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MASS SPECTROMETRIC STUDIES OF COALS AND COAL MACERALS*

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TABLE OF CONTENTS

1. INTRODUCTION

1.1. Focus

This paper will explore the characterization of coal-derived materials by High Resolution Mass Spectrometry (HRMS). Coals are very complex and heterogeneous on both a microscopic and molecular level. The microscopic heterogeneity can be reduced by working with macerals separated from the whole coal. Macerals are the microscopically identifiable plant remains which make up the organic portion of coals. The molecular make up of the various macerals can be traced back to the original biomolecules and biomacromolecules. The extent of alteration depends on both the rank of the coal and the type of maceral, some of which are more resistant than others. Data from both the analysis of whole coals and separated coals will be discussed.

Unlike many spectroscopic techniques the HRMS approach provides very detailed molecular information. A limitation of this technique is that the samples being analyzed must be either extracts of, or derived from coal by some process or reaction. Typical methods used to depolymerize coals are given in Table 1 along with references to HRMS studies on these products. We will concentrate on results produced by vacuum pyrolysis with both rapid and stepwise heating. Another important consideration is the mode of ionization used prior to mass analysis. Methods used include electron impact (normal (70eV) and low voltage), field ionization and other new approaches which are being explored. Many of the methods are designed to produce mostly molecular ions with little fragmentation from the ionization. Different internal standards are used for determining the precise mass measurements and for estimating yields of the various ions. As is the case with many methods, quantitation is difficult but necessary to provide meaningful information. Finally, both global and detailed data are necessary to advance our understanding of coal "structure" and reactivity.

1.2. Approaches

Pyrolysis High Resolution Mass Spectrometry (PyHRMS) has been applied to characterization of separated coal macerals and coal degradation products.(2,6-9) There are many papers on low resolution PyMS applied to coals(13) and one applied to these premium coals.(14) The PyMS approach can provide very detailed information on the molecules which are released in vacuum pyrolysis, however the probability of secondary reactions is a consideration and all interpretation must be made with this fact in mind. This approach yields more specific molecular data than any other method. A problem with low resolution PyMS is that in many if not most cases there may be several ions present with the same nominal mass but with different chemical compositions. This problem is eliminated by using a high resolution spectrometer that will resolve peaks which overlapped at lower resolution and thus yield more accurate information. Field Ionization Mass Spectrometry has been used extensively to characterized coal derived mixtures. However, only recently has it been used in a high resolution mode and applied to coal liquefaction products.(12) It appears to be a very promising approach to examine relatively large molecules produced by pyrolysis.

The complete set of Argonne Premium Coal Samples has been characterized using PyHRMS.(9) A major objective in that study was to examine differences in the heteroatom (oxygen, sulfur and nitrogen) containing molecules as a function of rank of the coals. Operating in the high resolution mode makes it possible to directly separate these species from each other and from the hydrocarbon molecules. In addition, many molecules, which can not be observed with gas chromatography by virtue of their size or polarity, can be observed with this method.

2. METHODOLOGY

2.1. Sample Preparation

The samples have been obtained from the Argonne Premium Coal Sample Program and the preparation of the samples has been described.(15) The appropriate elemental analyses for the samples are presented in Table 2. A second set of samples was obtained by extracting the original coals in refluxing pyridine under a nitrogen atmosphere. The residue was washed with dilute aqueous HCl and with methanol and dried in vacuo at 60°C. The maceral concentrates used as examples in this paper have been prepared by density gradient centrifugation.(16) Representative elemental analyses are shown in Table 2. These data have been included to show the distribution of heteroatoms in the coals and separated macerals. Complete analysis data for the macerals are presented elsewhere.(2,6)

Oxidative methods range in extent of depolymerization from aqueous sodium dichromate(1) to alkaline silver oxide.(2) The first method yields mostly aromatic carboxylic acids while the second gives a broad range of molecular weight acids including a large amount which resemble humic acids.

2.2. Data Acquisition

In HRMS analysis the scan rate depends on the resolution required; the higher the resolution the slower the scan rate. Therefore, the method of sample introduction will depend on the resolution. At lower resolution (<10,000), the sample can be directly inserted into the source either on a heated probe or on a high-temperature pyrolysis probe. However, at higher resolution (>10,000) the sample must be metered into the source such that the concentration is constant over the total scan time. For example, at a resolving power of 80,000 the scan rate is typically 1000 sec/decade so that a single scan can take up to 30 minutes. Normally, an all glass heated inlet system (AGHIS) is used. The inlet system was designed in this laboratory to use a quartz pyrolysis probe fitted with a platinum grid which was heated by a computer controlled DC power supply. A schematic of this inlet is shown in Figure 1. The inlet system was thermostated at 300°C and a silicon-carbide leak metered the sample into the mass spectrometer. Examples of operating conditions for HRMS data acquisition are shown in Table 3. Results from these different modes of operation will be discussed later. It should be noted that photographic detection is used in the PyFIMS experiments resulting in an average accuracy of ±0.003 mass units.(17)

2.3. Internal Standards

Two different types of internal standards are used in HRMS analysis. The first is used making precise mass measurements and the second, which can be used in pyrolysis experiments, is used for quantitation between different runs. Normally, perfluorokerosene is used as the mass standard in 70 eV experiments. Fluorinated carbon compounds have a negative mass defect which makes is possible to separate the sample (which consists of mainly positive mass defect species) from the standard peaks. However, PFK is for the most part, fully saturated and will not ionize under low voltage conditions. A mixture of aromatic compounds containing fluorine, iodine or bromine is used in this case. A complete list of these compounds is given in reference.(10)

The second internal standard is very important for comparing the results of the PyMS between the different rank coals. It allows a more quantitative comparison, while ideally not participating in any secondary reactions. Our standard appears to function very well. The Diels-Alder product shown below undergoes a thermally induced retro-reaction very cleanly at approximately 300°C to yield d_{10}-anthracene quantitatively. In the precise mass measurement mode it is easy to separate this ion from the coal pyrolysis products.

The mass spectra of the standard at 300°C is shown in Figure 2. Even at 70 eV the spectra are quite clean with the most abundant peak being the d_{10}-anthracene, while the maleic anhydride is converted into small molecules which do not interfere with the sample peaks. Normally the molecular ion peak at $m/z=286$ is not seen when the standard is pyrolized along with coal samples. Much of the data presented in this paper have been normalized to this standard. Since this standard is released at a lower temperature than the coal pyrolysis, one would expect no deuterium scrambling, which is what is observed experimentally. The peaks resulting from the standard are excluded from the final averaged spectra.

2.4. Data Reduction

Schmidt, et al.(10) have described in some detail a method for grouping the mass spectral data by general formula type and by hydrogen deficiency (HD). In this paper, we will use HD which corresponds to number of rings plus number of unsaturations ($HD = -2Z$), therefore each unit is worth two hydrogens. We analyze the data in a similar manner. First, empirical formulae are assigned for each peak using one of the groups in Table 4 for each assignments. Typically, each peak will have several possible formulas and normally >95% have at least one assigned. Next, the peaks are sorted by HD number and by group (Table 4) for the formulae which have the best fit between observed and calculated m/z ratios. Also taken into account is that analysis are the ^{13}C isotope peaks. Finally, the data is presented graphically and scanned to assure that the assignments make chemical sense. Normally for each group and HD combination a series of peaks differing by a methylene (14 mass units) is observed.

3. RESULTS AND DISCUSSION

3.1. Models

The objective of using model polymers in PyHRMS is two-fold. First, the results can be used to test the quantitation of the approach using systems which yield well-defined products. Second, the data can be used to help interpret results from much more complex systems such as coals. Initial results on two synthetic polymers have been reported.(18) The HRMS capability was very useful in uncovering a thermal rearrangement of the oxy-methylene linked polymer (I). The following rearrangement is known to be acid catalyzed; however, we have shown that it can occur thermally, leading to a much less reactive polymer as is shown in Figure 4.

A fragment with M/Z = 108 in pyrolysis can be due to a quinone, a cresol or a hydrocarbon. At low temperatures thermolysis of I yields quinones, while at higher temperature after the rearrangement to Ia, alkylphenols result. Due to the much stronger methylene-arylcarbon bond it is much more difficult to degrade the rearranged polymer (Ia), and lower yields are observed. The data which suggested this interpretation are shown in Figure 5. This type of rearrangement, which leads to less reactive species, could very well occur in pyrolysis of coal.

3.2. Macerals

Characterization of separated macerals has several related advantages. First, the heterogeneity of the material has been reduced. Second, macerals which occur in small amounts compared to the vitrinite can be examined without the problem of being observed by the major maceral, vitrinite. Several examples will be shown in which the nature of the heteroatoms in various macerals is compared.

It has been shown that the amount of organic sulfur varies between the different macerals isolated from the same coal.(2) From PyHRMS data, differences in the chemical structures of the organo-sulfur compounds can be observed. An example is shown in Figure 6 for a set of macerals from high-volatile bituminous coals. The liptinite pyrolysis products contain significant amounts of alkyl thiols or sulfide and thiophenes while the fusinite contains mostly polycyclic aromatics. Although sporinites tend to contain more sulfur than the associated vitrinites or inertinites, the forms appear to be of the more reactive type and should be more easily removed. It is interesting to note that aryl sulfides or thiols are important species in both sporinite and vitrinite, a result which has not been recognized in the past.

To further elucidate the structures found in resinite, sporinite, and vitrinite, a sample of an enriched liptinite separated by DGC was analyzed by PyMS. The data are sorted by both hydrogen deficiency and by heteroatom content. From this analysis, variations between the macerals (which can be designated by their density) for families of fragments, such as phenols can be observed. For example, in Figure 7 the percentage of total ion current for the phenols is shown for the sum of all scans for each density fraction. The three macerals can be easily distinguished. The phenolics are almost absent in resinites at low density. There is an increase in abundance in the region thought to contain sporinite and a rapid increase with density for the vitrinites. The distribution of phenolics determined by PyMS might prove to be useful for distinguishing different macerals. These data illustrate the utility of precise mass PyMS for maceral characterization. The technique can also be used to study coal and coal-model reactivity and products.

To modify the acid functionality in the macerals, the acidic hydrogens in the maceral concentrates were exchanged for metal ions.(19) Siskin and Aczel(20) have shown that treating a bituminous and a sub-bituminous coal with KOH reduces the yield of phenolic products in a 600°C pyrolysis under nitrogen. From studies on models, they found that potassium phenolates are very nonvolatile at that temperature and the phenols observed in the products result from cleavage of alkyl ether structures. A study by Schlosberg and Scouten(21) suggests that an opposite effect can be achieved by forming the calcium half-salt of phenols using calcium hydroxide. They found that the yield of phenols from coal liquids could be increased after treatment of the mixture with $Ca(OH)_2$. In our study, both the potassium and calcium half-salts were prepared for a vitrinite and the Ca salts for an additional set of macerals.

PyMS data on untreated macerals can not be used to distinguish between phenolic fragments resulting from hydroxybenzenes and those resulting from aryl ethers. Several experiments were performed to separate the two possible sources of phenol derivatives in the pyrolysis products. First, the reactivity of free phenols has been inhibited by the formation of their potassium salts and in the second set of experiments the tendency of phenols to polymerize was reduced by the formation of single calcium salts. The variation of yields with pyrolysis temperature for the alkylphenols from three Upper Elkhorn #3 seam vitrinite samples is shown in Figure 8. The intensities in the selected ion pyrograms were determined by summing the individual intensities of phenol and alkylphenol peaks for each scan. As predicted, the alkylphenol fragments from the Ca-exchange vitrinite were formed and volatilized at a much lower temperature than the raw vitrinite. While the effect was not as dramatic, the potassium-exchanged sample yielded alkylphenols at a higher temperature than the vitrinite. Upon examination of the distribution of the different fragment types averaged over all the mass scans, it was found that the Ca-exchanged sample yielded approximately twice the amount of single oxygen-containing fragments as the raw vitrinite, but the K-exchanged sample was very similar to the vitrinite. These results demonstrate that Ca can drastically reduce repolymerization of acidic oxygen-containing species during the pyrolysis of a vitrinite; however, the K-exchange does not affect the overall yield, but instead, just lowers the volatility.

