

COAL TAR ANALYSIS BY LC/MS

A.A. Herod, W.R. Ladner, B.J. Stokes

National Coal Board, Coal Research Establishment,
Stoke Orchard, Cheltenham, Glos. GL52 4RZ, UK

A.J. Berry and D.E. Games

Department of Chemistry, University College,
P.O. Box 78, Cardiff, CF1 1XL, UK

SUMMARY

The application of LC/MS to the analysis of an aromatic fraction of a hydroxyrolysis tar is described. The results are compared with those obtained by GC/MS, low eV probe mass spectrometry and field desorption mass spectrometry.

INTRODUCTION

The production of liquids from coal gives rise to complex intermediates which require detailed analysis to understand the processes occurring and to make effective use of the products. Analysis has hitherto been based on structural parameters from NMR methods (1) to give the average characteristics of the sample, supplemented by molecular information from GC and GC/MS. The gas chromatographic approach to molecular information is often hampered by lack of volatility and is generally limited to aromatic systems of five or six condensed rings with molecular weights up to about 300 (2). For samples with number average molecular weights over 300, the molecular information available through GC/MS describes less than half of the compounds present. To improve this situation we have investigated LC in conjunction with mass spectrometry for the analysis of coal tar.

Liquid chromatographic separations of coal-derived oils have been followed off-line by GC (3-6) and by probe-mass spectrometry (6). Directly combined LC/MS studies of coal-derived samples are rare (7,8), although LC/MS of standards found in coal tars (9) and of aromatic material from petroleum (10), as well as super-critical fluid chromatography/MS applied to a coal tar extract (11), have been described.

This paper describes the application of LC/MS to the analysis of an aromatic fraction of a hydroxyrolysis coal tar and compares the results with those obtained by GC/MS, by mass spectral probe at low ionising voltage and by field desorption mass spectrometry.

EXPERIMENTAL

Tar Sample and Fractionation

The tar chosen for study was produced by the hydroxyrolysis of a high volatile bituminous coal (82.9% C; 5.3% H) at 500°C in 150 bar hydrogen in a fixed bed reactor. The tar was first separated by solvent extraction into pentane solubles, asphaltenes (pentane insoluble-benzene soluble) and preasphaltenes (benzene insolubles); the pentane soluble fraction was further subdivided into saturates, aromatics and polars by column chromatography on silica (12). The separation scheme is shown in Figure 1 where yields for the various fractions are given relative to the starting weight.

Standard compounds

Standard compounds used to establish the mode of separation of the LC column were cyclohexane, perhydropyrene, benzene, toluene, pentyl benzene, sym-octahydrophenanthrene, naphthalene, methylnaphthalene, acenaphthene, diphenyl, dibenzofuran, 9,10 dihydroanthracene, fluorene, phenanthrene, methyl phenanthrene, pyrene, chrysene, perylene, dibenzanthracene and dibenzopyrene.

EQUIPMENT

The LC was performed using an analytical 3.9 x 300 mm stainless steel $10 \mu\text{m}$ Bondapak NH_2 column with hexane as the mobile phase pumped at 1 ml min^{-1} by a Waters 6000A pump. Detection was either by a variable wavelength Cecil 272 detector at 254 nm or a Finnigan 4000 mass spectrometer equipped with a moving belt interface and an Incos data system.

GC/MS examination was carried out using a Perkin-Elmer F17 gas chromatograph with a 42 m glass SCOT capillary column coated with SP2100 phase which was interfaced by a glass jet separator to a Kratos MS30 double beam mass spectrometer fitted with a DS55 data system. Mass spectrometric resolution of 3000 and a scan rate of 3 s/decade of mass enabled accurate mass measurement of all the spectral peaks. The gas chromatograph temperature-programme was from 85° to 285°C at 4°min^{-1} .

MS 30 examination of the aromatics (at 10 eV) was achieved using a solids injection probe heated from ambient temperature to 350°C . Field desorption mass spectrometry on the same sample was performed using a Varian CH_3 double focussing instrument.

RESULTS AND DISCUSSION

The full ultimate and proximate analyses of the coal and tar asphaltenes and aromatics are given in reference (1); the whole tar contained 82.2% C and 7.0% H while the aromatics fraction contained 87.5% C and 7.7% H. Number average molecular weights of the whole tar and the aromatics were 260 and 250 respectively.

