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DEVELOPMENT OF AN HPLC, GC/MS METHOD FOR ANALYSIS OF HYGAS OIL SAMPLES

by

Leo A. Raphaelian

ENERGY & MINERAL RESOURCES PROGRAMS

ENERGY & ENVIRONMENTAL SYSTEMS DIVISION
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National Technical Information Service
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5285 Port Royal Road
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NTIS price codes
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Distribution Category:
Coal Conversion and
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ANL/EMR-4

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June 1979

Work Sponsored by

U.S. Department of Energy
Assistant Secretary for Energy Technology
Office of Fossil Energy Programs

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DEVELOPMENT OF AN HPLC GC/MS METHOD FOR ANALYSIS OF HYGAS OIL SAMPLES

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ABSTRACT

Direct analysis of a HYGAS oil sample by gas chromatography/mass spectrometry (GC/MS) or capillary column GC/MS is difficult for at least two reasons: (1) due to the large number (probably over 400) of compounds present in the mixture, many overlapping peaks occur, resulting in mass spectra that are often confusing, and (2) moderately to highly polar compounds are not easily chromatographable.

In Part 1 of this study, high performance liquid chromatographic (HPLC) methods for separating the complex HYGAS oil samples into fractions were investigated. A satisfactory separation of a HYGAS oil sample into seven fractions varying from non-polar or weakly polar to highly polar was achieved on a μBondapak CN column with a complex gradient of hexane to THF.

In Part 2, derivatization as a means for making polar compounds more amenable to identification by capillary column GC/MS was explored. With the use of standard phenols, carboxylic acids, amines, and alcohols, it was found that BSA (a silylating agent) was most effective in derivatizing phenols and alcohols and Methyl-8 Concentrate (an alkylating agent) was most effective in derivatizing carboxylic acids and amines. The lower limit of detection by capillary column GC/MS was in the range of less than 10 to 20 ng/μL per underivatized compound.

In Part 3, a preliminary study of the methods developed in Parts 1 and 2, namely HPLC separation into fractions and derivatization of the polar fractions, was undertaken on an authentic HYGAS oil sample to determine whether the methods would make the sample more amenable to analysis by capillary column GC/MS. It was found that, with HPLC, the complex mixtures of HYGAS oil samples are separated into simpler complex mixtures and, with derivatization of the polar fractions, the identification by capillary column GC/MS of polar compounds not normally chromatographable was enhanced. Many previously unreported hydroxy PNAs were found.

1 SEPARATION INTO FRACTIONS BY HPLC

1.1 INTRODUCTION

1.1.1 Objective

The objective of this part of the study was to determine whether high performance liquid chromatography (HPLC) could be used to separate HYGAS oil samples into fractions that would be more amenable to analysis by capillary column gas chromatography/mass spectrometry (GC/MS) than the bulk sample.

1.1.2 Background

In preliminary analyses by GC/MS, it was found that HYGAS oil samples contain a variety of compounds including toluene, the start-up and make-up oil, aromatic hydrocarbons, phenols, anilines, pyridines, thiophenes, benzonitriles, and PNAs. Direct analysis of the mixture by GC/MS is at best difficult for at least two reasons: (1) due to the large number (probably over 400) of compounds present in the mixture, many overlapping peaks occur, resulting in mass spectra that are often confusing; (2) capillary columns that give good separation of non-polar compounds are not adequate for the separation of polar compounds. Therefore, there is a definite need for a preliminary separation of the complex mixtures in HYGAS oil samples.

Ideally, for use in capillary column GC/MS, the preliminary separation scheme (fractionation) should give non-polar or very weakly polar, weakly polar, moderately polar, polar, and very polar fractions. Alternatively, a separation scheme that would provide fractions of classes of compounds, such as hydrocarbons, alcohols, phenols, amines, etc., would also be useful, particularly for use in developing specific derivatizations.

For the separation of petroleum, fractional distillation, extraction, complex formation, and column chromatography, including adsorption, partition, and gel permeation, are among the methods that have been used. Each method has certain advantages and disadvantages. With fractional distillation, the toluene, which represents a major portion of a HYGAS oil sample, could be removed. However, this method suffers from the fact that any distillation, fractional or otherwise, requires heat and decomposition and reaction between components in the mixture typically takes place, altering the composition. With such extractions as the acid/base liquid-liquid type, recoveries of individual components of the mixture are not only variable but also often low, particularly with polar compounds; moreover, some matrix effects frequently occur affecting recoveries. Complex formation is not only too limited to be of use but also not applicable in this case since the complexes would not be chromatographable by GC. Column chromatography, although useful, suffers from being long and tedious and requires the use and workup of large amounts of solvent; it is not recommended for a large number of samples.

It can be stated, generally, that separations that can be done by column chromatography can also be done considerably better by HPLC. When

compared to column chromatography, HPLC gives much better resolution, much shorter run times, and much less solvent. However, the amount of sample that can be processed per run is considerably less than with column chromatography. To overcome this disadvantage, several runs of the sample can be made with the attendant advantages of time, workup of much less solvent, and resolution.

In the petroleum field, HPLC has been used predominantly for identification of components in a mixture[1,2] or for fingerprinting oil samples.[3] Little attention has been paid to the use of HPLC as a means of performing gross separation 4-6 although, in certain instances, investigators have isolated peaks and identified the compound or compounds by GC/MS or mass spectrometry. Although HPLC/MS instruments are available, HPLC does not have the resolution capillary column GC and, as a result, HPLC/MS is not as useful as capillary column GC/MS for the analysis of complex mixtures.

As mentioned, HYGAS oil samples contain a variety of compounds with a wide range of polarities, with toluene as the major component. Since many of the compounds of interest are present only in low concentrations, the problem of isolating and separating into fractions sufficient quantities of these compounds for capillary column GC/MS analysis must be addressed.

The use of HPLC for preliminary fractionation of samples from coal conversion plants was based on the following calculations and assumptions (Fig. 1.1). Typically, complex mixtures that are to be analyzed by capillary column GC/MS are concentrated or diluted to give a range of concentration for each compound of 500 pg/μL to 200 ng/μL. The average component in such a mixture has a concentration of 20 ng/μL with the majority of the components falling in the range of 10-50 ng/μL. If one assumes that the average component has a concentration of 20 ng/μL in the sample to be injected into the capillary column of the GC/MS and there are 100 components in the mixture of one of the five fractions, then there would be 2 μg/μL for each fraction or 1 mg for the five fractions. If one assumes that 95% of the HYGAS sample is toluene, to identify the remaining components, one would require 20 mg of sample. The limit for HPLC high resolution micro columns is 20-60 mg of sample. Thus, a separation in just one HPLC run of a HYGAS sample into five fractions suitable for analysis by capillary column GC/MS appeared to be well within the realm of possibility.

1.1.3 HPLC Method Development

Several approaches to the separation of HYGAS oil samples into fractions suitable for analysis by capillary column GC/MS can be considered. First, with reverse phase HPLC, using μBondapak C_{18}, for example, polar compounds readily pass through the column and relatively non-polar compounds are retained and separated. Thus, a fairly easy separation of polar compounds from non-polar compounds is accomplished. However, since aqueous systems are used in this case, an additional step of liquid-liquid extraction, whose deficiencies have been pointed out above, would be required.