The reactivity of the alkylaryl ethers in these samples should not be affected by the potassium or calcium at these lower temperatures. In the case of the K-exchanged sample, the study by Siskin and Aczel(20) would suggest that phenol fragments seen in the initial portion of the peak would result from ether cleavage. For the Ca-exchanged samples it appears that the phenolates are thermally cleaved from the macromolecules at a lower temperature than are phenols. This suggests that the alkylaryl ether products would appear at the high end of the temperature distribution. These results indicate that the products represented by the shaded area in Figure 8 may be mainly the result of alkylaryl ether cleavage.

The Ca-modified sample of the Illinois #2 vitrinite yielded similar results to those just discussed. However, with Brazil Block vitrinite the Ca-exchanged maceral pyrogram appeared to be very similar to the raw material. One possible explanation for this result is that this vitrinite apparently has been heavily weathered. The study by Liotta and coworkers(22) suggests that extensive ether formation is possible with oxidative weathering. Any alkylaryl ethers formed would be unaffected by the calcium. Also, these ethers would tend to be on the surface and, therefore, more easily released.

An interesting pattern emerges upon examination of the variation between the different phenol/alkylphenol fragments for the various macerals and modified macerals. Averaged intensity values which have been normalized to give 100 for the largest are shown in Table 6. For all three raw vitrinites, the methylphenol (M-1) peak is the largest, while for all the Ca-exchanged vitrinites, a three-carbon phenol (M-1) peak dominates. Although it is not entirely clear why we see this result, there is a possible explanation. Lignin is a major precursor to vitrinite and the fundamental monomer of softwood lignin is a three-carbon chain, methoxyhydroxybenzene. Our work has suggested that upon coalification the methoxyl is rapidly lost, yielding an alkylphenol as the major structural unit. oxidative degradation studies demonstrate that these units can still exist in some modified forms in coals. It is possible that the C_3-phenol fragment seen in the PyMS of the Ca-vitrinites is derived from lignin. Since the Ca-exchange lowers the temperature at which fragments are seen, less degradation occurs, which may account for the appearance of C_3-phenols. If lignin-derived structures are responsible for some of these results, one would expect these structures to be less abundant in both sporinite and the fusinite samples, which is what has been observed.

The sporinite sample behaved very differently from the vitrinite. The yield of phenols was very similar for the Ca-modified and unmodified samples. This result would imply that alkylaryl ethers dominate the oxygen-containing structures that lead to these products seen in vacuum pyrolysis. The products also contain a significant amount of multi-ring mono-oxygen species. This may result from dehydrogenation of oxygen containing hydroaromatics. Also, it should be noted that there are a significant number of fragments that contain three oxygens, more so than for any of the other macerals we have studied.

The fusinite sample results are similar to those of the vitrinites, but the overall yields are less and the yields of phenolics relative to other species are less. However, it is known that even inertinites which are 100% pure will react thermally, as we have shown for short contact-time liquefaction. The yield of phenolics was enhanced by the Ca exchange and they appear at a temperature very similar to that found for the vitrinite.

By combining chemical modifications of acidic oxygen sites with PyMS, relative abundances of phenolic and alkylaryl ethers in macerals can be studied. The macerals do exhibit differences which can be rationalized to some extent by their source of organic macromolecules. The exchange with calcium lowers the temperature necessary for the release of the phenol fragments from vitrinites and may reduce secondary retrogressive reactions.

3.3 Premium Coals

Recently we have concentrated on characterization of the eight Premium Coal Samples listed in Table 2. The focus on this small number of samples is important in that comparisons with other chemical and spectroscopic data are facilitated. Also, these samples are homogeneous and have been protected from oxygen. Results from three sets of experiments will be discussed, including: flash pyrolysis(9), linear heating of fresh coals, and pyrolysis of mild oxidation products.(7)

As one would expect, the aromaticity of the hydrocarbons observed in 600°C flash pyrolysis increases with increasing carbon content. For coals with less than ~85% carbon, one to two ring aromatics are the major products. For greater than ~85%, three, four, and five ring compounds increase in abundance. An example of a high rank coal is shown in Figure 9. Two ring compounds are most abundant (HD=7), but the amount of 3-ring and 4-ring are very close. Series of peaks separated by methylenes (14 mass units) are observed up to HD=20. The aromatics are highly alkylated with up to 12 alkyl carbons. Initial tandem MS results suggest that these are mostly methyl groups.

Much of the oxygen functionality is related to the original lignin, especially in lower rank coals. The series of peaks from the lignite which contain either one or two oxygens is shown in Figure 10. As has been shown in selective oxidation experiments(7), hydroxy- or dihydroxy-benzene are the most abundant series.

The alteration of oxygen containing lignin structures can be observed as the coals increase in rank. However, in pyrolysis the absolute yields of oxygen containing products, excluding small gases, does not follow the rank sequence in the coals. The molecules containing two oxygens more closely resemble the original lignin and decrease witih rank. Distribution of all possible heteroatoms and hydrocarbons are shown in Figure 11 for the lignite coal. Significant amounts of the aromatic oxygen species have a HD number between four and six. Two oxygens species most abundant group are single ring compounds. Three oxygen containing compounds occur in the higher HD number region. It is interesting to note that three oxygen compounds are more abundant than two oxygen containing species in the high rank lv bituminous coal (APCS #5). Examination of the data suggests that these molecules are fairly larger heteroaromatics similar in size and hydrogen deficiency to the dominant aromatic hydrocarbons observed in this coal.

Coals vacuum pyrolysis products tend to be rich in heteroatoms, epecially high sulfur, high volatile bituminous coals.(8) The data in Figure 12 are presented for two reasons. First, it demonstrates that diverse mix of molecules, five of the six series peaks contain heteroatoms. Also, note that these are not all just regular methylene series, but in two cases $C_{20}H_{10}O$ and $C_{20}H_{26}$ are related to terpenoids. Second, this is a good demonstration of the power of high resolution operation. At nominal mass resolution, most of the possible information would be lost.

The Diels-Alder adduct internal standard has been used in all of the flash pyrolysis experiments, but also has proven useful in the linear ramp heating experiments. An example of reproducibility is shown in Figure 13. Both the overall yields with time are quite reproducible, as are the individual mass assignments. If the standard is well coated onto the coal particles, loss of some of these particles prior to pyrolysis does not affect the outcome of the experiment.

The slowly heating method gives results similar to the flash pyrolysis, but, in addition, yields temperature dependence information. As is seen in Figure 14, oxygen species are more abundant than polycyclic aromatic hydrocarbons. However, in the higher rank coals, several interesting differences can be noted in Figure 15. The dihydroxybenzenes disappear, and napthalenes are much more abundant, but the phenols, although lower in abundance, are still significant. Also, surprisingly the napthalene evolve over a very broad temperature range. Those found at the lower temperature are most likely small molecules trapped within the matrix.

A danger in pyrolysis experiments of insoluble solids, is the certain occurrence of secondary reactions. Mild oxidative degradation has been used to form a soluble , but high molecular weight product which can be pyrolyzed under less severe conditions.(8) PyMS of the humic products results in volatilization at lower temperatures than with the coal or maceral, as is shown in Figure 16. Comparing the pyrolysis products between the two samples, the most striking difference is the reduction in aliphatics in the humic acid fraction. Figure 17 shown the distribution of hydrocarbons found as a function of HD number. However, in each case the contribution of fragments with more than one aromatic ring was small, 5.6% for the coal and 4.6% for the oxidation product. This suggests that single ring aromatics dominate in this coal and apprears to be true for coals of similar rank.

4. CONCLUSIONS

High resolution mass spectrometry has proven to be very useful in tthe characterization of complex materials such as coals. In the past, the method was used for examining process derived liquids, but it is also a useful tool in the analytical pyrolysis mode. Results from PyHRMS suggest that a significant number of "monomers" in coals contain multiple heteroatoms. The amount can be rank dependent in some cases, but they are found in all coals. This very detailed information needs to be correlated with results from other methods.

In the future, the trend is toward other soft-ionization techniques. FIHRMS appears promising and needs to be exploited. We are working on FABHRMS techniques to characterize relatively high molecular coal derived products. Laser ionization combined with high resolution time-of-flight MS could have some very interesting applications in coal characterization. Better structural data can be obtained by tandem HRMS. Precise mass ions are selected in the first section, fragmented in a collision cell and the fragmentation pattern recorded. Such an approach would be very useful for large molecules where a empirical formula can yield a large number of possible structures.

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REFERENCES

1. R. Hayatsu, R. G. Scott, L. P. Moore, and M. H. Studier, Aromatic Units in Coal, *Nature* **257**, 378-380 (1975).
2. R. E. Winans, R. Hayatsu, R. G. Scott, and R. L. McBeth, Reactivity and Characterization of Coal Macerals, in: *Chemistry and Characterization of Coal Macerals* (R. E. Winans and J. C. Crelling, eds.), ACS Symposium Series No. 252; American Chemical Society, Washington, D.C. pp. 137-155 (1984).
3. R. Hayatsu, R. G. Scott, and R. E. Winans, Oxidation of Coal, in: *Oxidation in Organic Chemistry* (W. S. Trahanovsky, ed.), Part D, pp. 279-352, Academic Press (1982).
4. C. M. White, L. J. Douglas, M. B. Perry, and C. E. Schmidt, Characterization of Extractable Organosulfur Constitutents from Bevier Seam Coal, *Energy Fuels* **1**, 222-226 (1987).
5. R. Hayatsu, R. E. Winans, R. G. Scott, L. P. Moore, and M. H. Studier, Trapped Organic Compounds and Aromatic Units in Coals, *Fuel* 57, 541-548 1978.
6. R. E. Winans, R. G. Scott, P. H. Neill, G. R. Dyrkacz, and R. Hayatsu, Characterization and Pyrolysis of Separated Coal Macerals, *Fuel Proc. Tech.* **12**, 77-88 (1986).
7. R. E. Winans, R. Hayatsu, R. L. McBeth, R. G. Scott, and R. E. Botto, Aromatic Structures in Whole Coals and Coal Macerals, *Prepr. Am. Chem. Soc., Div. Fuel Chem.* **33(1)**, 407-414 (1988).

8. R. E. Winans and P. H. Neill, Multiple Heteroatom Containing Sulfur Compounds in Coal, in: *ACS Symposium Series, Geochemistry of Sulfur in Fossil Fuels*, (W. L. Orr and C. M. White, eds.), submitted (1989).

9. R. E. Winans, R. L. McBeth, and P. H. Neill, Characterization of the Argonne Premium Coal Samples by Pyrolysis High Resolution Mass Spectrometry, *Prepr. Am. Chem. Soc., Div. Fuel Chem.* **33(3)**, 85-90 (1988).

10. C. E. Schmidt, R. F. Sprecher, and B. D. Batts, Low-Voltage, High-Resolution Mass Spectrometric Methods for Fuel Analysis: Application to Coal Distillates, *Anal. Chem.* **59(17)**, 2027-33 (1987).

11. T. Aczel, S. G. Colgrove, and S. D. Reynolds, High Resolution Mass Spectrometric Analysis of Coal Liquids, *Prepr. Am. Chem. Soc., Div. Fuel Chem.* **30(1)**, 209-20 (1985).

12. H.-R. Schulten and A. Marzec, Liquefaction Behaviour of Coals Studied by Field Ionization Mass Spectrometry and Chemometrics, in: 1987 International Conference on Coal Science (J. A. Mouljin, K. A. Nater and H. A. G. Chermin, eds.), pp. 215-218, Elsevier, Amsterdam (1987).