LC of standards and aromatic fraction

The LC/UV separation of some of the standards is shown in Figure 2. This separation gave a linear relationship between log capacity factor (corrected for column dead volume) and the number of double bonds in the standard compound as indicated in Figure 3. Thus, the elution volume is controlled by the aromaticity of the compound and classes of similar compounds elute together with their alkyl derivatives. This separation is significantly different from that obtained by GC where the compounds elute in approximate boiling point order which means that long chain alkyl aromatics coelute with unsubstituted but much more condensed aromatics. Figure 4 shows that the LC/UV and LC/MS profiles of the aromatic fraction are similar; any differences are due to the changes in UV adsorbance with increasing aromaticity compared with the total ion current. The first peaks in the LC/MS profile correspond to cycloalkanes, including the biomarkers, pentacyclic triterpanes such as hopanes revealed by an intense m/z 191, which have no significant UV adsorption. Their presence indicates that the saturates/aromatics split is not complete, possibly because the boiling range of the sample exceeds that originally intended for the method (12).

Figures 5 to 8 show mass spectra of some of the more prominent peaks in the total ion current profile of Figure 4. In each spectrum we have linked the fragment or molecular ion peaks for the various Z series of hydrocarbons by

solid lines. Z is defined by the general hydrocarbon formula C_nH_{2n+Z} and denotes the hydrogen deficiency compared with alkanes (where Z = +2) since each double bond or ring adds (-2) to the Z number. The graphically represented Z series indicate the range of homologues present in the spectrum but not the aromatic structure since all structural isomers elute close together. The mass spectra reveal that homologous series are prominent and extensive; Table 1 numerises the Z series found with the maximum alkyl chain homologues detected. Other evidence for long alkyl chains ($> C_{20}$), for example, from NMR analysis is given in reference 1. Long Z series aliphatic and aromatics were also found in off-line LC-field ionisation MS on two non-distillable SRC-I coal liquids(5), these extended to over mass 700 and revealed long homologous series for the different Z series. This similarity is not surprising since the SRC-I process and hydrolysis at 500°C use very similar severities of treatment.

GC/MS

The GC/MS study revealed a complex alkylated aromatic mixture but only extending to about mass 240. The total ion current profile in Figure 9 shows that the number of structural isomers of overlapping alkylated aromatic types was so great that the GC resolution was insufficient to cope and broad multiple peaks were evident. The main unsubstituted aromatics are indicated in the Figure and components found are listed in Table 2 which shows that there are numerous highly alkylated aromatics.

Mass Spectrometry Probe

Figure 10 shows an averaged mass spectrum of the aromatic fraction obtained by low ionising voltage probe MS. It reveals a complex series of aromatic molecular ions with components such as alkyl-naphthalenes, alkyl-diphenyls, alkyl-perylenes etc. up to mass 600, the upper limit of the mass range. The average molecular weight, calculated as the 50% intensity of the averaged spectrum is 260, i.e. close to the number average molecular weight determined isopiesticly.

Field Desorption Mass Spectrometry

Figure 11 shows the field desorption spectrum. There is no significant intensity below mass 200 but a complex series of masses extending, at low intensities, beyond mass 1000; the low molecular weight material observed by LC/MS and GC/MS has presumably been pumped away in the mass spectrometer.

GENERAL DISCUSSION

This study indicates that on-line LC/MS gives chemical information on the coal-derived aromatics which has not previously been obtained by other methods. On the other hand, probe experiments have revealed the presence of high molecular weight material which is not detected by LC/MS, most probably because this material was not volatilised from the moving belt interface and therefore did not enter the ion source (13).

The complex alkylated aromatics with evidence of the biomarkers pentacyclic triterpanes of the hopane type indicate that there has not been undue degradation of the molecular structures and evidence from NMR (1) indicates that the loss of hydroaromatic groups by aromatisation is one of the main reactions taking place during mild hydrolysis; the small quantity of low carbon number hydrocarbon gas (less than 5 wt % daf coal) produced during the hydrolysis reinforces this view.

Alkylated material, including up to C₁₀ - alkyl naphthalenes, has also been observed (14-16) to evaporate from coals at low temperatures (>300°C) and has been described as the remains of the oil produced during coalification the bulk of which has migrated from the coal measures to oil and gas fields. The aromatics fraction described in this work probably corresponds to a slightly modified, wider molecular weight range fraction of the oil remnant.