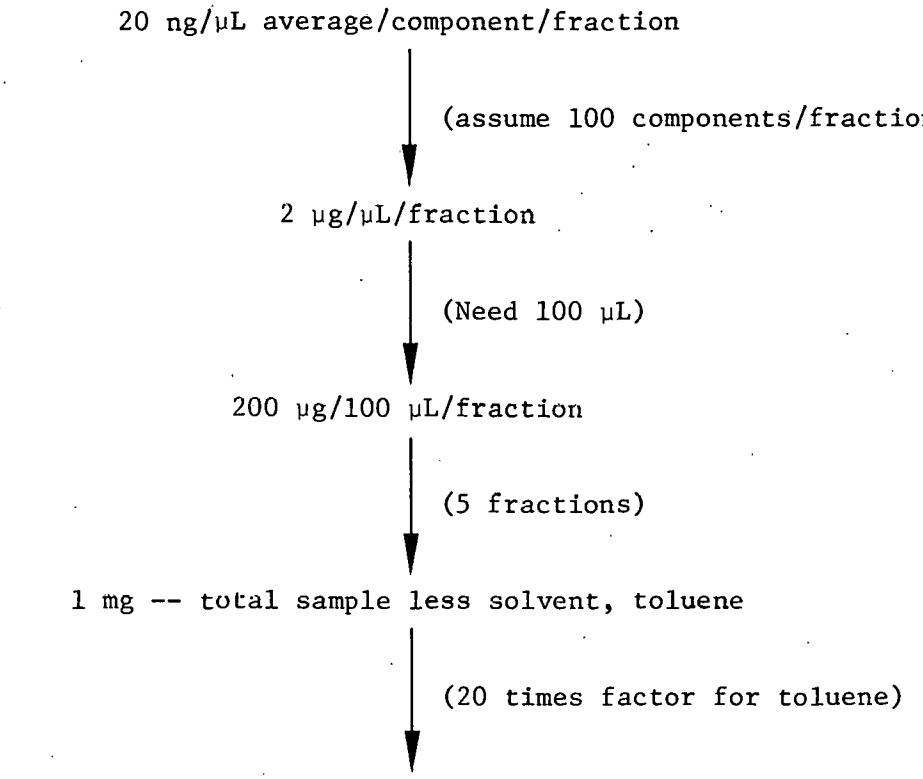

Fig. 1.1. Schematic Diagram Illustrating Amount of Sample Required for Separation into Five Fractions Suitable for Analysis by Capillary Column GC/MS

Having considered reverse phase HPLC, one can deduce criteria desirable in the HPLC method for separating HYGAS oil samples into fractions suitable for use in capillary column GC/MS. Ideally, the preliminary separation scheme (fractionation) should give nonpolar or very weakly polar, weakly polar, and moderately polar, polar, and very polar fractions in typical organic solvents that are suitable for GC/MS and derivatization and that are easily removed by evaporation such as pentane, hexane, acetonitrile, methylene chloride, and THF. It would be preferable also to remove the toluene as a separate fraction so that sufficient quantities of the other components in the HYGAS oil samples could be identified by capillary column GC/MS.

Of the high resolution micro columns available from Waters Associates, Inc. (Table 1.1), the following columns were considered potentially most useful for separating the HYGAS oil samples into fractions.

Table 1.1. Specifications of Waters Micro Columns (3.9 mm ID × 30 cm) (Data from Waters Associates, Inc.)

Column	Polarity	Plates/Meter at Specified Linear Velocity	Sample Loading Limit (mg)
μBondapak C_{18}	Very low	9000 at 0.44 cm/sec	20-60
μBondapak Phenyl	Low	9000 at 0.53 cm/sec	20-60
μBondapak CN	Medium	9000 at 0.53 cm/sec	20-60
μBondapak NH_2	High	9000 at 0.44 cm/sec	20-60

It would be expected that μBondapak NH_2 columns (in this case, the normal phase mode) would be most useful for providing good separations of relatively non-polar compounds, whereas the more polar compounds would remain on the column and require elution by backwashing. On the other end of the polarity scale, μBondapak C_{18} columns are too non-polar to be useful for separations in the normal phase mode and, therefore, were not investigated in this study. It appeared that the μBondapak Phenyl and μBondapak CN columns were the most promising for bringing about the separation into fractions of weakly polar through highly polar compounds. Although some separation of relatively non-polar compounds, which, aside from the solvent toluene, represent a large portion of a HYGAS oil sample, would take place, resolution would not be expected to be good.

Therefore, the study of methods development of a separation of HYGAS oil samples into fractions suitable for analysis by capillary column GC/MS and/or for derivatization and subsequent analysis by capillary column GC/MS would involve the following:

1. Investigation of the separation ability of μBondapak NH_2, μBondapak CN, and μBondapak Phenyl columns with solvents easily removed by evaporation and suitable for use in capillary column GC/MS and/or for derivatization and use in capillary column GC/MS.

2. Development of a means of separating the major component, toluene, from the rest of the compounds present so that sufficient concentrations of compound are available in each of five fractions for analysis by capillary column GC/MS and/or for derivatization and subsequent analysis by capillary column GC/MS.

1.2 EXPERIMENTAL PROCEDURES

1.2.1 HYGAS Oil Sample

The HYGAS oil sample (72/H/G/O/3), a further description of which can be found in Appendix A, was filtered with a sample clarification kit (Waters Associates, Inc., Milford, MA 01757) to remove unreacted coal.

1.2.2 Standard Solutions

With the exception of gallic acid monohydrate, each of the standards was dissolved in benzene. Gallic acid monohydrate was dissolved in THF. The source of the standards is shown in Table 1.2.

1.2.3 Solvents

For the preparation of standards, Burdick & Jackson Solvents (Burdick & Jackson Laboratories Inc, Muskegon, Michigan 49442) were used. For the mobile phase in HPLC runs, Waters solvents were used. They were hexane (No. 84911), 2,2,4-Trimethylpentane (No. 84915), THF (UV) (No. 84901), methylene chloride (No. 84913), and acetonitrile (No. 84905). Where low concentrations of THF in hexane were used, such as 1, 2.5, 5, and 10%, the solvents were premixed because solvent gradients at low concentrations led to erractic mixing of solvents.

1.2.4 HPLC Columns

The HPLC columns were from Waters and were 3.9 mm ID × 30 cm: μBondapak NH_2 (No. 84040), μBondapak Phenyl (No. 27198), and μBondapak CN (No. 84042).

1.2.5 Equipment

The HPLC equipment was Waters, consisting of two 6000A Solvent Delivery Systems, a 660 Solvent Programmer, U6K Universal Liquid Chromatograph Injector, 440 Absorbance Detector (UV), and R-400 Differential Refractometer (ΔRI). Detection was done at 254, 313, and 365 nm in the UV.

The flow rate of each pump was determined by measuring the volume of solvent at exhaust with a stop watch after which adjustments were made to give the desired flow rate. A six-way Valco air-activated selenoid valve was used for backflushing. Flow programming was done by connecting pump "A" to the "B" inlet of the solvent programmer normally used for solvent gradients.