13. G. S. Melcalf, W. Windig, G. R. Hill, and H. L. C. Meuzelaar, Characterization of U. S. Lignites by Pyrolysis Mass Spectrometry and Multivariate Analysis, *Int. J. Coal Geol.* 7, 245-268 (1987).

14. Y. Yun and H. L. C. Meuzelaar, Simultaneous Thermogravimetric and Mass Spectrometric Observations on Vacuum Pyrolysis of Argonne PCSP Coals, *Prepr. Am. Chem. Soc., Div. Fuel Chem.* **33(3)**, 75-84 (1988).

15. K. S. Vorres and S. K. Janikowski, The Eight Coals in the Argonne Premium Coal Sample Program, *Prepr. Am. Chem. Soc., Div. Fuel Chem.* **32(1)**, 492-499 (1987).

16. G. R. Dyrkacz and E. P. Horwitz, Separation of Coal Macerals, *Fuel* 61, 3-12 (1982).

17. H.-R. Schulten, Pyrolysis and Soft Ionization Mass Spectrometry of Aquatic/Terrestrial Humic Substances and Soils, *J. Anal. Appl. Pyrol.* 12, 149-186 (1987).

18. T. G. Squires, B. F. Smith, R. E. Winans, R. G. Scott, and R. Hayatsu, Structure and Reactivity of Coal Model Polymers, in: 1983 International Conference on Coal Science, pp. 292-295, Pittsburgh (1983).

19. R. E. Winans, R. G. Scott, P. H. Neill, G. R. Dyrkacz, R. L. McBeth, and R. Hayatsu, Characterization and Reactivity of Hydroxyls and Ethers in Coal Macerals, in: 1985 International Conference on Coal Science, pp. 687-690, Pergamon, Sydney (1985).

20. M. Siskin and T. Aczel, Pyrolysis Studies on the Structure of Ethers and Phenols in Coals, in: 1981 International Conference on Coal Science, pp. 651-656, Gluchauf, Essen (1981).

21. R. H. Schlosberg and C. G. Scouten, The Organic Chemistry of Calcium: A New Phenol Separation/Recovery Approach, *Prepr. Am. Chem. Soc., Div. Fuel Chem.* 28(1), 180-187 (1983).

22. R. Liotta, G. Brons, and J. Isaacs, Oxidative Weathering of Illinois No. 6 Coal, *Fuel* 62, 781-791 (1983).

TABLE 1. Approaches used to Prepare Samples for HRMS Analysis.

Method	References
Oxidation	(1),(2),(3)
Extraction	(4),(5)
Vacuum Pyrolysis	(2),(6),(7),(8),(9)
Liquefaction	(10),(11),(12)

TABLE 2. Elemental Analysis for the Coal and Maceral Samples.

Sample	Name	%C(maf)	Per 100 Carbons H	N	S	O
1	Upper Freeport mvB	85.5	66.0	1.55	0.32	6.59
2	Wyodak-Anderson SubB	75.0	85.6	1.28	0.23	18.0
3	Herrin hvCB	77.7	77.2	1.51	1.15	13.0
4	Pittsburgh hvAB	83.2	76.7	1.69	0.40	7.96
5	Pocahontas lvB	91.0	58.5	1.25	0.21	2.04
6	Blind Canyon hvBB	80.7	85.7	1.67	0.17	10.8
7	Stockton-Lewiston hvAB	82.6	76.3	1.62	0.30	8.93
8	Beulah-Zap Lignite	72.9	79.5	1.35	0.36	20.9
	Illinois No. 2 Vitrinite	73.9	85.4	1.28	0.81	18.4
	Brazil Block Sporinite	78.6	113.6	1.20	0.76	10.7
	Upper Elkhorn Sporinite	80.9	94.2	1.59	0.51	9.3
	Ohio No. 5 Alginite	81.6	133.7	.73	-	-
	Upper Elkhorn Inertinite	70.9	63.8	1.45	4.66	16.2
	Illinois No. 2 Fusinite	79.3	48.0	0.54	1.89	12.3

TABLE 3. Modes of Operation for HRMS.

Spectrometer	Resolution	Sample Temperature (°C)	Heating Rate °C/Min.	Ionization Mode	Reference
Kratos MS 25	5,000	200-800	50	70 eV	(2),(6)
Kratos MS 50	40,000	200-800	50	70 eV	(7)
Kratos MS 50	40,000	600	rapid	70 eV	(9)
Kratos MS 50	25,000	300	-	Low eV	(9)
Kratos MS 50	80,000	300	-	Low eV	(8)
MAT 731	10,000-30,000	50-750	60	FI	(12),(17)

TABLE 4. Heteroatom and Combination of Heteroatoms Searched for in HRMS Data.

Hydrocarbons		Sulfur	31.972072
Oxygen	15.994915	Two Sulfurs	63.944144
Two Oxygens	31.989830	Sulfur-Oxygen	47.96699
Three Oxygens	47.984745	Sulfur-Two Oxygens	63.961905
		Sulfur-Three Oxygens	79.956820
Nitrogen	14.003074	Sulfur-Nitrogen	45.975146
Two Nitrogens	28.006148	Sulfur-Two Nitrogens	59.97822
Nitrogen-Oxygen	29.997989	Sulfur-Nitrogen-Oxygen	61.970061
Nitrogen-Two Oxygen	45.992904		

TABLE 6. Averaged Relative Abundances for the Phenol and Alkylphenol Peaks.

Sample	Maceral M/Z =	94	107	108	121	122	135	136
Illinois #2	Vitrinite	38	100	48	45	29	28	--
Illinois #2	Vit. Ca	94	87	45	19	13	100	--
Brazil Block	Vitrinite	36	100	50	36	29	61	11
Brazil Block	Vit. Ca	61	55	21	21	--	100	--
Upper Elkhorn	Vitrinite	27	100	53	41	41	5	5
Upper Elkhorn	Vit. Ca	22	69	42	32	19	100	8
Upper Elkhorn	Vit. K	37	100	57	45	39	16	4
Brazil Block	Sporinite	33	100	56	49	42	35	25
Brazil Block	Spor. Ca	65	100	84	89	68	92	26
Illinois #2	Fusinite	20	100	55	30	5	50	10
Illinois #2	Fus. Ca	51	100	54	37	26	86	6

FIGURE CAPTIONS

Figure 1. AGHIS with the interface for the pyrolysis probe.

Figure 2. Reversible Diels-Alder adduct used as a quantitation standard.

Figure 3. Mass spectra of the pyrolysis standard.

Figure 4. Thermal rearrangement of oxy-methylene linked polymer(I).

Figure 5. Selected ion chromatogram for quinone and alkylphenol fragments from PyHRMS of Polymer I.

Figure 6. Distribution of sulfur compounds determined from PyHRMS for four maceral samples.

Figure 7. Selected phenolic fragment data from PyMS and maceral samples separated from a liptinite concentrate. The dashed line divides the liptinites from the vitrinites.

Figure 8. Total ion pyrogram for vitrinite and two exchanged vitrinites.

Figure 9. Hydrocarbon peaks sorted by hydrogen deficiency from PyHRMS of APCS #5, low volatile bituminous coal.

Figure 10. Peaks containing one, two or three oxygens from PyHRMS of APCS #8, lignite coal.

Figure 11. Area chart of the distribution of the various heteroatoms from PyHRMS of APCS #8, lignite coal.

Figure 12. Selected ion spectra for six series which have a peak at m/z=266 for LVHRMS of APCS #3, Herrin Seam coal pyrolysis product.

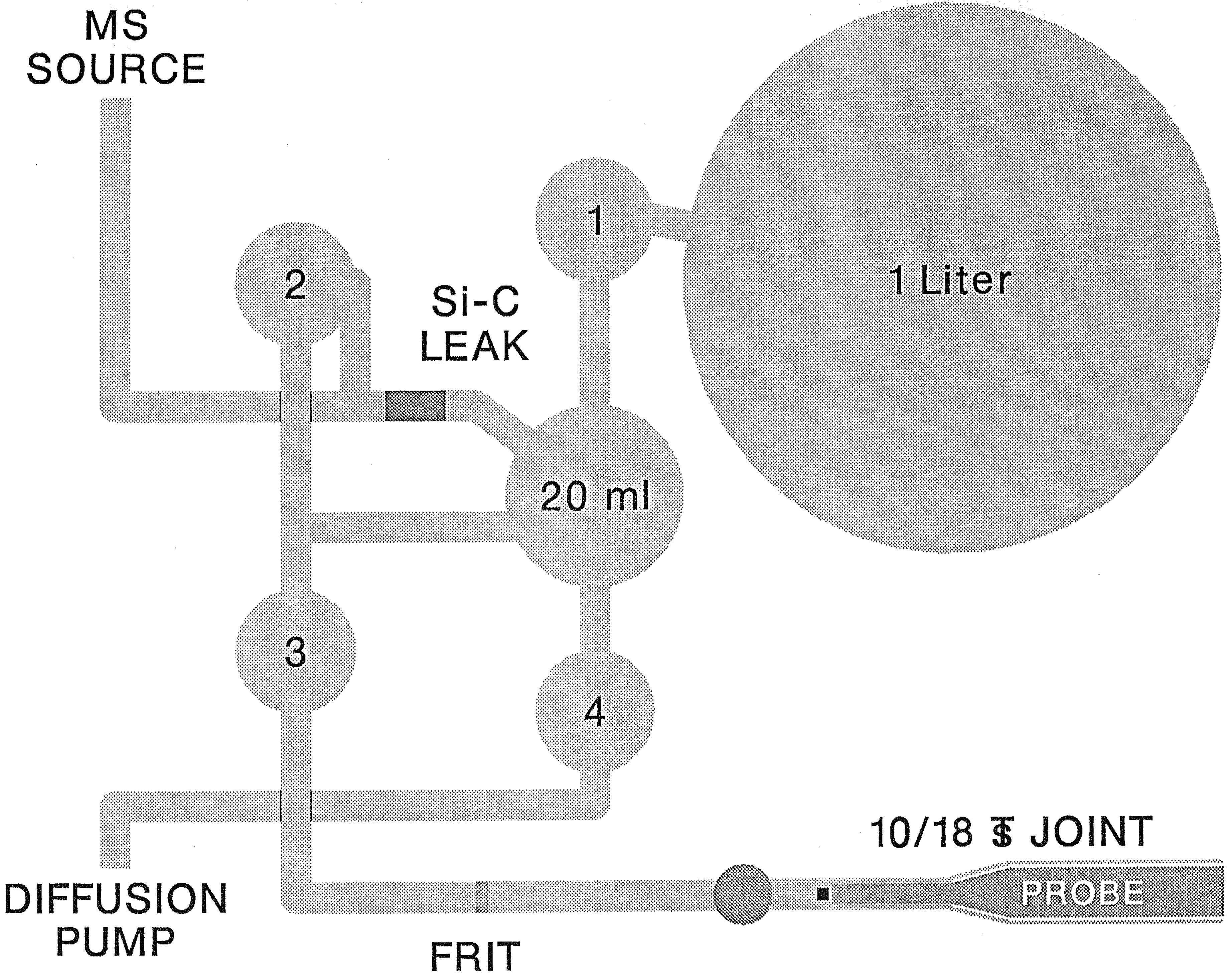
Figure 13. Selected ion pyrogram of dihydroxylbenzenes relative to the Diels-Alder standard for linear heating (50°C/min.) of APCS #2, the subbituminous coal.