CONCLUSIONS

LC/MS gives significant chemical information on a wide boiling sample of aromatics derived from coal by revealing both the extent of the homologous series, up to C₂₀ alkyl substituents, and the size of the aromatic systems, up to seven rings. This information is not revealed by other techniques such as NMR, MS, or GC/MS. Although the method works satisfactorily on-line, there is still discrimination against high molecular weight material.

ACKNOWLEDGEMENTS

The work was carried out as part of the analytical support for the IEA coal pyrolysis project being undertaken by Bergbau Forschung in Germany. A.J. Berry acknowledges financial support from SERC. The views expressed are those of the authors and not necessarily those of the Board.

REFERENCES

1. C.E. Snape, W.R. Ladner and K.D. Bartle, *Fuel* **64**, 1394, 1985.
2. P. Burchill, A.A. Herod and R.G. James in *Carcinogenesis*, Vol.3, Polynuclear Aromatic Hydrocarbons ed. P.W. Jones and R.I. Freudenthal, Raven Press NY, p.35, 1978.
3. B.A. Drew and S.C.F. Robinson, *Fuel* **64**, 861, 1985.
4. R.B. Lucke, D.W. Later, C.W. Wright, E.K. Chess and W.C. Weimer, *Anal. Chem.* **57**, 633, 1985.
5. H. Uchino, S. Yokoyama, M. Satou and Y. Sanada, *Fuel* **64**, 842, 1985.
6. T.W. Allen, R.J. Hurtubise and H.F. Silver, *Anal. Chem.*, **57**, 666, 1985.
7. W.A. Dark, W.H. McFadden and D.L. Bradford, *J. Chrom. Sci.* **15**, 454, 1977.
8. W.A. Dark and W.H. McFadden *J. Chrom. Sci.* **16**, 289, 1978.
9. K.J. Krost, *Anal. Chem.*, **57**, 763, 1985.
10. R.W. Smith, D.E. Games and S.F. Noel, *Int. J. Mass Spectrom. and Ion Physics* **48**, 327, 1983.
11. R.D. Smith, H.T. Kalinoski, H.R. Udseth and B.W. Wright, *Anal. Chem.*, **56**, 2476, 1984.
12. K.D. Bartle, W.R. Ladner, T.G. Martin, C.E. Snape and D.F. Williams, *Fuel* **58**, 413, 1979.
13. D.E. Games in 'Soft Ionisation Biological Mass Spectrometry', *Proc. Chem. Soc. Symposium on Advances in Mass Spec. Soft Ionisation Methods*, ed. H.R. Morris London, p.54, July 1980.
14. A.A. Herod, N.J. Hodges, E. Pritchard and C.A. Smith, *Fuel* **62**, 1331, 1983.
15. A.A. Herod and C.A. Smith, *Fuel* **64**, 281, 1985.
16. A.A. Herod, W.R. Ladner and B.J. Stokes, *Proc. 10th Int. Mass Spec. Conf. Swansea, UK, Paper 400, 9-13 September 1985.*

TABLE 1

Aromatic types detected by LC/MS

Mass of parent of homologous series	Z No. $C_n H_{2n+Z}$	Name of one isomeric structure	Maximum alkyl chain detected
78	-6	Benzene	>15
118	-8	Indan	>20
116	-10	Indene	>20
128	-12	Naphthalene	>21
154	-14	Diphenyl	>19
166	-16	Fluorene	>19
178	-18	Phenanthrene	>12
204	-20	Phenyl-naphthalene	12
202	-22	Pyrene	15
228	-24	Chrysene	11
226	-26	Benzo(ghi)fluoranthene	11
252	-28	Benzopyrene	10
278	-30	Dibenzanthracene	10
276	-32	Naphthylphenanthrene	7
302	-34	Dibenzopyrene	8
300	-36	Coronene	9

TABLE 2

Aromatic types detected by GC/MS

Mass of parent of homologous series	Z No. $C_n H_{2n+Z}$	Name of one isomeric structure	Maximum alkyl chain detected
78	-6	Benzene	5
118	-8	Indan	5
116	-10	Indene	0*
128	-12	Naphthalene	6
154	-14	Diphenyl	5
166	-16	Fluorene	4
178	-18	Phenanthrene	4
204	-20	Phenyl-naphthalene	2
202	-22	Pyrene	2

* Components of Z = -10 are not normally detected at masses less than mass 186 corresponding to octahydro-phenanthrene although indene is the lowest "parent" of the series.

