deep into the respiratory tract and are of concern for their health impact.

6. Certified Reference Materials, when available, should be used as internal quality assurance tools by all laboratories involved in the Kuwait Oil Well Fire measurement activities. A listing of NIST Standard Reference Materials appropriate for the smoke related activities is available upon request.

**ACKNOWLEDGEMENTS:** James Brown measured the  $\text{CO}_2$  concentration in the bag samples and Nelson Bryner and Randall Lawson assisted in the preparation of the smoke particulate and gas sampling equipment.

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#### Table Captions

Table 1	Analysis of Smoke from Kuwait Oil Fires
Table 2	PAH Concentration Observed in Kuwait Air Filter Samples
Table 3	Masses of PAHs Observed in Kuwait XAD Samples
Table 4	Comparison of PAH Content of Smoke, Dust, and Oil
Table 5	Gas Chromatographic and Mass Spectrometric Conditions used for PAH Measurements of the Kuwait Samples

#### Figure Captions

Figure 1	Map indicating ambient (1) and plume (2) sampling sites relative to the Kuwait International Airport.
Figure 2	Photograph showing whitish ground level smoke and black smoke from a combination jet-pool fire. The plume sample was collected 1 meter above the ground near the right hand side of the picture.
Figure 3	Negative Ion Mass Spectrum of Ambient Kuwait Smoke

Figure 4 Positive Ion Mass Spectrum of Ambient Kuwait Smoke

Figure 5 Transmission Electron Micrographs of Ambient Kuwait Smoke. Left picture 6,000X, middle 20,000X of same agglomerate, Right 30,000X of second agglomerate.

#### APPENDIX: PAH ANALYSIS

The PTFE filters were transferred to 50 mL centrifuge tubes, spiked with 10  $\mu$ L of a standard containing 7 perdeuterated PAHs and extracted ultrasonically in 25 mL dichloromethane (DCM) for 20 min. A particulate matter Standard Reference Material with known PAH concentrations (SRM 1649, Urban Dust/Organics) was processed through the same procedure as the filter samples and served as a quality assurance sample. The filters were removed from the tubes and the extracts were centrifuged at approximately 10,000 g's for 1 min. This centrifugation did not clarify the extracts so they were concentrated under  $N_2$  to < 2 mL and passed through a 0.2  $\mu$ m pore syringe filter (Anotop 10). The filter and SRM extracts were finally concentrated to  $\leq 100 \mu$ L in 4 mL amber vials prior to GC-MS quantification.

The upstream and downstream segments of each XAD-2 tube were processed separately to check for breakthrough of any PAHs collected in the vapor phase. The XAD-2 cartridges were scored above the upstream segment of sorbent and the different segments were spiked with the perdeuterated PAH standard described above and extracted ultrasonically for 15 min with 10 mL DCM in 15 mL centrifuge tubes. The XAD-2 extracts were transferred to other 15 mL tubes and concentrated under  $N_2$  to  $\leq 100 \mu$ L.

Two microliter volumes of each sample extract was injected onto the GC column. Details of both the GC and MS conditions are specified in Table 5. Each sample was analyzed one time, using a PAH standard solution (prepared at NIST) as a calibrant.

Table 1. Analysis of Smoke from Kuwait Oil Well Fires

PROPERTY	PLUME	AMBIENT	LAB. SCALE <sup>a</sup>
PARTICULATE CONCENTRATION	21 $\pm$ 1 mg/m <sup>3</sup> 15 $\pm$ 1 mg/m <sup>3</sup> <sup>b</sup>	0.6 $\pm$ 0.3 mg/m <sup>3</sup>	100-200 mg/m <sup>3</sup>
CO <sub>2</sub> Concentration	650 ppm	350 ppm	1000-2000 ppm
Smoke Yield	0.11 g smoke/g oil <sup>c</sup>	-	0.09 - 0.15 g sm./g oil
Organic Fraction	92 $\pm$ 3 % <sup>d</sup>	72 $\pm$ 5 %	14 - 21 %

<sup>a</sup> Lab. Scale refers to data for Alberta sweet and Arabian light crude pool burns at the scale of 0.6 to 3 m in diameter [6,7].

<sup>b</sup> The error bounds are based on the uncertainty in the gravimetric determination of smoke particulate collected.

<sup>c</sup> This value represents an upperbound.

<sup>d</sup> The error bounds reflects the precision of the analysis.