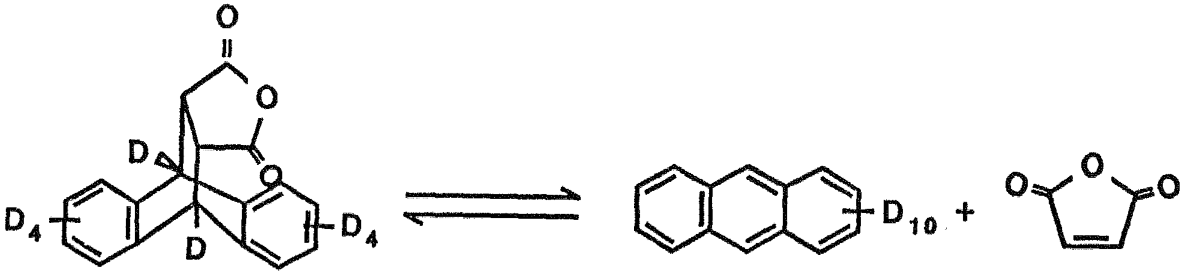
Figure 14. Selected ion pyrograms relative to the standard for linear heating (50°C/min.) of APCS #2, the subbituminous coal.

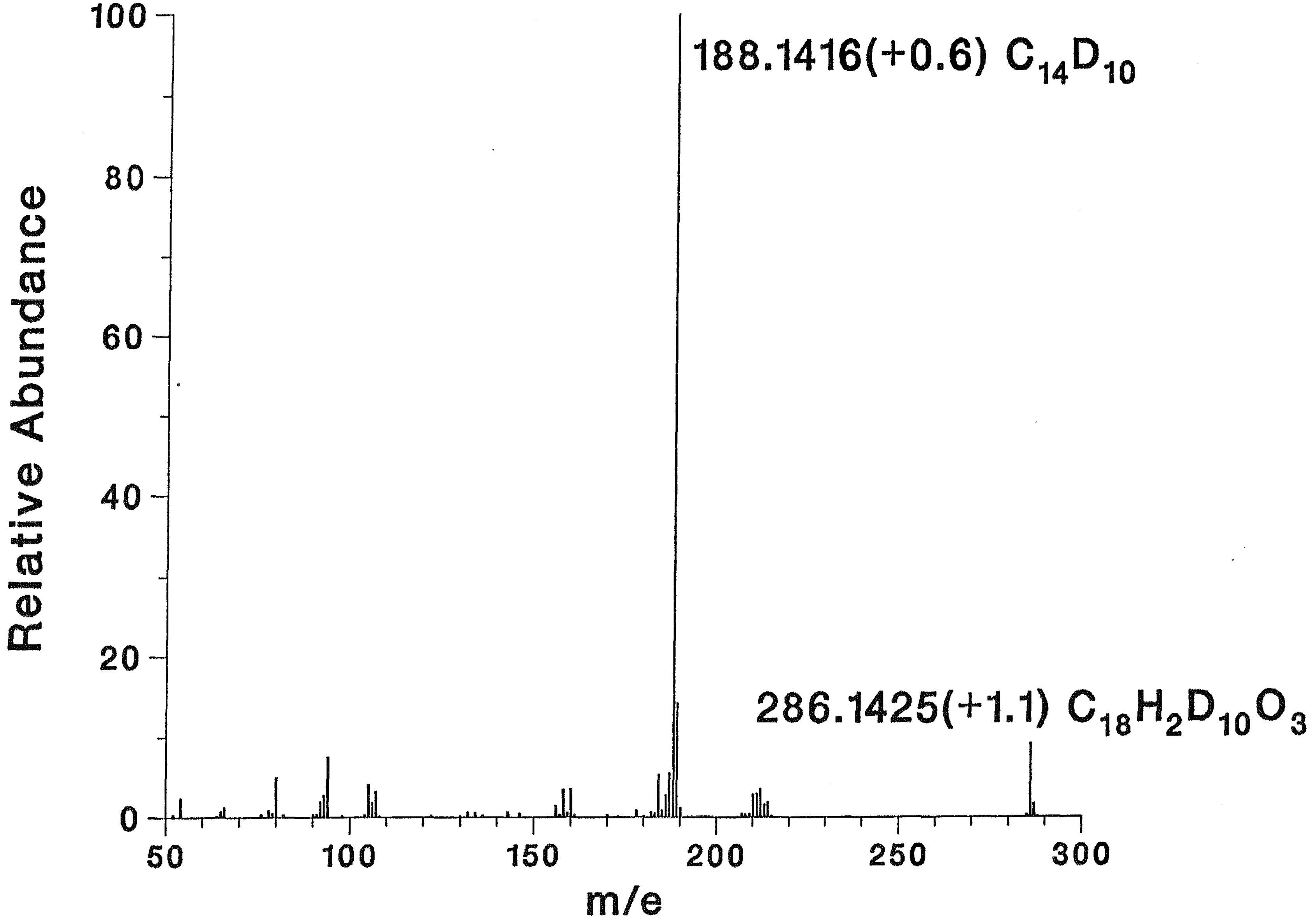
Figure 15. Selected ion pyrograms relative to the standard for linear heating (50°C/min.) of APCS #1, medium volatile bituminous coal.

Figure 16. Total ion current (TIC) pyrograms from PyHRMS (50°C/min.) of APCS #2 subbituminous coal and its methylated Ag_2O oxidation product.

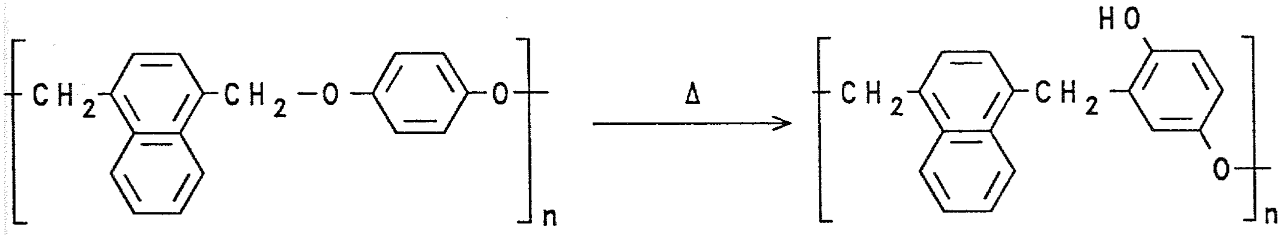
Figure 17. Distribution of hydrocarbons with respect to hydrogen deficiency for the average of the data shown in Figure 15.