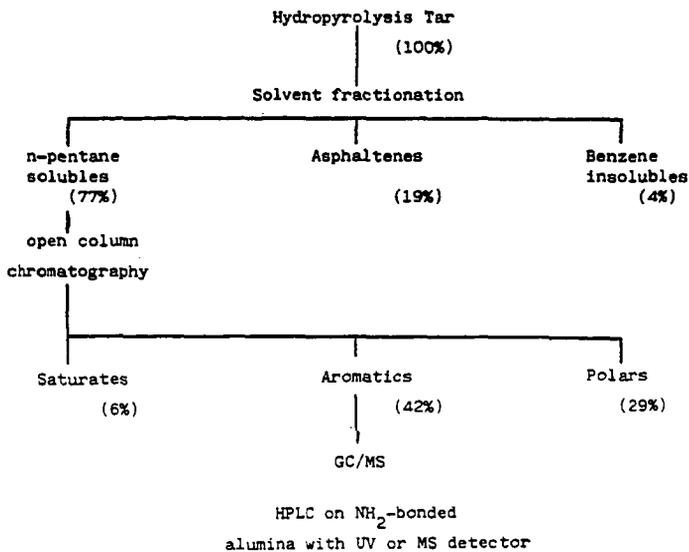


Figure 1: Separation Scheme

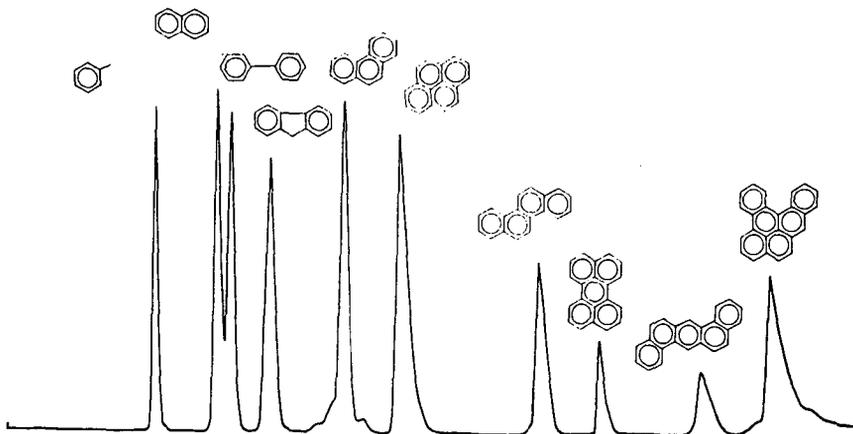


Figure 2: LC/UV separation of some standards

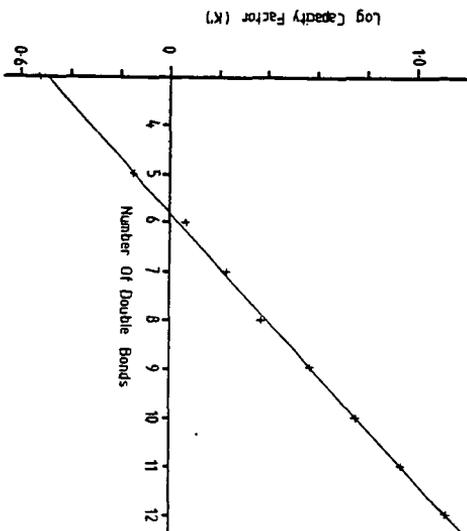


Figure 3: Relationship between number of double bonds in various aromatic molecules and log capacity factor (K'), where $\log k' = 1 + [(V_R - V_M) / V_M]$; V_R and V_M are the elution volumes of the aromatic and cyclohexane respectively.