1.3 RESULTS AND DISCUSSION

1.3.1 Separation of Non-Polar and Weakly Polar Compounds with μBondapak NH_2

Dark[3] has done an extensive study of the differences in petroleum-based products with μBondapak NH_2, and n-heptane as solvent, at a flow rate of 2 mL/min. Although the method is useful for fingerprinting (for which it was intended), it was found that separation of low PNAs was not sufficient, particularly for collection of fractions. Thus, with constant flow rate, the alkyl benzenes and lower PNAs tend to come together making separation into fractions and collection of those fractions difficult and the higher PNAs take a long time to come off the column, resulting in excessively long runs.

Table 1.2. Sources of Standards

Compound	Company	Specification	Catalog Number or Kit Number
aniline-2,3,4,5,6-d_5	Aldrich	99 + atom %	17,569-2
anthracene	Analabs	99% (min)	RNH004
anthracene-d_{10}	Stohler	98 atom %	D33
benzaldehyde	Aldrich	98 + %	B133-4
2,3-benzanthracene	Analabs	99% (min)	RNH060
benz(a)phenanthrene	RFR	95% (min)	RAH-7
benz(a)pyrene	Analabs	98% (min)	RNH033
benzoic acid	Aldrich	99%	10,947-9
benzonitrile	Aldrich	99%	B895-9
benzyl alcohol	Aldrich	99 + %	B1,620-8
benzyl amine	Aldrich	99%	18,570-1
chrysene	Analabs	99% (min)	PRH012
o-cresol	Polyscience	Qual	170BX
1,2,3,4-dibenzanthracene	Analabs	99% (min)	RNH016
1,2,5,6-dibenzanthracene	Analabs	99% (min)	RNH017
dibenzofuran	Aldrich	98%	13,568-2
2,6-dimethyl aniline	Eastman	--	1736
9,10-dimethyl anthracene	RFR	99% (min)	RAH-24
7,12-dimethyl-2,3-benzanthracene	ACL	--	--
9,10-dimethyl-2,3-benzanthracene	ACL	--	--
3,6-dimethyl phenanthrene	ACL	--	--
gallic acid monohydrate	Aldrich	--	14,791-5
2,4-lutidine	Aldrich	96 + %	L360-9
2-methyl anthracene	Analabs	99% (min)	RNH039
1-methyl naphthalene	Aldrich	97%	M5,680-8
2-methyl-1-naphthol	Aldrich	98%	16,284-1
1-methyl phenanthrene	Analabs	99% (min)	RNH044
2-methyl phenanthrene	Analabs	99% (min)	RNH045
1-methyl pyrene	ACL	--	--
3-methyl pyrene	ACL	--	--
naphthalene	Aldrich	98%	18,560-4

Table 1.2. (Contd.)

Compound	Company	Specification	Catalog Number or Kit Number
1-naphthalene acetic acid	Aldrich	99%	N386-4
1-naphthol	Aldrich	99 + %	N199-2
pentacene	Analabs	98% (min)	RNH048
perylene	Analabs	99% (min)	RNH049
phenanthrene	Aldrich	98 + %	P1,140-9
phenol	Polyscience	Qual	170BX
2-picoline	Aldrich	98%	10,983-5
pyrene	Analabs	99% (min)	RNH057
pyridine	Fisher	ACS	P-368
quinoline	Aldrich	96%	Q125-5
2,3,5-trimethyl naphthalene	Aldrich	--	T7,740-2
triphenylene	Analabs	99% (min)	RNH064
2,4-xylenol	Polyscience	Qual	170BX

Aldrich Chemical Co., 940 West Saint Paul Avenue, Milwaukee, WI 53233

Analabs, Inc., 80 Republic Drive, North Haven, CT 06473

Stohler Isotope Chemicals, 92 Beckwith Place, Rutherford, NJ 07070

RFR Corp., 1 Main Street, Hope, R.I. 02831

Polyscience Corp., 8366 Gross Point Road, Niles, IL 60648

Eastman Kodak Co., Rochester, N.Y. 14650

ACL: Benzene solutions (1.00 mg/mL) from Analytical Chemistry Laboratory, Argonne National Laboratory

Fisher Scientific Co., Fair Lawn, N.J. 07410

Since it was desirable to modify this procedure to spread out the separation of the alkyl benzenes and lower PNAs, a study was made of the effect of flow rate on the retention time of some model PNAs, benzene, naphthalene, anthracene, chrysene, and 1,2,3,4-dibenzanthracene (Table 1.3). As might be expected, with constant flow rate, retention time increases with lower flow rates and decreases with higher flow rates.

For the best separation, it would appear that if one were to program the flow of solvent such that it is initially low and increases progressively, a separation of the lower PNAs could be accomplished while performing the separation of the higher PNAs in a reasonable amount of time. (A slow solvent gradient was unacceptable because it tended to push everything off the column.) Curve 10 on the Waters Model 660 Solvent Programmer, with a slowly rising exponential-type slope, was chosen for the flow programming. The results of three such runs on the five model compounds are shown in Table 1.3. After a number of runs with a variety of PNAs, it appeared that the best separation could be achieved with curve 10 flow programmed from 1-4 mL over a time period of 20 minutes. The retention times of a number of PNAs and benzene under these conditions are shown in Table 1.4. It can be seen that retention time falls into a series of groups, as shown in Table 1.5, and the condensed 4-ring PNAs fall nicely between 3 and 4-ring PNAs and the condensed 5-ring PNAs fall between the 4 and 5-ring PNAs.

The use of the μBondapak NH_2 as a stationary phase was excellent for the separation of non-polar or weakly polar compounds; however, with polar compounds, the phase was too retentive and, although moderately polar compounds might pass through the column with a gradient, highly polar compounds would be retained. It is possible to backwash the highly polar compounds but no separation into fractions of the polar compounds would be achieved. An example of this is shown in Figs. 1.2 and 1.3. It can be seen that the polar compounds came off the column after backwash as one broad peak.

Table 1.3. HPLC Retention Times of a PNA Mixture with μBondapak NH_2 Column and Hexane as Solvent as a Function of Flow Rate and Flow Programming

Flow (mL/min)	Time (min)	Curve	Retention Time (Minutes)				
			Benzene	Naphthalene	Anthracene	Chrysene	1,2,3,4-Dibenz-Anthracene
1.0	--	--	4.2	5.2	6.7	10.4	16.5
1.5	--	--	2.8	3.3	4.3	5.5	10.3
2.0[a]	--	--	2.1	2.5	3.2	5.0	7.8
2.5	--	--	1.7	2.0	2.6	4.0	6.3
3.0	--	--	1.4	1.7	2.2	3.3	5.3
4.0	--	--	1.1	1.3	1.7	2.5	4.0
1.0 to 4.0	20	10	4.2	5.0	6.5	10.0	14.8
2.0 to 4.0	5	10	2.1	2.5	3.2	4.6	6.0
2.0 to 4.0	4	10	2.1	2.5	3.2	4.2	5.7

[a]Two runs, almost identical retention times.