MS
SOURCE
1
1 Liter
2
Si-C
LEAK
20 ml
3
4
10/18 $ JOINT
PROBE
DIFFUSION
PUMP
FRIT


O
O
O
D
D
D4
D4
D10
+
O
O
O

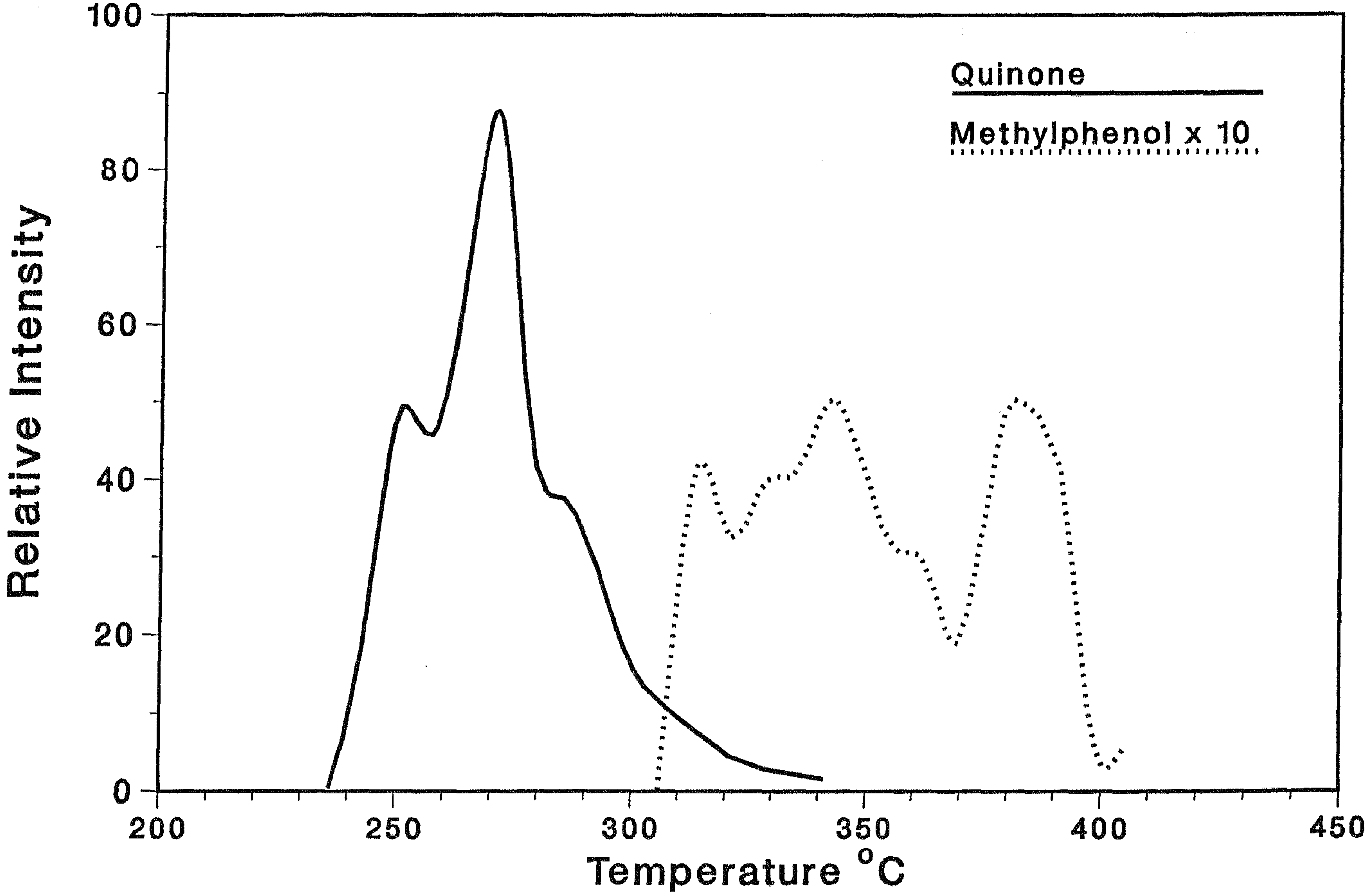


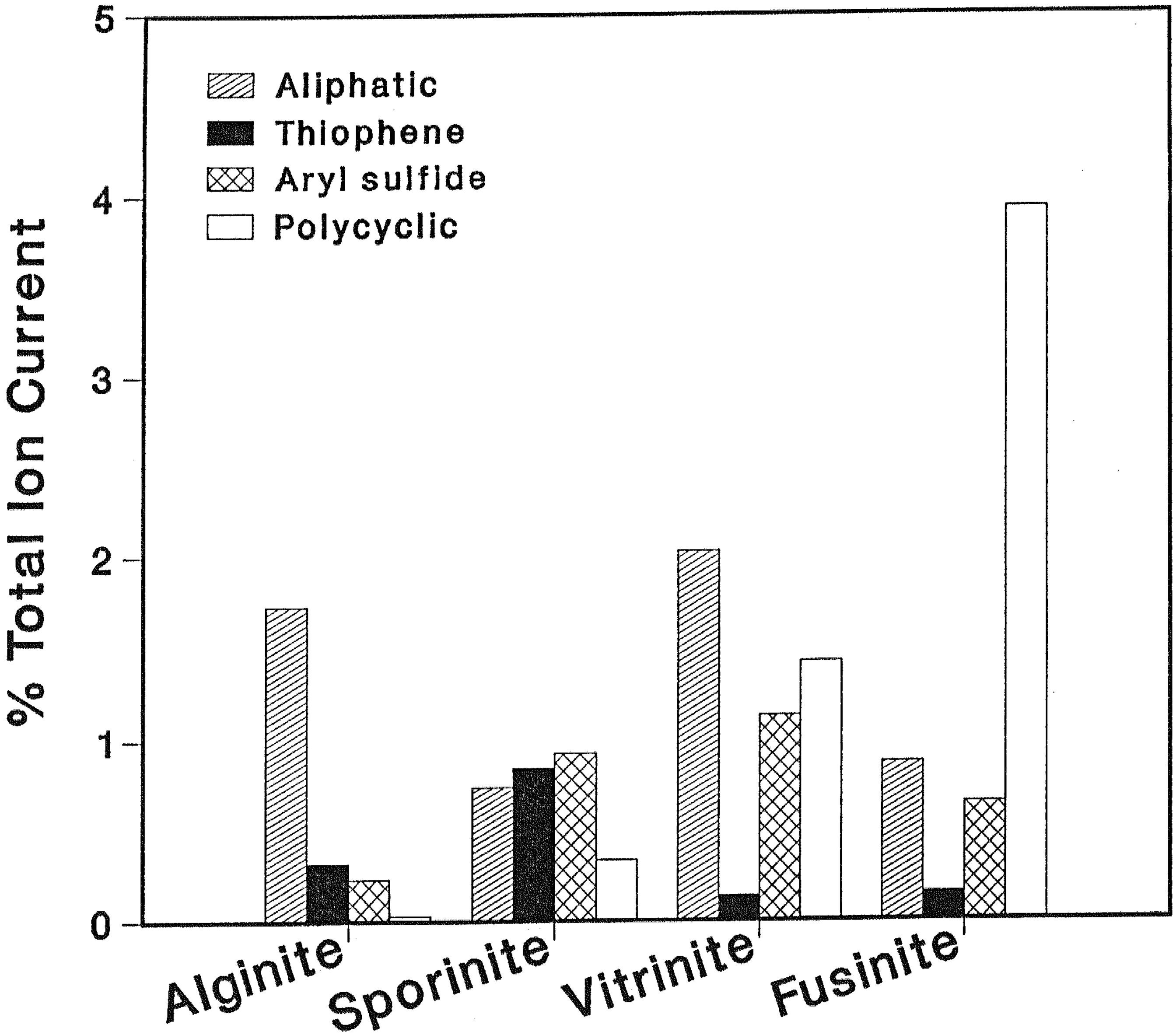
188.1416(+0.6) $C_{14}D_{10}$
286.1425(+1.1) $C_{18}H_2D_{10}O_3$
Relative Abundance
100
80
60
40
20
0
50
100
150
200
250
300
m/e



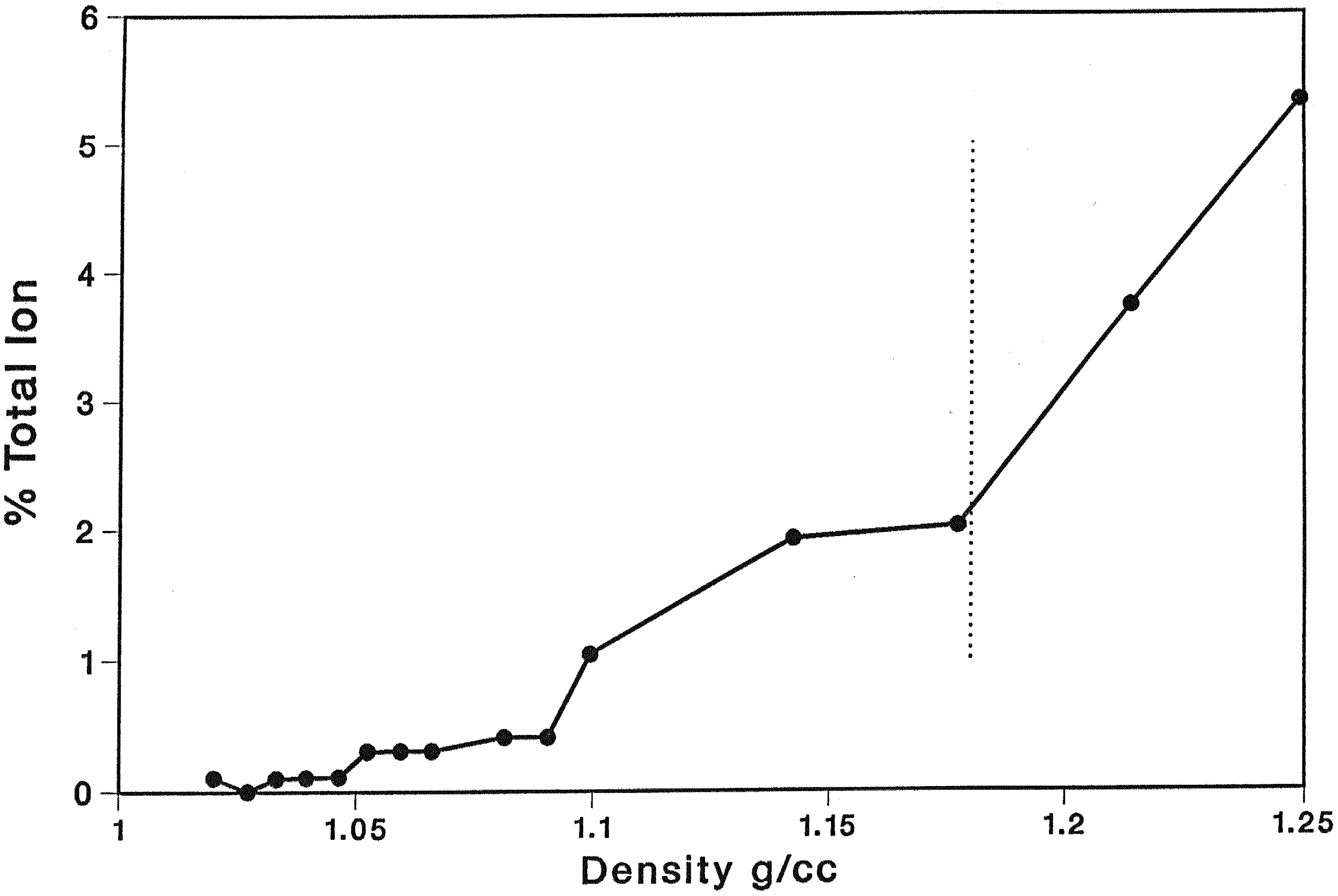
I.

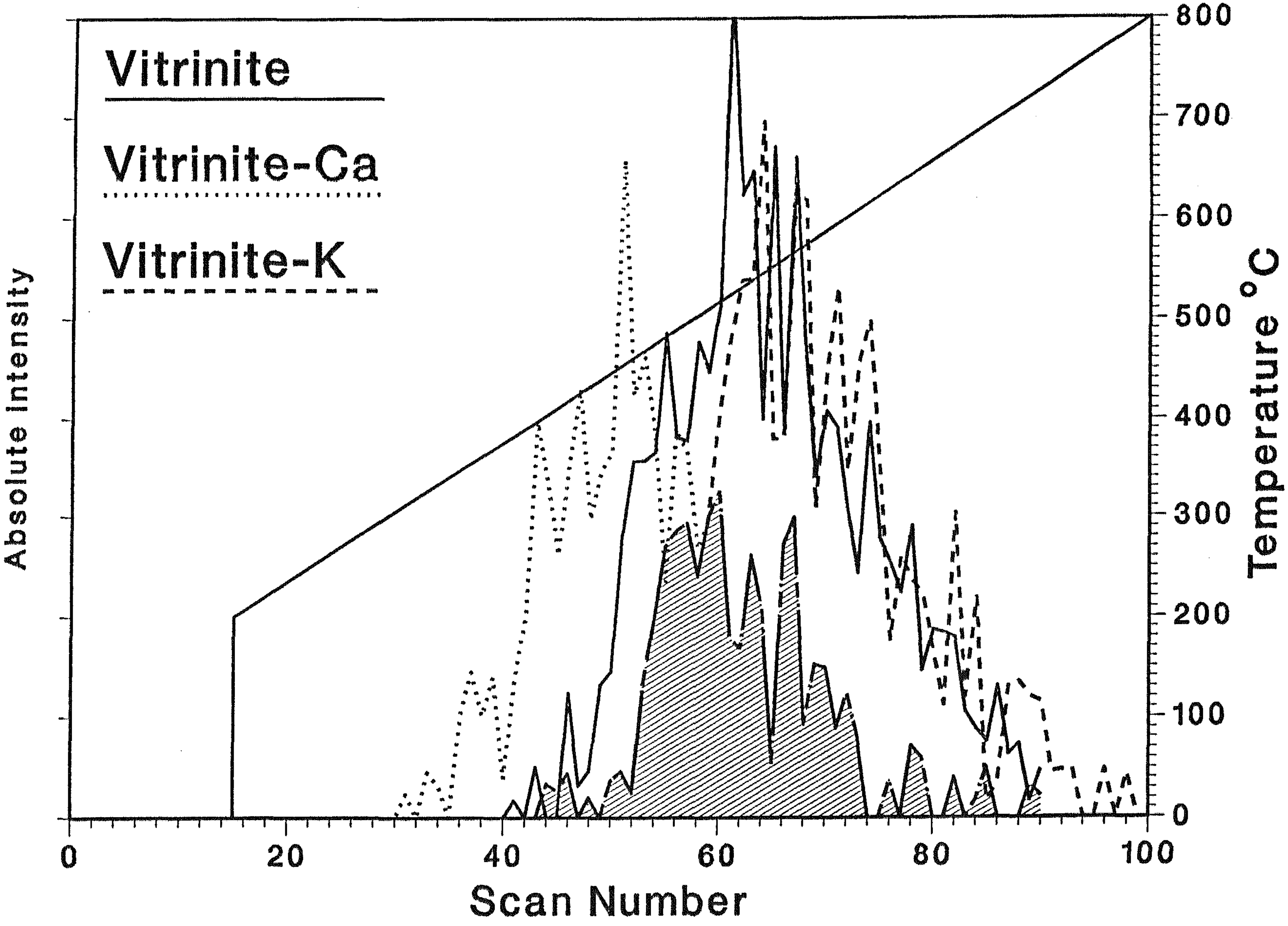
II.