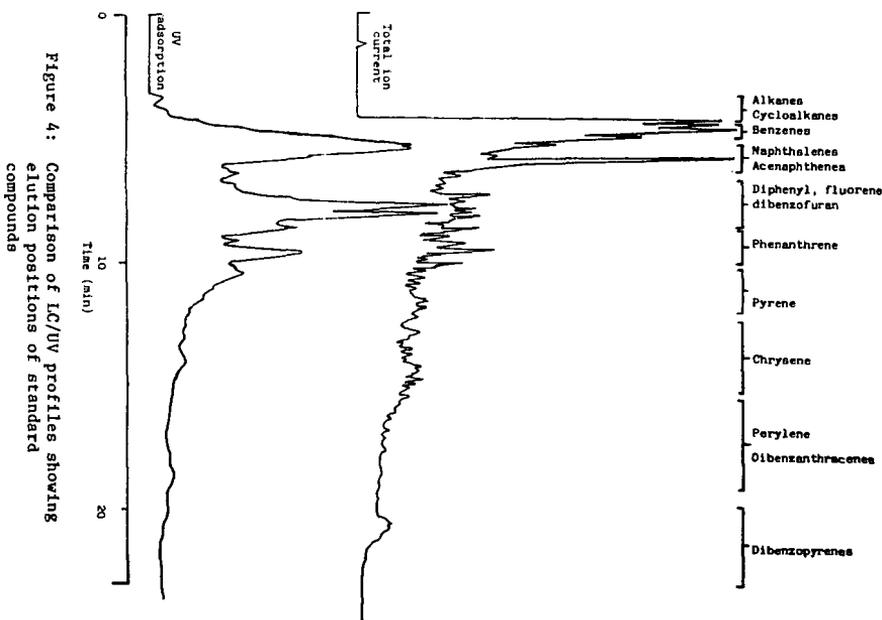


Figure 4: Comparison of LC/UV profiles showing elution positions of standard compounds