Table 2. PAH Concentrations Observed in Kuwait Oil Fire Particulate Samples<sup>a</sup>  
(ng/mg unless noted otherwise)

PAH	<u>FILTER Blnk (ng)</u>	<u>PLUME<sup>b</sup></u>	<u>AMBIENT(ng)<sup>c</sup></u>	<u>SRM 1649<sup>d</sup></u>
phenanthrene	2.3	100	< 2.3	5.0 (4.5)
anthracene	< 1	30	< 1	0.62 (0.6)
fluoranthene	< 1	76	< 1	7.1 (7.1)
pyrene	< 1	84	< 1	6.1 (7.2)
benz[a]anthracene	< 1	28	< 1	2.7 (2.6)
chrysene	< 1	34	< 1	3.3 (3.6)
benzo[b]fluoranthene	< 1	17	< 1	5.8 (6.2)
benzo[k]fluoranthene	< 1	9.0	< 1	2.0 (2.0)
benzo[e]pyrene	< 1	21	< 1	3.6 (3.3)
benzo[a]pyrene	< 1	19	< 1	2.7 (2.9)
perylene	< 1	5.8	< 1	0.77 (0.8)
indeno[1,2,3-cd]pyrene	< 1	13	< 1	3.1 (3.3)
benzo[ghi]perylene	< 1	15	< 1	4.2 (4.5)

<sup>a</sup> Uncertainties estimated from the measurement precision to be  $\pm 10$  % of the listed concentrations or masses.

<sup>b</sup> Plume sample - filter #11.

<sup>c</sup> Ambient sample - filter #12.

<sup>d</sup> Concentrations in parentheses are the assigned values for Standard Reference Material 1649 [Urban Dust/Organics], analyzed for quality control purposes.

Table 3. Masses of PAHs Observed in Kuwait XAD Samples<sup>a</sup>

PAH	XAD BLANK	PL.XAD UP <sup>b</sup>	PL XAD DOWN <sup>b</sup>	AM. XAD UP <sup>c</sup>	AM. XAD DOWN <sup>c</sup>
phenanthrene	< 0.5	400	55	17	< 0.5
anthracene	< 0.5	50	4.4	< 0.5	< 0.5
fluoranthene	< 0.5	32	2.3	0.69	< 0.5
pyrene	< 0.5	26	1.9	0.92	< 0.5
benz[a]anthracene	< 0.5	0.71	< 0.5	< 0.5	< 0.5
chrysene	< 0.5	0.78	< 0.5	< 0.5	< 0.5

<sup>a</sup> Uncertainties estimated from the measurement precision to be  $\pm 10\%$  of the listed masses.

<sup>b</sup> Plume XAD - Sample #11.

<sup>c</sup> Ambient XAD - Sample #12.

Table 4. Comparison of PAH Content of Smoke, Dust, and Oil<sup>a</sup>

Sample	Total PAH/g sample <sup>b</sup>	benzo [a] pyrene/g sample
Kuwait whitish smoke	490 µg, (16 µg/m <sup>3</sup> ) <sup>c</sup>	19 µg, (0.3 µg/m <sup>3</sup> )
Lab. Scale <sup>d</sup>	4800-5200 µg	180 - 240 µg
Alberta sweet crude	1400 µg	less than 3 µg
urban dust standard	about 50 µg	2.7 µg

<sup>a</sup> Uncertainties estimated from the measurement precision to be  $\pm 10\%$  of the listed masses.

<sup>b</sup> The total PAH refers to PAHs collected on the filter and does include the contribution of the volatile fraction listed in Table 3.

<sup>c</sup> The numbers in () refer to the mass concentrations of PAH in air.

<sup>d</sup> The results for the lab scale burns and the crude oil are taken from reference [6].

Table 5. Gas Chromatographic and Mass Spectrometric Conditions used for PAH Measurements of the Kuwait Samples

#### Gas Chromatography

Column: 25 m x 0.2 mm (0.15 µm phase) Smectic liquid crystalline phase

Carrier: He, 6 psi head pressure

Temperature Program: 37 °C (2 min hold), 30 °C/min, 200 °C, 3 °C/min, 270 °C (hold)

Injector: Cool on-column.

Detector Temperature: 270 °C.

#### Mass Spectrometry

Electron Multiplier Voltage: 2500 V.