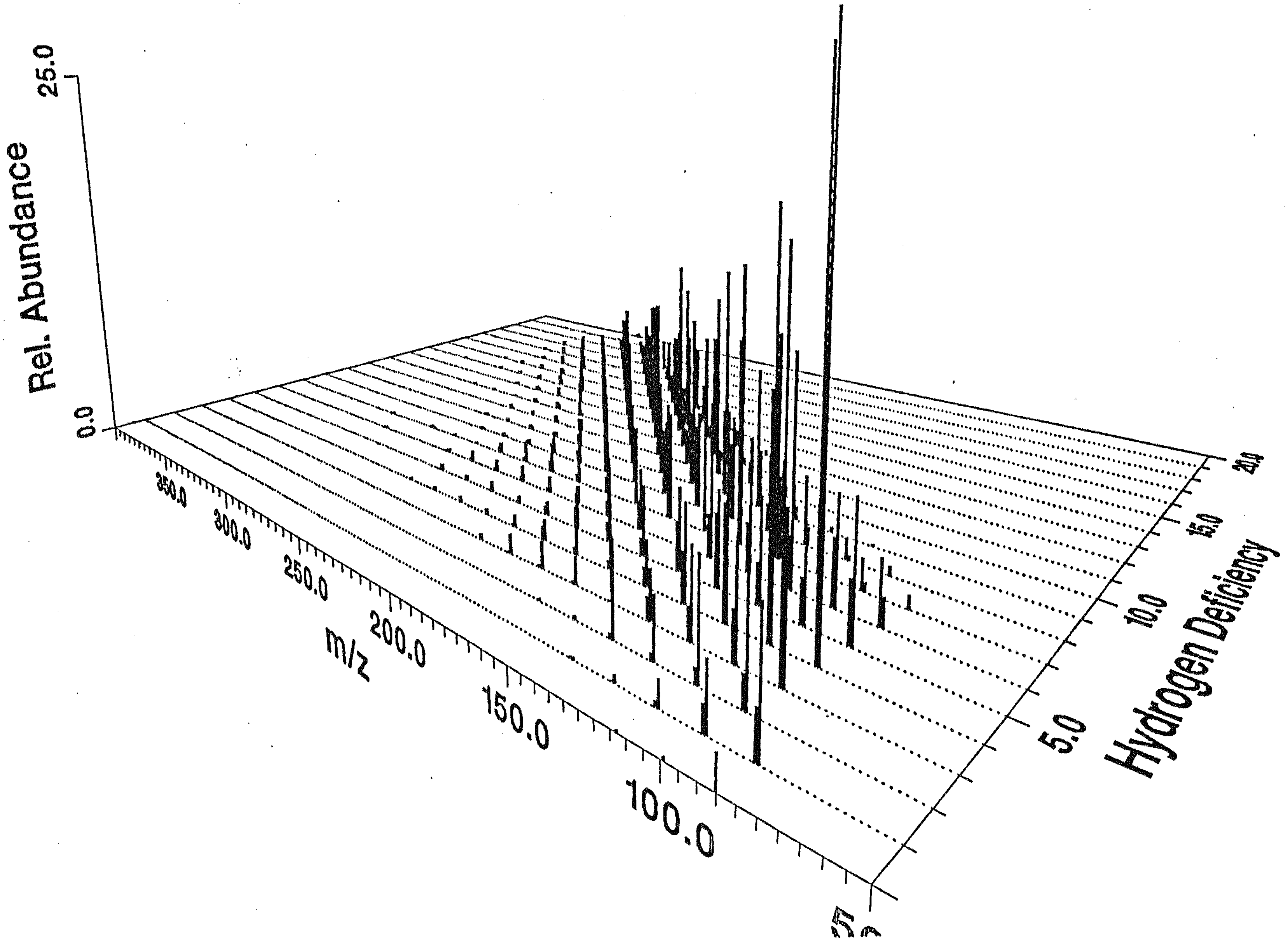

Quinone
Methylphenol x 10
Relative Intensity
0
20
40
60
80
100
200
250
300
350
400
450
Temperature °C

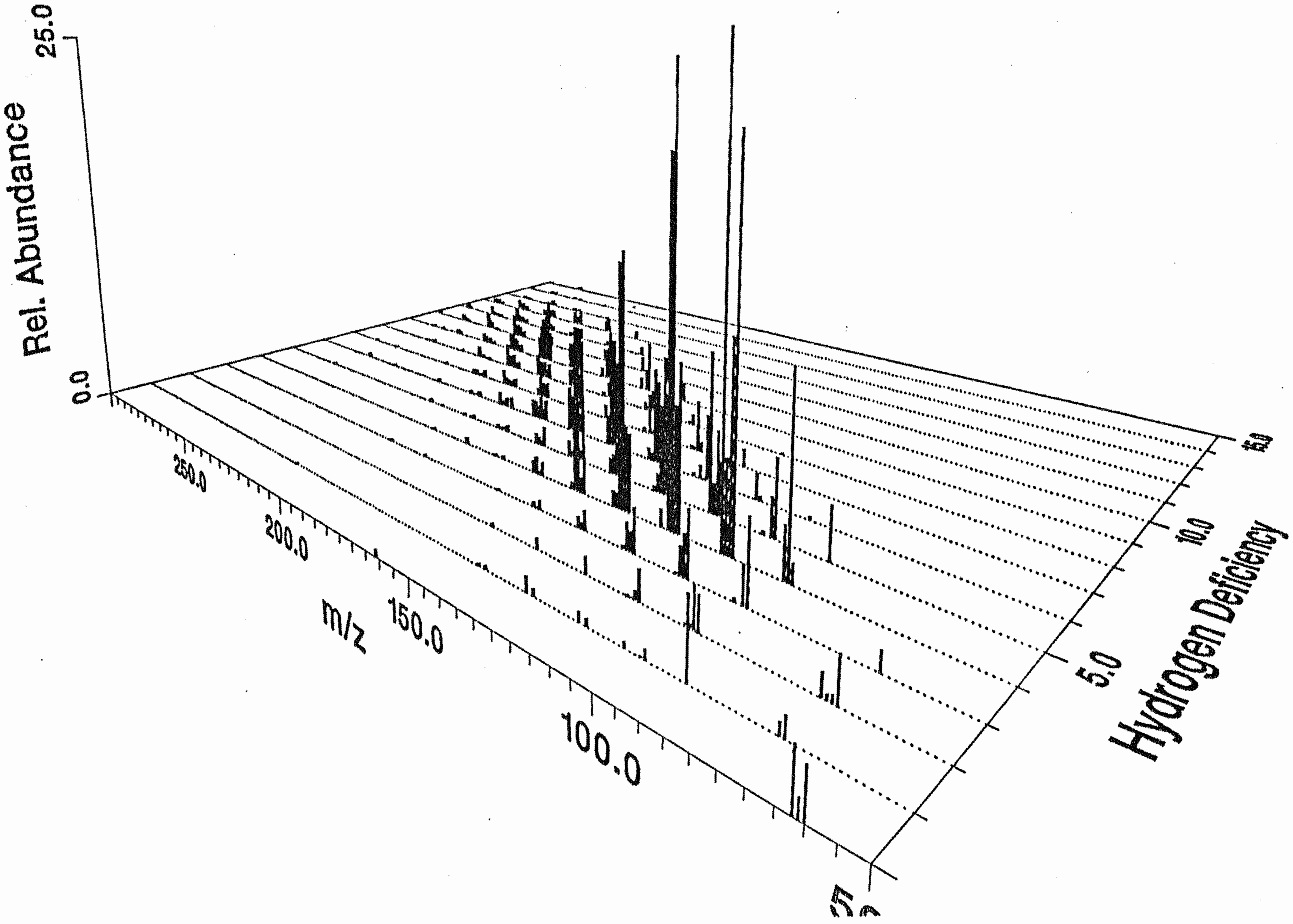


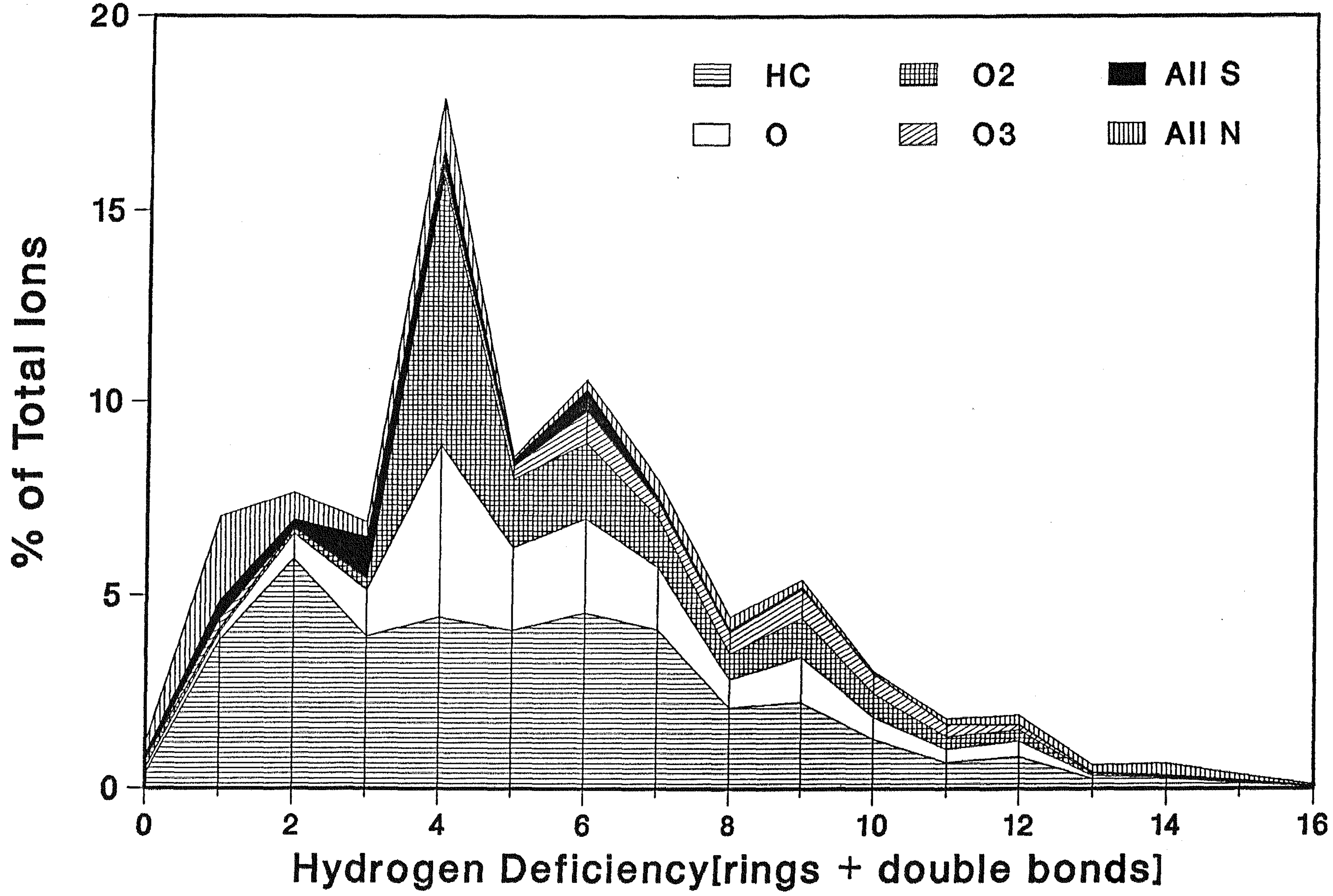
% Total Ion Current
0
1
2
3
4
5
Aliphatic
Thiophene
Aryl sulfide
Polycyclic
Alginite
Sporinite
Vitrinite
Fusinite