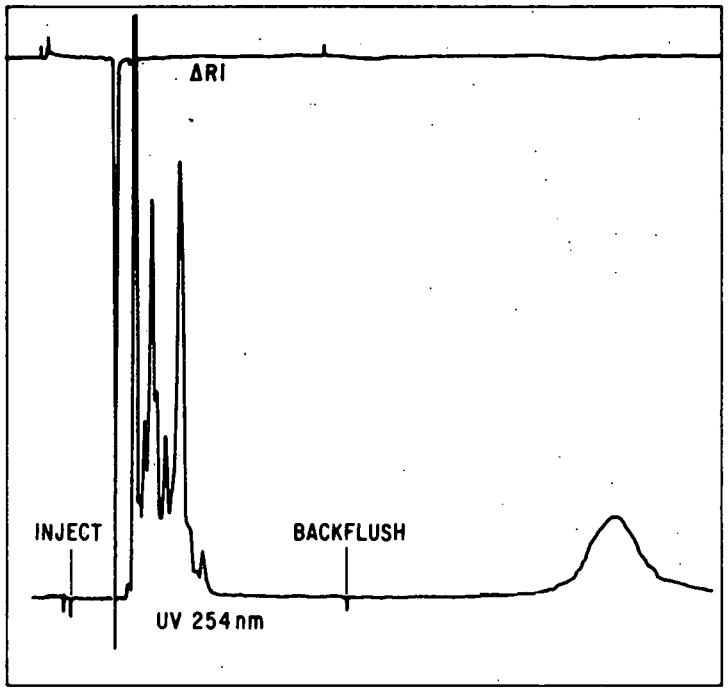

Fig. 1.2. HPLC of HYGAS Oil Sample, 72/H/G/O/3, Using a μBondapak NH_2 Column, Heptane Solvent, a 1.5 mL/min Flow Rate and Detection by ΔRI and UV at 254 nm

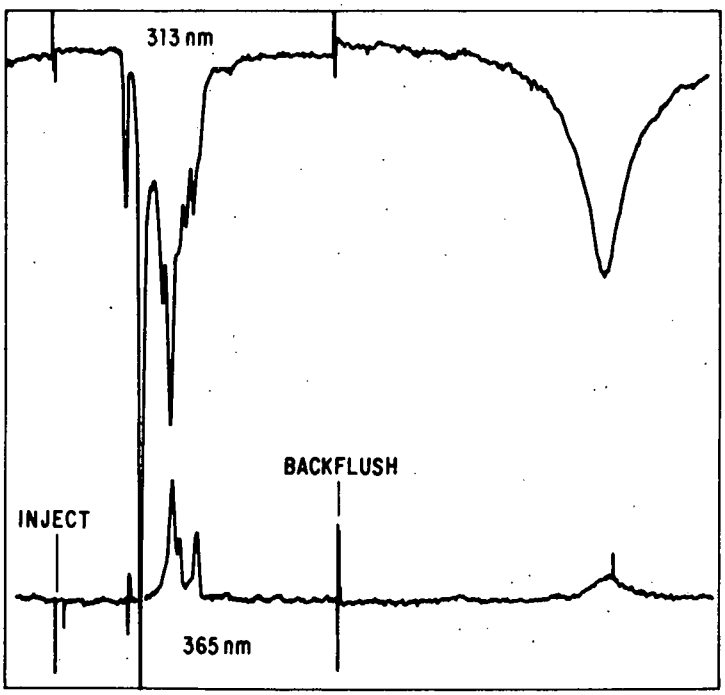

Fig. 1.3. HPLC of HYGAS Oil Sample, 72/H/G/O/3, Using a μBondapak NH_2 Column, Heptane Solvent, a 1.5 mL/min Flow Rate, and Detection by UV at 313 and 365 nm

Table 1.4. HPLC Retention Times of Selected PNAs with μBondapak NH_2 Column and Hexane as Solvent, Flow Programmed from 1-4 mL/min, Curve 10, 20 min

Compound	No. of Rings	Retention Time (min)
Benzene	1	4.2
Naphthalene	2	5.0
1-Methyl naphthalene	2	5.0
2,3,5-Trimethyl naphthalene	2	5.8
Anthracene	3	6.9
2-Methyl anthracene	3	6.8
m-Dimethyl anthracene	3	7.3
Phenanthrene	3	7.3, 7.5
1-Methyl phenanthrene	3	7.5
2-Methyl phenanthrene	3	7.3
3,6-Dimethyl phenanthrene	3	7.2
2,3-Benzanthracene	4	10.7
7,12-Dimethyl-2,3-Benzanthracene	4	9.3
9,10-Dimethyl-2,3-Benzanthracene	4	7.8[a]
Chrysene	4	10.9
Triphenylene	4	10.9
1,2-Benz(a)phenanthrene	4	10.4
Pyrene	4 (c)	7.7, 7.8
1-Methyl pyrene	4 (c)	8.3
3-Methyl pyrene	4 (c)	8.0
Pentacene	5	13.7
1,2,3,4-Dibenzanthracene	5	14.5
1,2,5,6-Dibenzanthracene	5	14.7, 15.1
Perylene	5 (c)	12.1
Benz(a)pyrene	5 (c)	11.5

[a]Appears not to be designated compound

(c) Condensed ring system

Table 1.5. Retention Time Range of Selected PNAs as a Function of the Number of Rings (μBondapak NH_2, Hexane Solvent, Flow Programmed 1-4 mL/min, 20 min, Curve 10)

Number of Rings	Retention Time Range (Minutes)	
	Noncondensed	Condensed
1	4.2 (1)	NA
2	5.0-5.8 (3)	NA
3	6.8-7.5 (7)	--
4	9.3-10.9 (5)	7.7-8.3 (3)
5	13.7-15.1 (3)	11.5-12.1 (2)

( ) Number of compounds from which range was determined

NA Not Applicable

Thus, μBondapak NH_2 can be used to separate non-polar and weakly polar compounds into fractions but is ineffective with moderately and highly polar compounds. Such a separation into fractions can be very useful for identifying a complex mixture that contains predominantly compounds that are relatively non-polar, since GC conditions can be tailor-made to each fraction. It would be particularly useful for identifying the higher PNAs.

1.3.2 Separation of Medium and Highly Polar Compounds into Fractions with μBondapak Phenyl and μBondapak CN

1.3.2.1 Specific Problems To Be Addressed in the Separation

Whereas HPLC with a μBondapak NH_2 column affords a good separation of non-polar compounds, it is not useful, as stated, for separating the polar compounds into fractions. It appeared that the weakly polar stationary phases, μBondapak Phenyl and μBondapak CN, might be more useful in this regard. The best approach appeared to be to try to get the non-polar compounds to elute initially as one fraction and then to do a separation into fractions of the compounds of varying polarity with typical normal phase HPLC and gradient elution. Therefore, several criteria, as listed below, had to be met in the separation:

1. The non-polar and weakly polar compounds should elute in one fraction, preferably along with toluene, the major component of HYGAS recycle oil, since a suitable chromatographic method could then be worked out for these compounds,

2. The moderately and highly polar compounds should be separated into at least 4-6 fractions,

3. The highly polar must elute from the column so that there is no need for backwashing,

4. The separation into fractions should be complete in a reasonable amount of time (say, within one hour), and

5. The separation of a HYGAS oil sample should yield fractions of sufficient quantity so that analyses by GC/MS and/or derivatization and analyses by GC/MS could be done satisfactorily.