Selected Ion Monitoring Program:

<u>Time (min)</u>	<u>Masses Monitored (amu)</u>
3 - 16	178, 188, 202, 212
16 - 26	228, 240
26 - 44	252, 264
44 - 65	276, 288

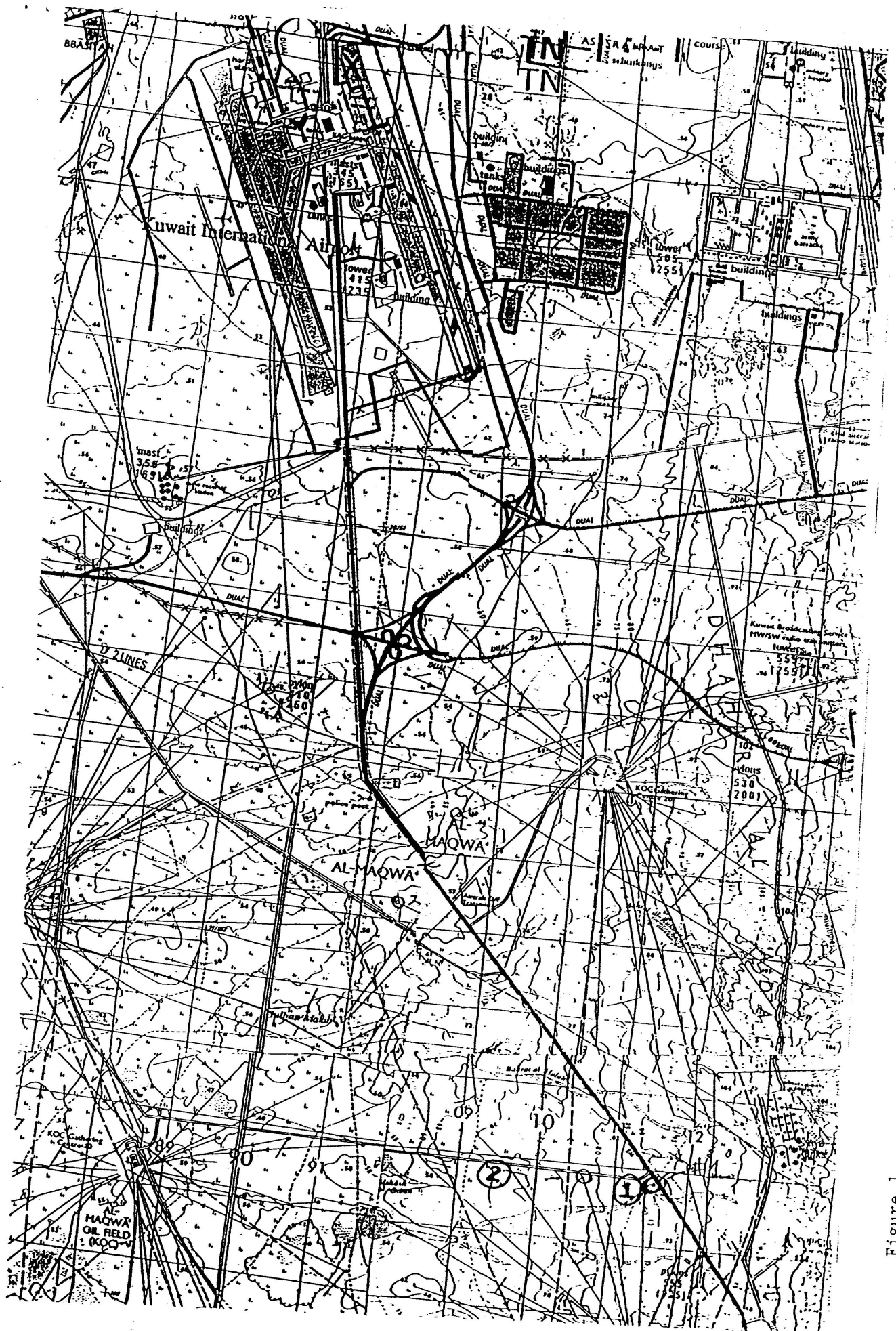


Figure 1.