% Total Ion
6
5
4
3
2
1
0
1
1.05
1.1
1.15
1.2
1.25
Density g/cc

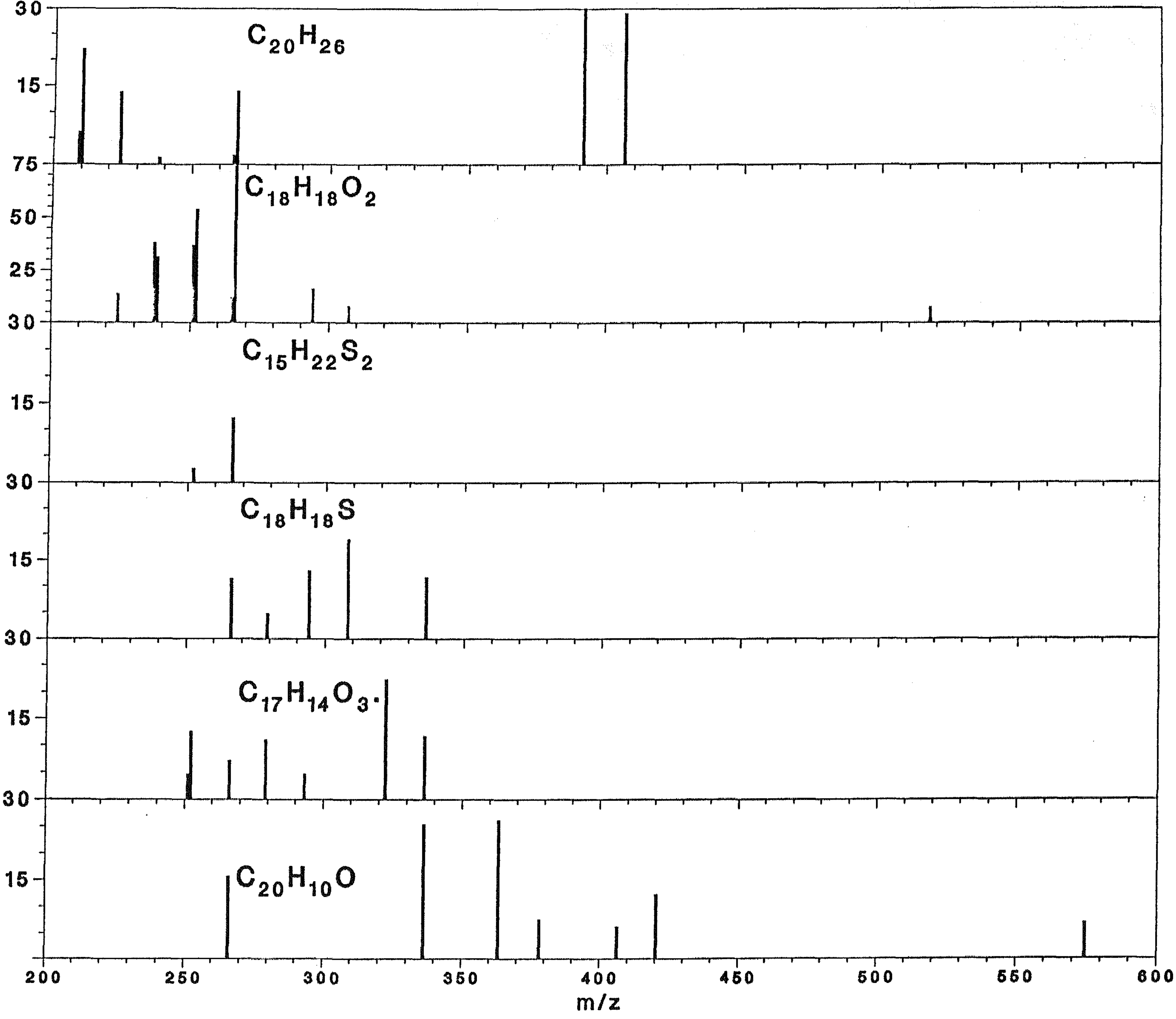

Vitrinite
Vitrinite-Ca
Vitrinite-K
Absolute Intensity
Temperature °C
Scan Number
0
20
40
60
80
100
0
100
200
300
400
500
600
700
800

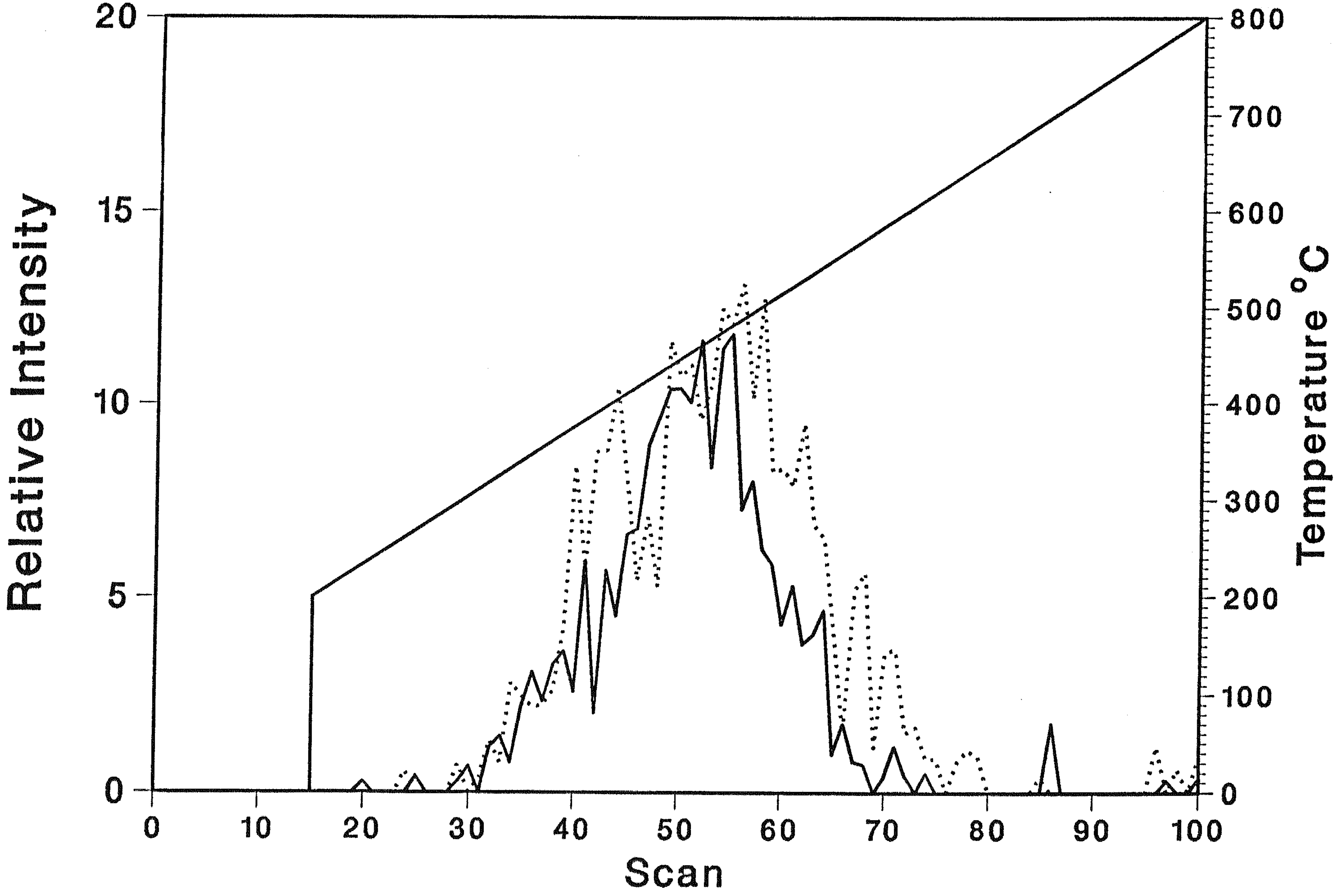

Rel. Abundance
25.0
0.0
350.0
300.0
250.0
200.0
150.0
100.0
m/z
20.0
15.0
10.0
5.0
Hydrogen Deficiency


Rel. Abundance
25.0
0.0
250.0
200.0
150.0
m/z
100.0
15.0
10.0
5.0
Hydrogen Deficiency

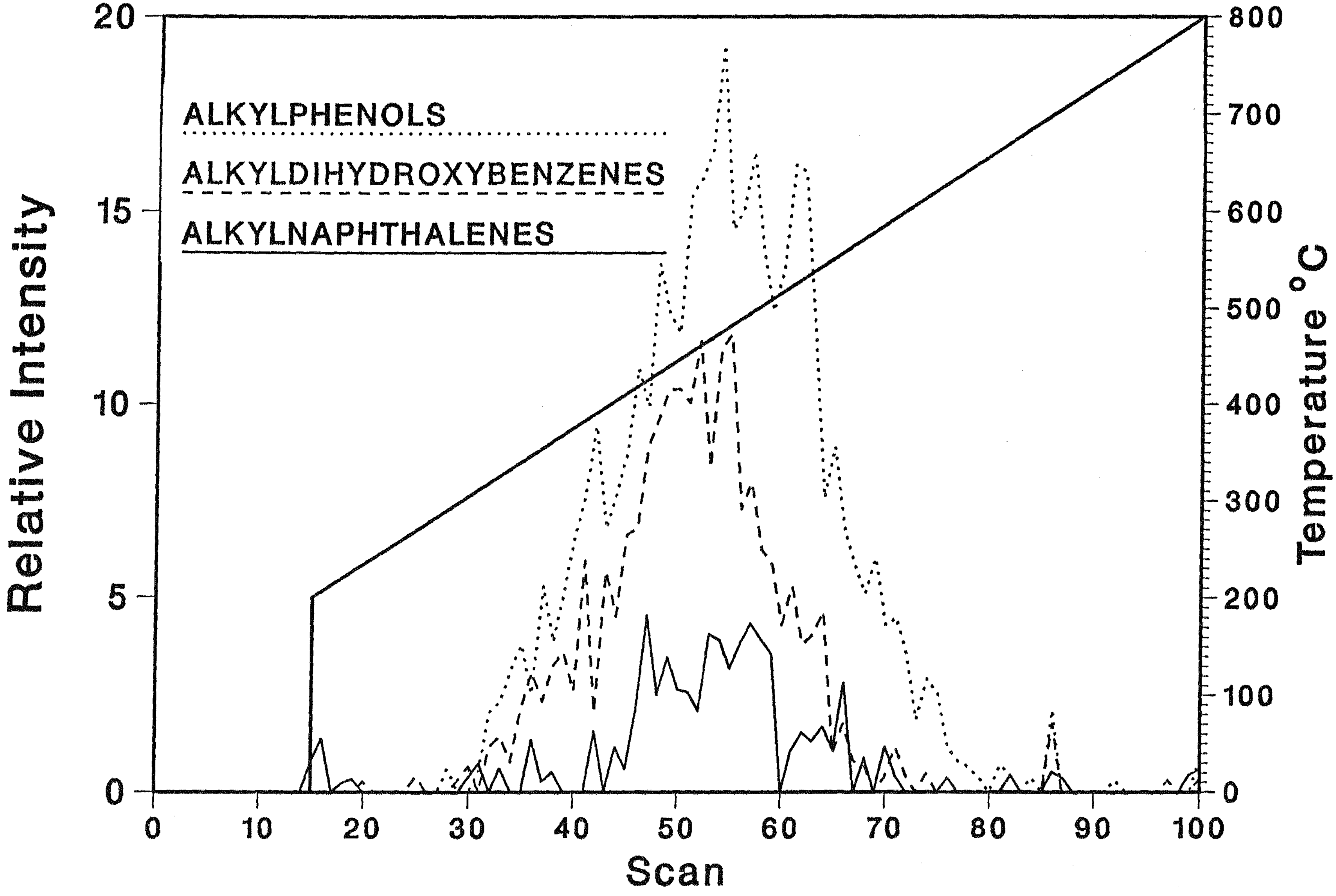


20
15
10
5
0
% of Total Ions
0
2
4
6
8
10
12
14
16
Hydrogen Deficiency[rings + double bonds]
HC
O
O2
O3
All S
All N