In such an HPLC study, the variables are numerous; for example, solvents, gradient curve, time of start of gradient, and duration of gradient. Although a considerable number of experiments were performed, only a few are described here.

1.3.2.2 Development of a Method

In initial experiments with a variety of standard polar compounds, it was found that gradients of hexane (a non-polar solvent) to acetonitrile (a moderately polar solvent) and hexane to methylene chloride (a polar solvent)

did not work as well as a gradient of hexane to THF (a polar solvent). With a linear 10-min gradient, hexane to 25% THF in hexane, a group of compounds with varying polarity can be separated on μBondapak Phenyl and μBondapak CN as shown in Table 1.6. The μBondapak CN column appears to provide a little better separation of the relatively non-polar compounds, dibenzofuran, benzaldehyde, and benzonitrile, than of the more polar compounds. The μBondapak Phenyl column also appears to be more retentive than the μBondapak CN column. Although separation appears fairly good for these model polar compounds with a 20 μL HYGAS oil sample it is poor (with a μBondapak CN column) because of the complexity of the sample (Fig. 1.4). The polar compounds come off the column too quickly and are not separated into fractions. Even with a slower change in concentration of THF (linear gradient, 0-5% THF in hexane in 20 min, 5-10% THF in 10 min, and 10-100% THF in 10 min), bunching of the polar compounds still occurs at the beginning of the chromatogram and separation is poor (Fig. 1.5). If one uses pure hexane for 5 min and then runs the same program as in the preceding example, separation of the non-polars from the polars appears adequate but separation of the polars into fractions is inadequate (Fig. 1.6). To spread out the polar compounds, one can hold off the above gradient for 16 min (Fig. 1.7). The moderately polar to highly polar compounds (center of chromatogram, around 25 min Fig. 1.7) can then be spread out by going to a slower initial gradient, 0% for 16 min, 0-1% in 10 min, 1-5% in 10 min, 5-10% in 10 min, and 10-100% THF

Table 1.6. Retention Times of Selected Compounds on μBondapak Phenyl and μBondapak CN; Linear Gradient, Hexane to 25% THF in Hexane in 10 min, Flow 2 mL/min

Compound	Retention Time (Minutes)	
	μBondapak Phenyl	μBondapak CN
Benzene	1.7	1.7
Dibenzofuran	2.2	2.1
Benzaldehyde	5.5	3.1
Benzonitrile	5.8	3.8
2-Methyl-1-naphthol	5.8	6.9
o-Cresol	5.8	6.6
2,6-Dimethyl aniline	6.0	3.3
Phenol	6.2	7.6
Benzoic acid	7.3	6.8
Quinoline	8.0	6.0
2-Picoline	8.6	5.8
Pyridine	8.7	6.5
2,4-Lutidine	9.7	6.6

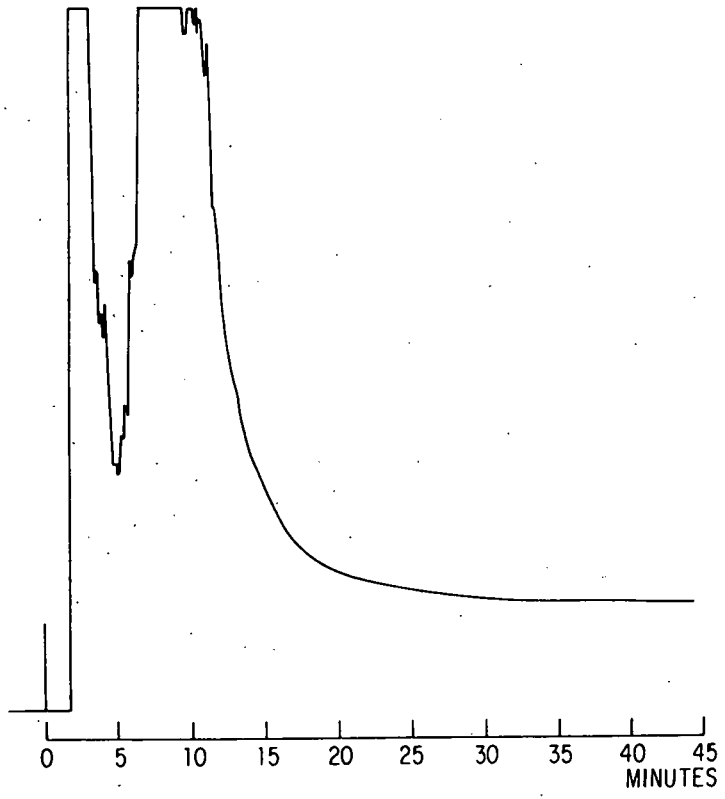

Fig. 1.4

HPLC of 20 µL HYGAS Oil Sample, 72/H/G/O/3, µBondapak CN Column, 2 mL/min Flow, Linear (Curve 6) Gradient, 0-25% THF in Hexane in 10 min, UV Detection at 254 nm

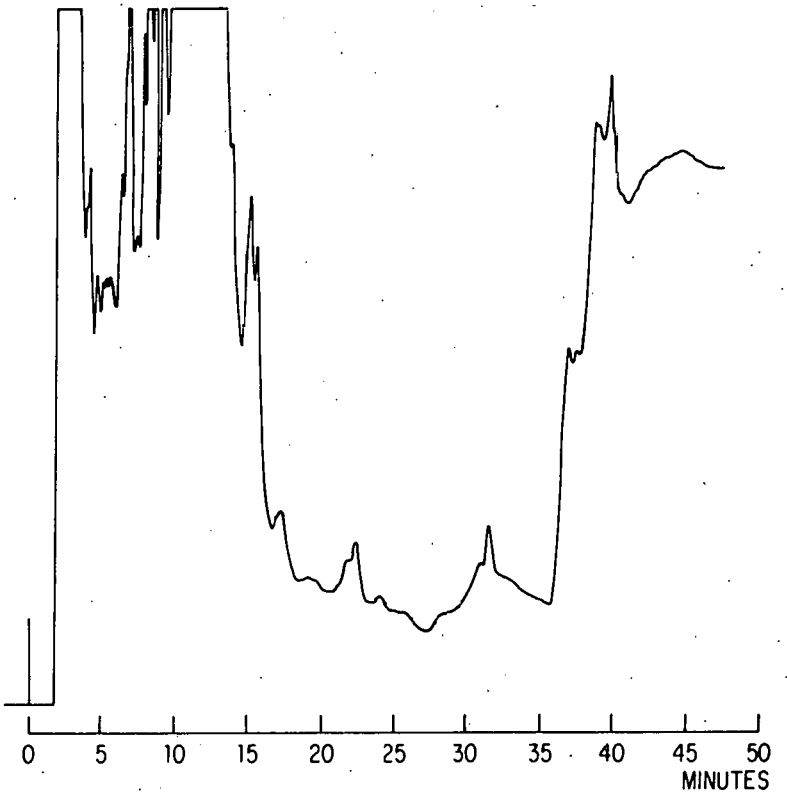

Fig. 1.5

HPLC of 20 µL HYGAS Oil Sample, 72/H/G/O/3, µBondapak CN Column, 2 mL/min Flow, Linear (Curve 6) Gradient, 0-5% in 20 min, 5-10% in 10 min, 10-100% THF in Hexane in 10 min, UV Detection at 254 nm