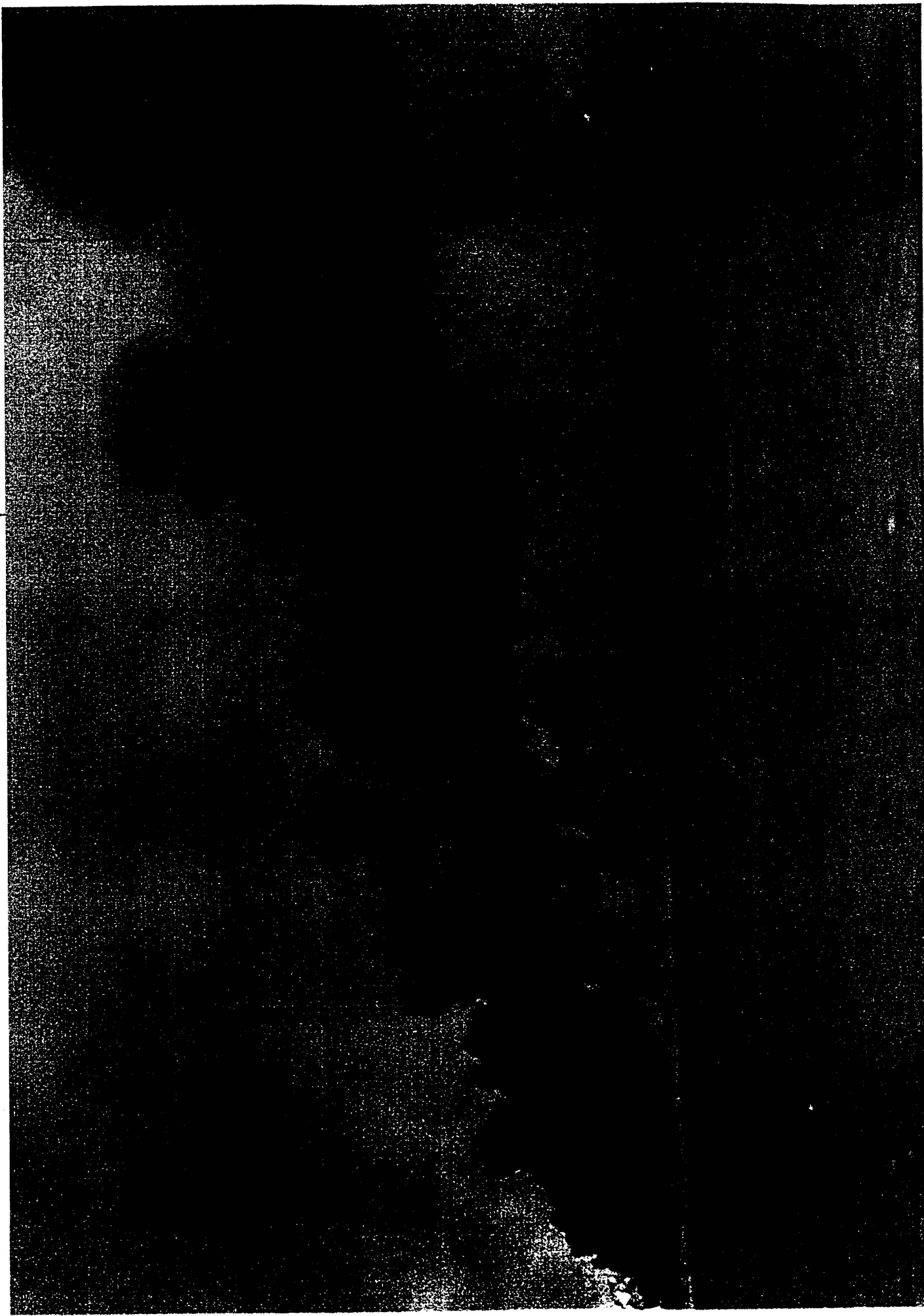


Figure 2.

Kuwaiti Soot  
(negative ion mass spectrum)