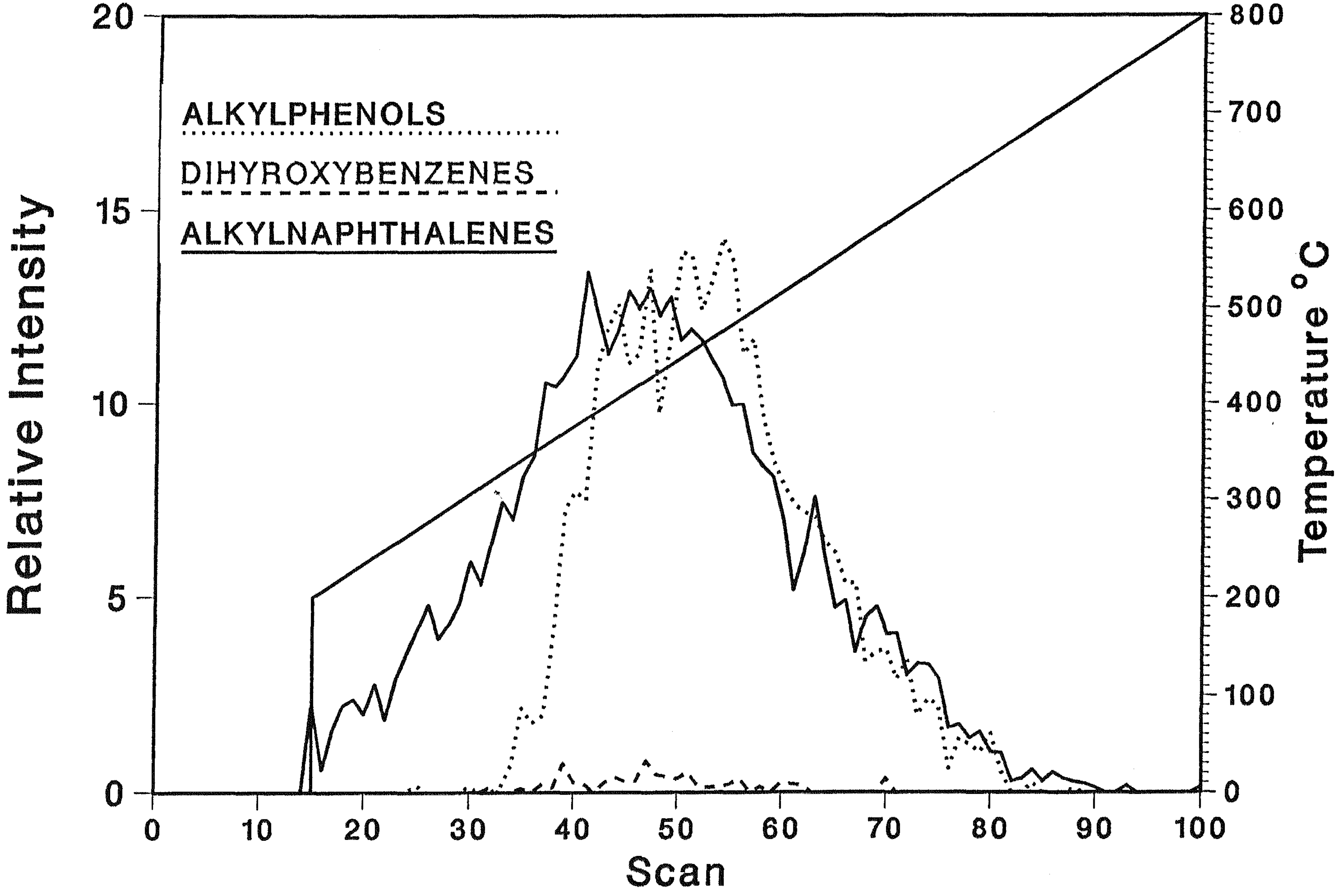

30
15
75
50
25
30
15
30
15
30
15
30
15
$C_{20}H_{26}$
$C_{18}H_{18}O_2$
$C_{15}H_{22}S_2$
$C_{18}H_{18}S$
$C_{17}H_{14}O_3$·
$C_{20}H_{10}O$
200
250
300
350
400
450
500
550
600
m/z

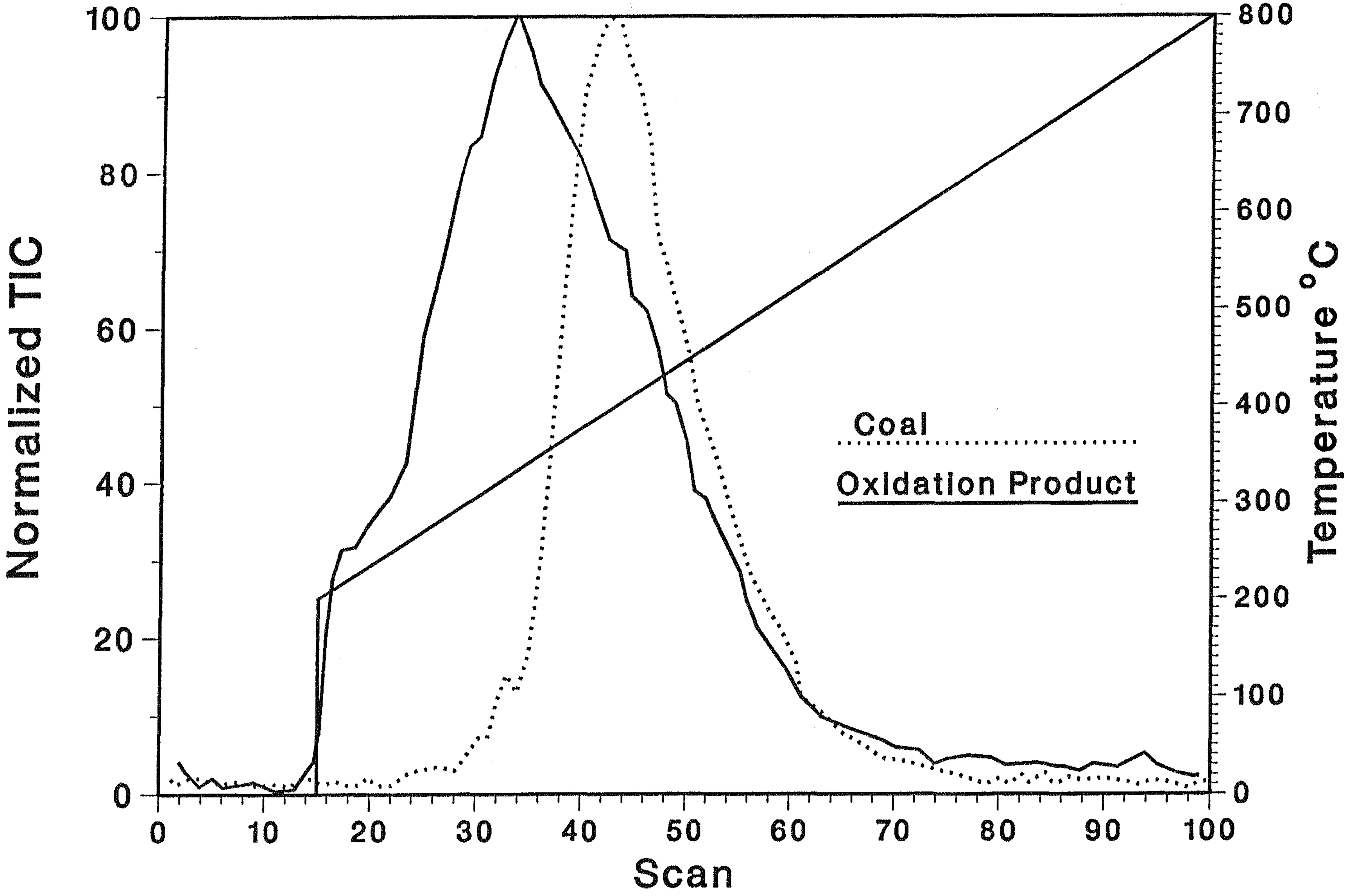


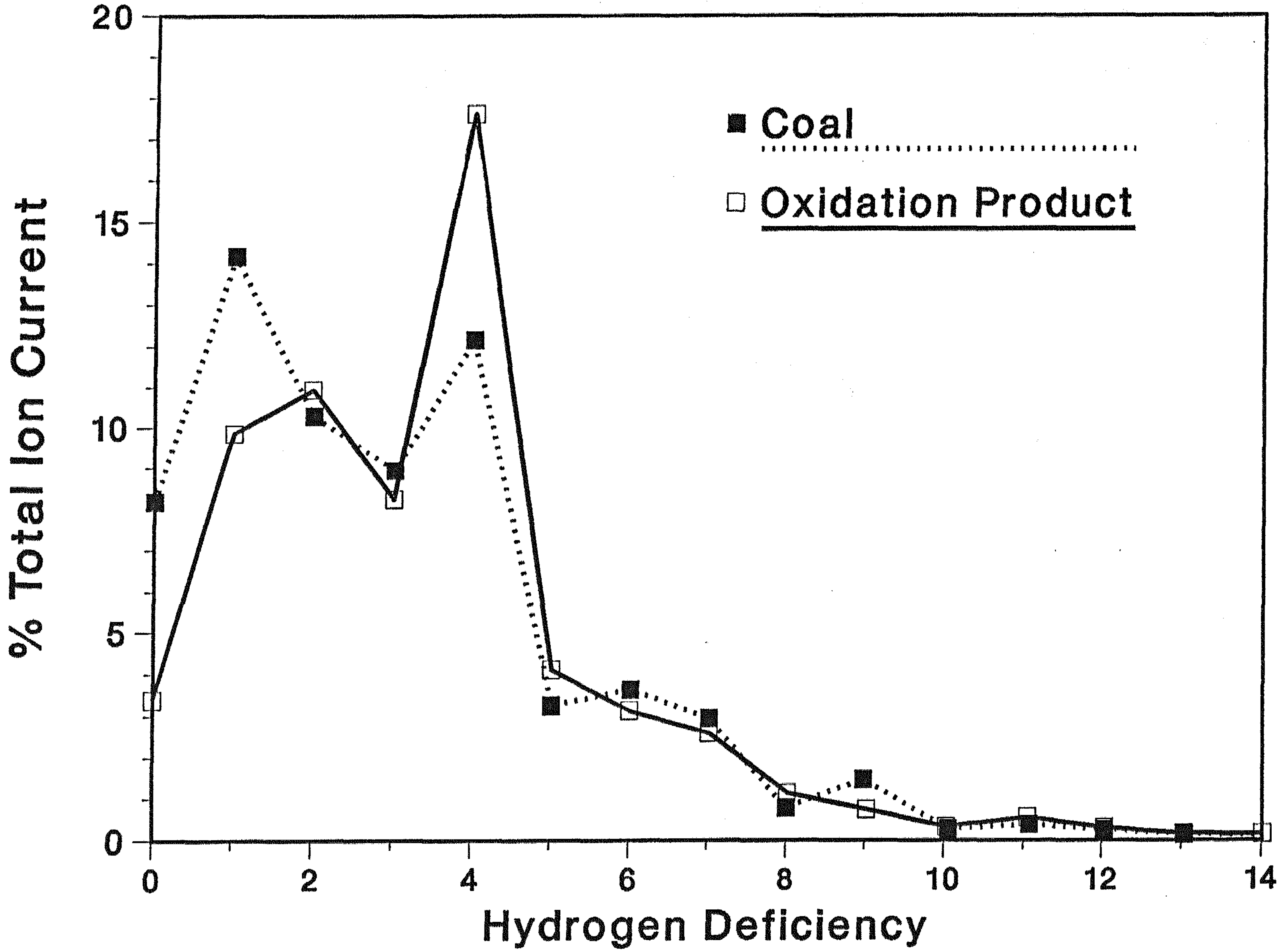
Relative Intensity
0
5
10
15
20
Scan
0
10
20
30
40
50
60
70
80
90
100
Temperature °C
0
100
200
300
400
500
600
700
800



ALKYLPHENOLS
ALKYLDIHYDROXYBENZENES
ALKYLNAPHTHALENES
Relative Intensity
20
15
10
5
0
Temperature °C
800
700
600
500
400
300
200
100
0
Scan
0
10
20
30
40
50
60
70
80
90
100


ALKYLPHENOLS
DIHYROXYBENZENES
ALKYLNAPHTHALENES
Relative Intensity
0
5
10
15
20
Scan
0
10
20
30
40
50
60
70
80
90
100
Temperature °C
0
100
200
300
400
500
600
700
800


Normalized TIC
Temperature °C
Scan
0
10
20
30
40
50
60
70
80
90
100
0
20
40
60
80
100
0
100
200
300
400
500
600
700
800
Coal
Oxidation Product



% Total Ion Current
20
15
10
5
0
0
2
4
6
8
10
12
14
Hydrogen Deficiency
■ Coal
□ Oxidation Product