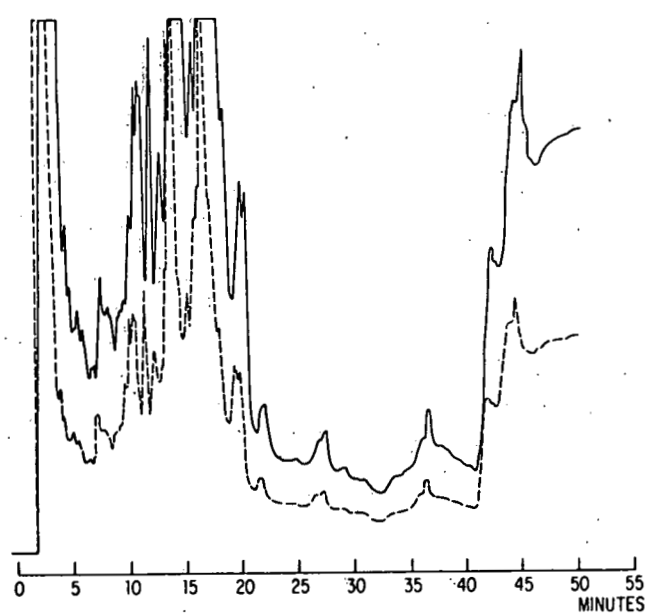

Fig. 1.6

HPLC of 20 µL HYGAS Oil Sample, 72/H/G/O/3, µBondapak CN Column, 2 mL/min Flow, Hexane for 5 min, Linear (Curve 6) Gradient, 0-5% in 20 min, 5-10% in 10 min, 10-100% THF in Hexane in 10 min, UV Detection at 254 nm

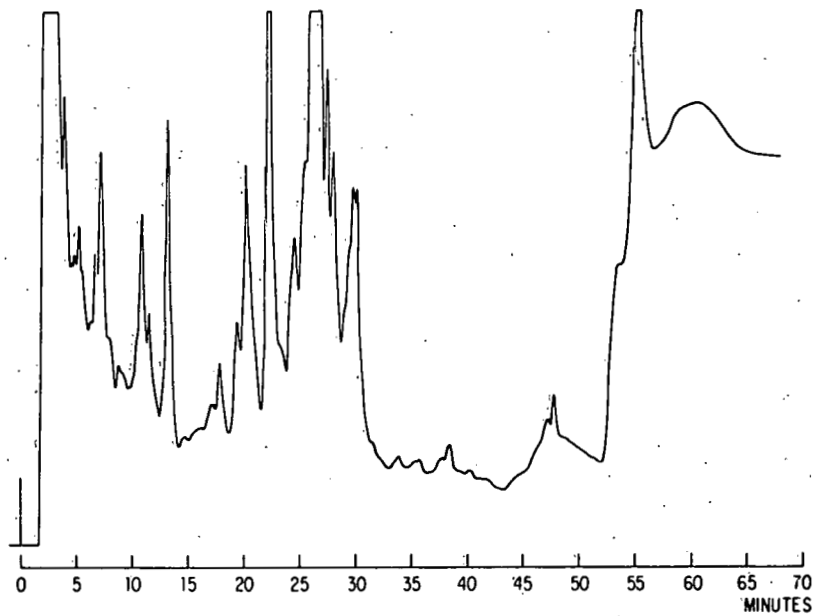

Fig. 1.7

HPLC of 20 µL HYGAS Oil Sample, 72/H/G/O/3, µBondapak CN Column, 2 mL/min Flow, Hexane for 16 min, Linear (Curve 6) Gradient, 0-5% in 20 min, 5-10% in 10 min, 10-100% THF in Hexane in 10 min, UV Detection at 254 nm

in hexane in 10 min (Fig. 1.8). Finally, in order to make the very polar compounds elute quickly without affecting the separation of the moderately polar compounds, the following gradient was used: 0% THF for 16 min, 0-1% THF in hexane in 10 min, 1-5% in 10 min, and 5-100% THF in hexane in 10 min (Fig. 1.9); this sequence gives a satisfactory separation of the HYGAS oil sample into fractions. (Under similar conditions, not quite as nice a separation is achieved with a μBondapak Phenyl column; Fig. 1.10.)

The preceding chromatograms were run with 20 μL (equivalent to approximately 20 mg) of HYGAS oil sample injected on the column. Although 20 mg is sufficient sample for carrying out a separation of a HYGAS oil sample into five fractions and for analysis by capillary column GC/MS and/or derivatization and subsequent analysis by capillary column GC/MS of each of the fractions, it appeared worthwhile to determine how much sample could be injected on the μBondapak CN column before overloading and loss of resolution takes place. Conceivably, with large quantities of sample, the toluene, the major component of the mixture and the first peak in the chromatogram, could be separated provided there was not excessive tailing of the toluene peak and resolution of the more polar compounds was not lost. Initially, a study of toluene itself was done; as can be seen in Table 1.7, the tailing becomes excessive at above 200 μL. It is possible that the toluene solvent could have an effect on the resolution of the polar compounds because toluene is more polar than the initial elutant, hexane; hence, an investigation of an actual HYGAS oil sample was undertaken. Figures 1.9 and 1.11-1.13 are chromatograms of 20, 50, 100, and 200 μL of HYGAS oil sample as injected on-column and Figs. 1.14-1.16 are comparisons of 20 vs 50 μL, 50 vs 100, and 100 vs 200, respectively, with the attentuation adjusted so that the chromatograms would be approximately equivalent in intensity. Some loss of resolution is apparent with 200 μL injected on the column but little loss of resolution appears with 100 μL.

To make certain that highly polar compounds will pass through the column, gallic acid was used as a test compound. (Gallic acid is a particularly attractive compound for such a test because besides being polar it also has several sites capable of being adsorbed on the stationary phase.) Since gallic acid is insoluble in non-polar and weakly polar solvents, the test was run with a relatively polar mobile phase. Table 1.8 shows no hold-up with 100% THF and only a slight holdup with a linear gradient from 40% to 100% THF in hexane in 10 min. Thus, it is expected that even the most polar compounds will elute from the column with approximately 30-40% THF in hexane. The retention times of a number of polar compounds run under the same conditions as the HYGAS sample (100% hexane for 16 min, linear gradient to 1% THF in hexane in 10 min, 1-5% THF and 5-100% THF in 10 min) are shown in Table 1.9.