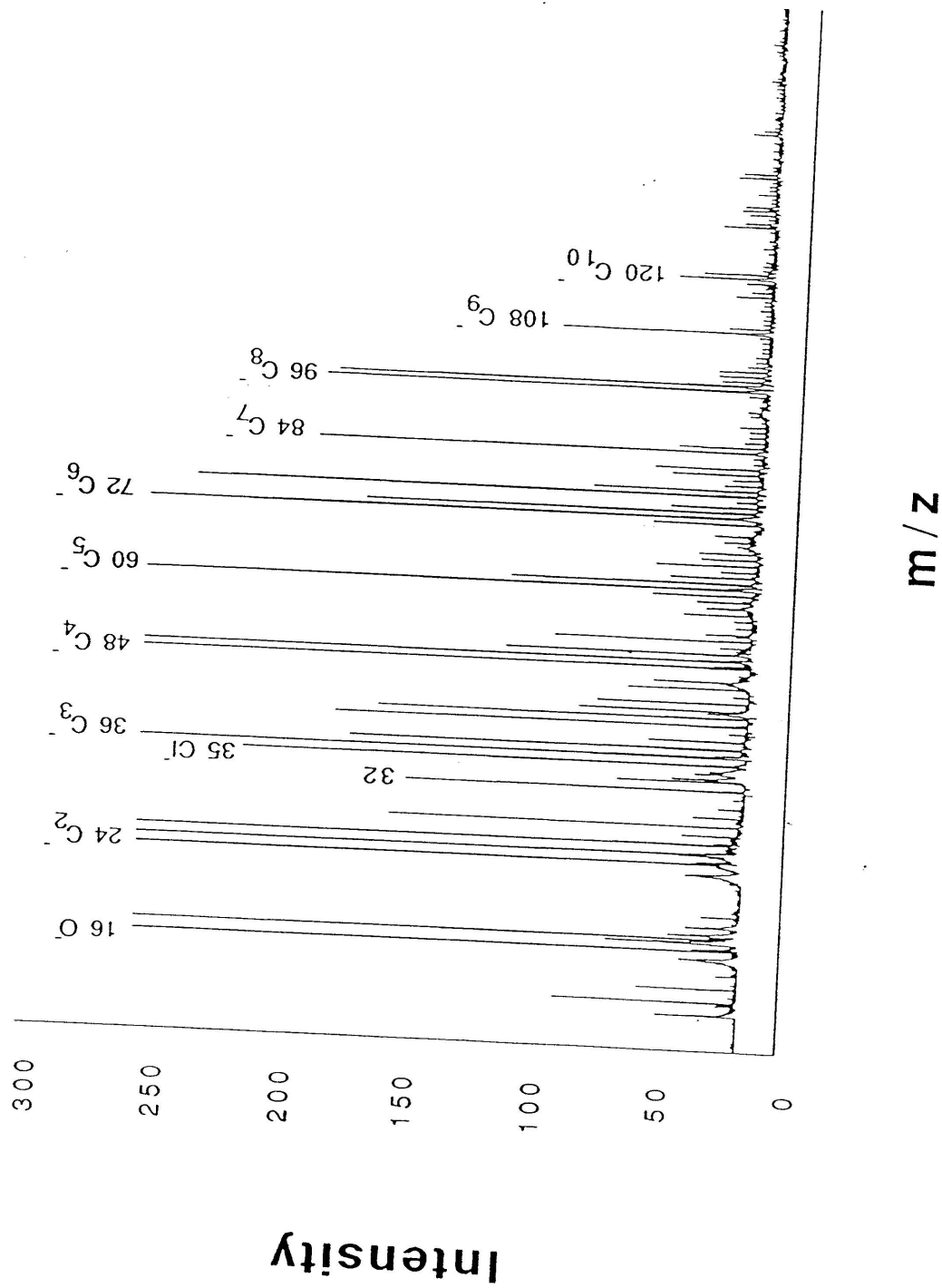


Figure 3.

Kuwait Sample  
(positive ion, high mass region)