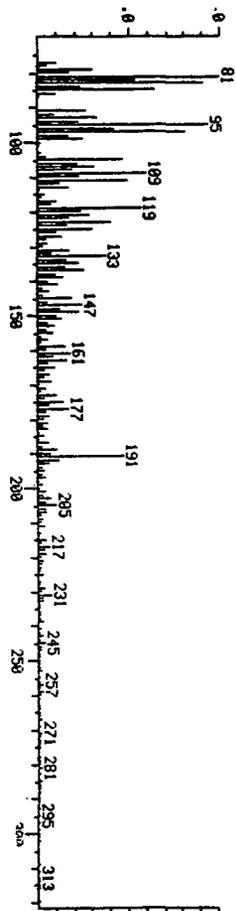


Figure 5: Mass spectrum of saturates showing m/z 191

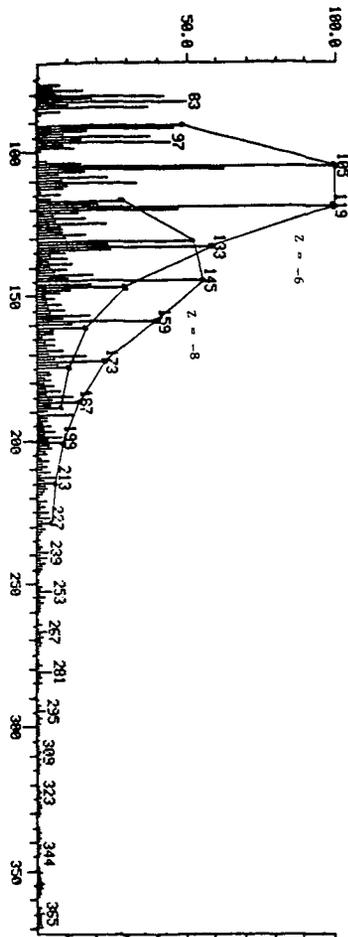


Figure 6: Mass spectrum showing Z=-6 and Z=-8 fragment ions

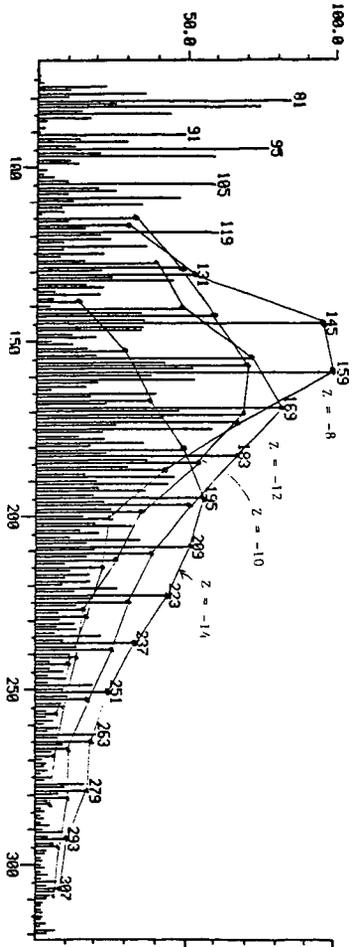


Figure 7: Mass spectrum showing Z=-8, Z=-10, Z=-12, and Z=-14 fragment ions

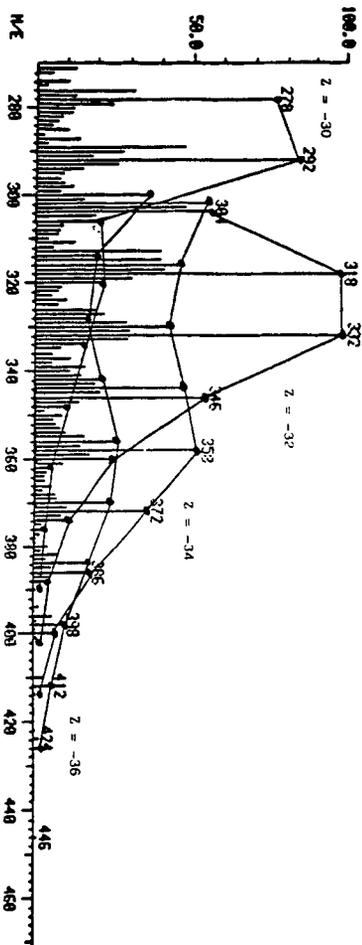


Figure 8: Mass spectrum showing Z=-30, Z=-32, Z=-34 and Z=-36 molecular ions

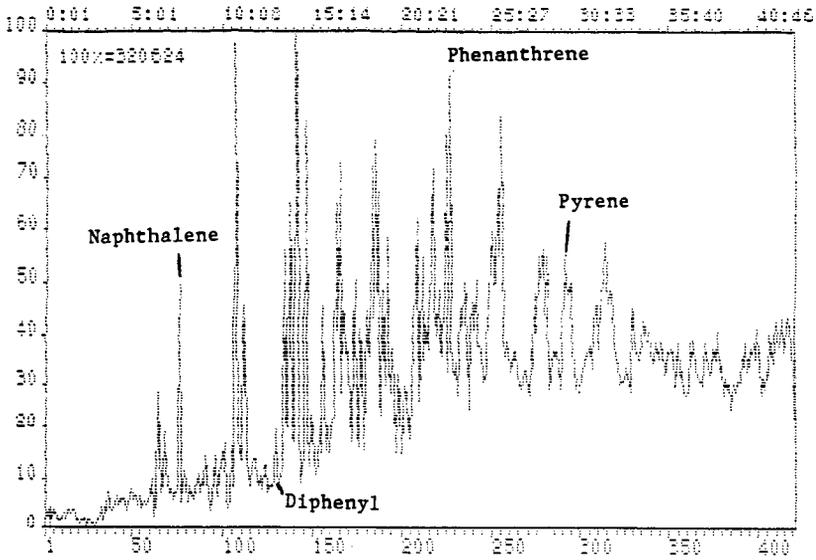


Figure 9: Aromatics by GC/MS

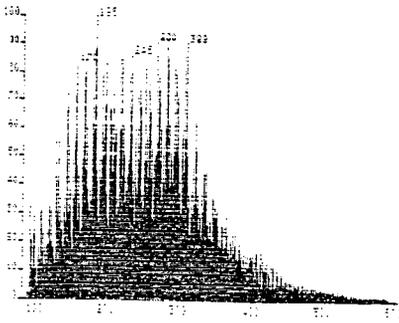


Figure 10: Averaged spectrum at low eV of aromatics

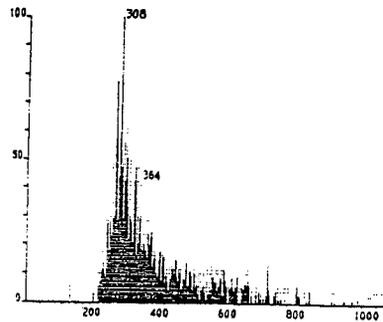


Figure 11: Field desorption profile of aromatics