1.3.3 Summary and Conclusions

Based on the results of this study,

1) μBondapak NH_2 is an excellent stationary phase for the separation of non-polar or weakly polar compounds into fractions but is not suitable for the separation of more polar compounds. Such a separation can be very useful for identifying a complex mixture

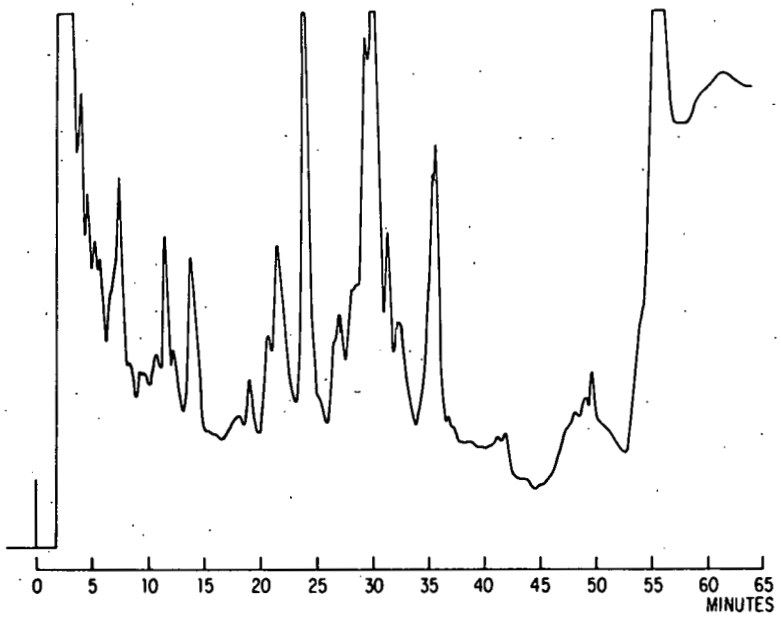

Fig. 1.8

HPLC of 20 µL HYGAS Oil Sample, 72/H/G/O/3, µBondapak CN Column, 2 mL/min Flow, Hexane for 16 min, Linear (Curve 6) Gradient, 0-1% in 10 min, 1-5% in 10 min, 10-100% THF in Hexane in 10 min, UV Detection at 254 nm

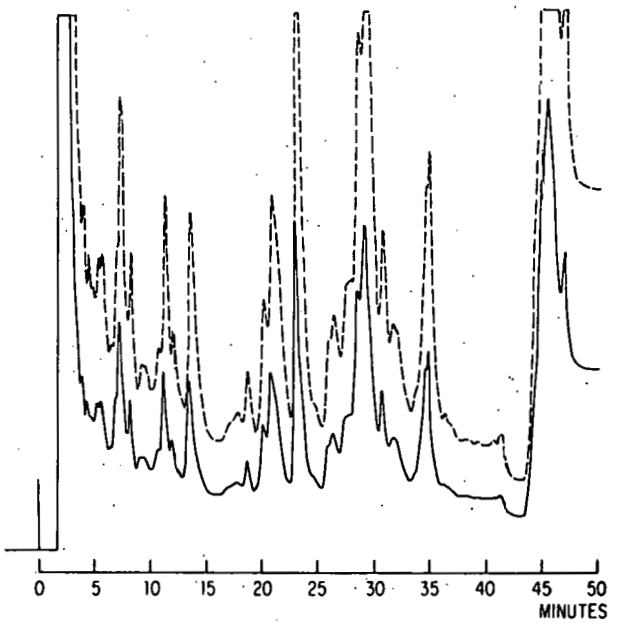

Fig. 1.9

HPLC of 20 µL HYGAS Oil Sample, 72/H/G/O/3, µBondapak CN Column, 2 mL/min Flow, Hexane for 16 min, Linear (Curve 6) Gradient, 0-1% in 10 min, 1-5% in 10 min, 5-100% THF in Hexane in 10 min, UV Detection at 254 nm

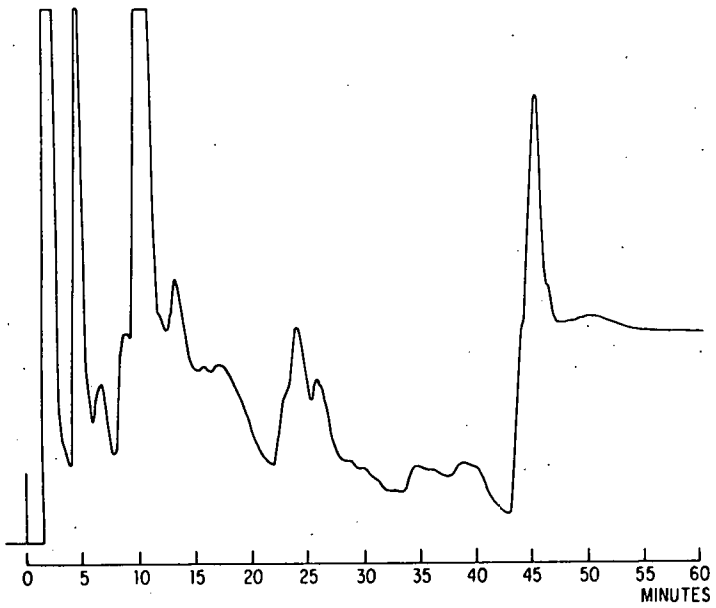

Fig. 1.10

HPLC of 20 µL HYGAS Oil Sample, 72/H/G/O/3, µBondapak Phenyl Column, 2 mL/min Flow, Hexane for 16 min, Linear (Curve 6) Gradient, 0-1%, 1-5%, 5-100% THF in Hexane in 10 min, UV Detection at 254 nm

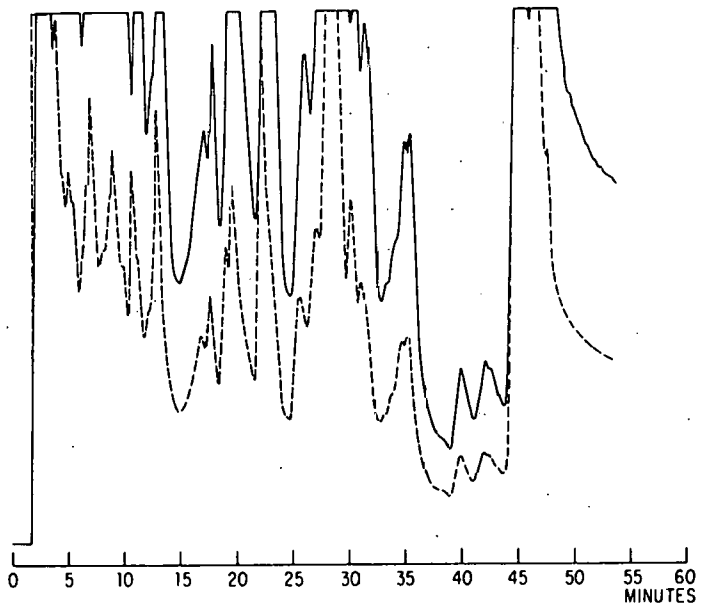

Fig. 1.11

HPLC of 50 µL HYGAS Oil Sample, 72/H/G/O/3, µBondapak CN Column, 2 mL/min Flow, Hexane for 16 min, Linear (Curve 6) Gradient, 0-1% 1-5%, 5-100% THF in Hexane in 10 min, UV Detection at 254 nm