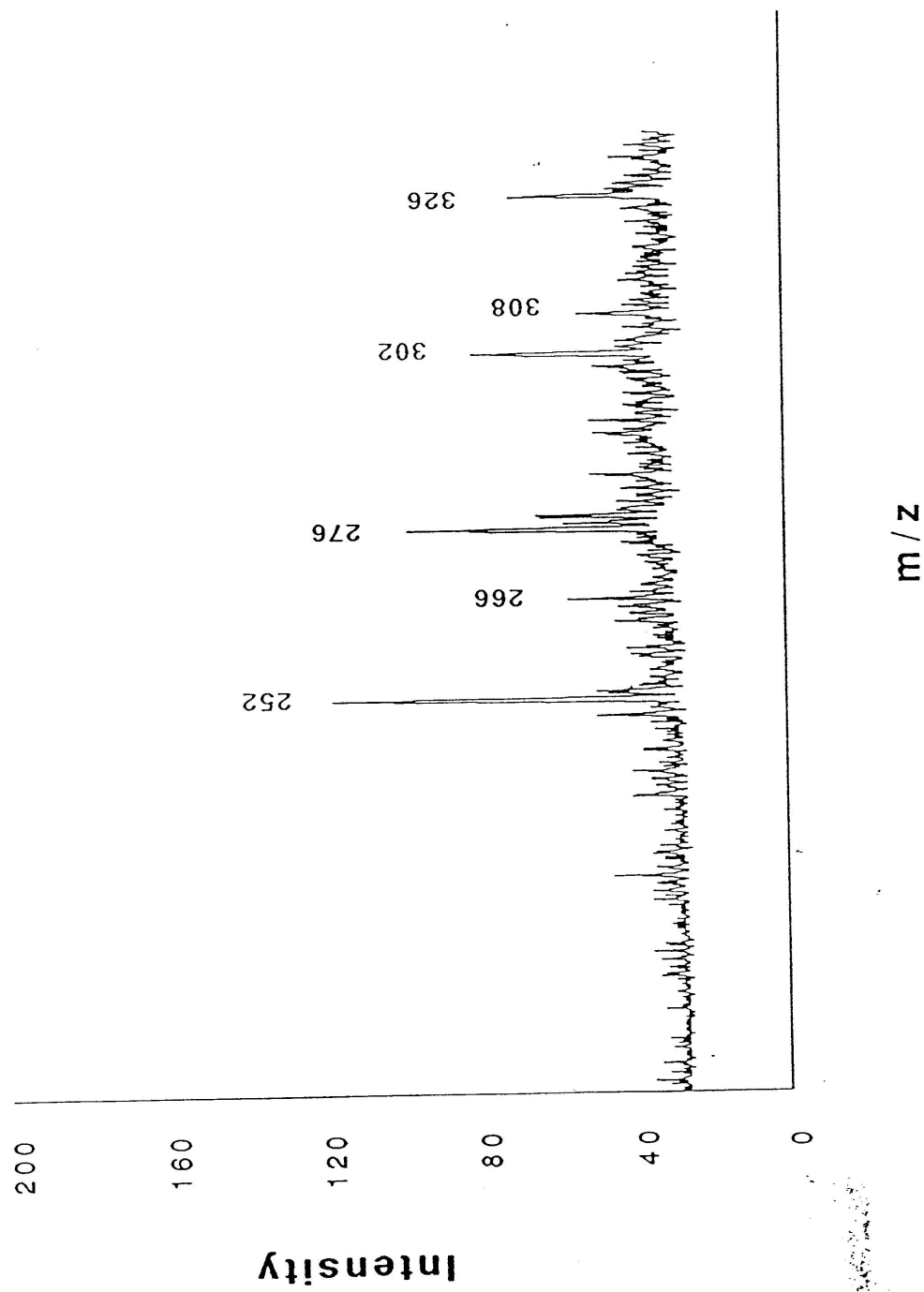


Figure 4.

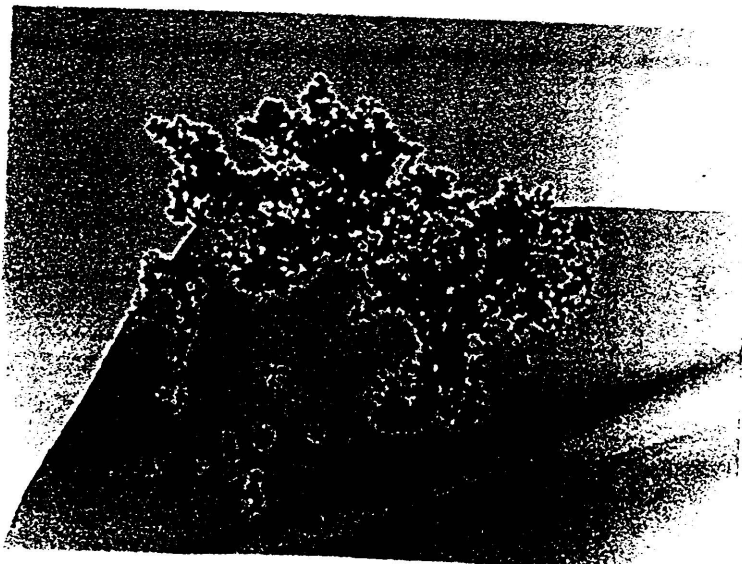


Figure 5.