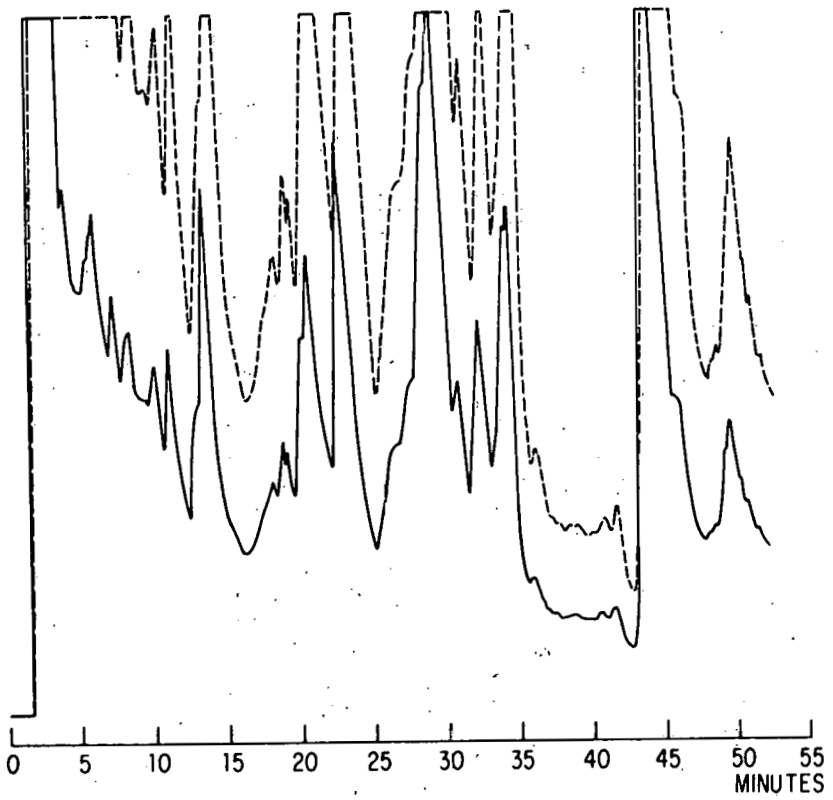

Fig. 1.12

HPLC OF 100 µL HYGAS Oil Sample, 72/H/G/O/3, µBondapak CN Column, 2 mL/min Flow, Hexane for 16 min, Linear (Curve 6) Gradient, 0-1% in 10 min, 1-5% in 10 min, 5-100% THF in Hexane in 10 min, UV Detection at 254 nm

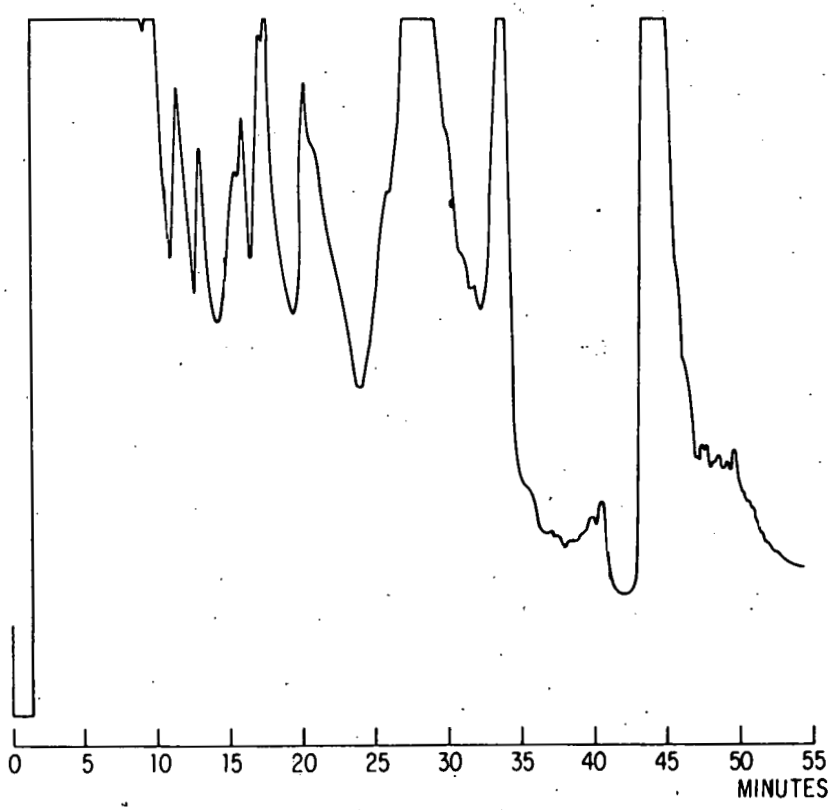

Fig. 1.13

HPLC of 200 µL HYGAS Oil Sample, 72/H/G/O/3, µBondapak CN Column, 2 mL/min Flow, Hexane for 16 min, Linear (Curve 6) Gradient, 0-1% in 10 min, 1-5% in 10 min, 5-100% THF in Hexane in 10 min, UV Detection at 254 nm

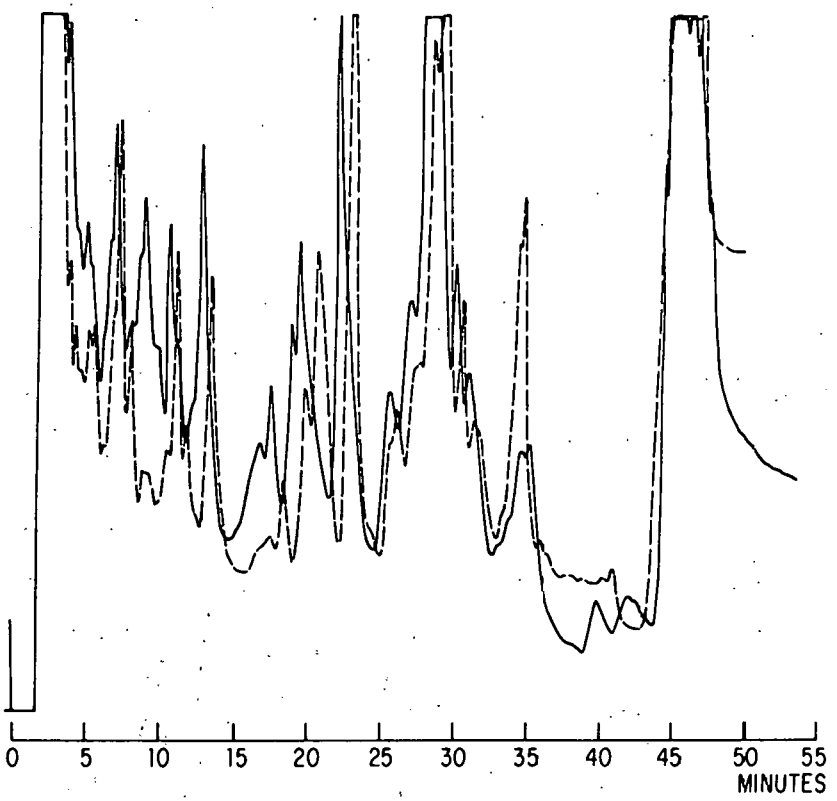

Fig. 1.14

Comparison of HPLC Chromatograms of 20 µL (Dashed) and 50 µL (Solid) HYGAS Oil Sample, 72/H/G/O/3, µBondapak CN Column, 2 mL/min Flow, Hexane for 16 min, Linear (Curve 6) Gradient, Hexane to 1% THF in Hexane in 10 min, 0-1%, 1-5%, 5-100% THF in Hexane in 10 min, UV Detection at 254 nm, Curves Offset

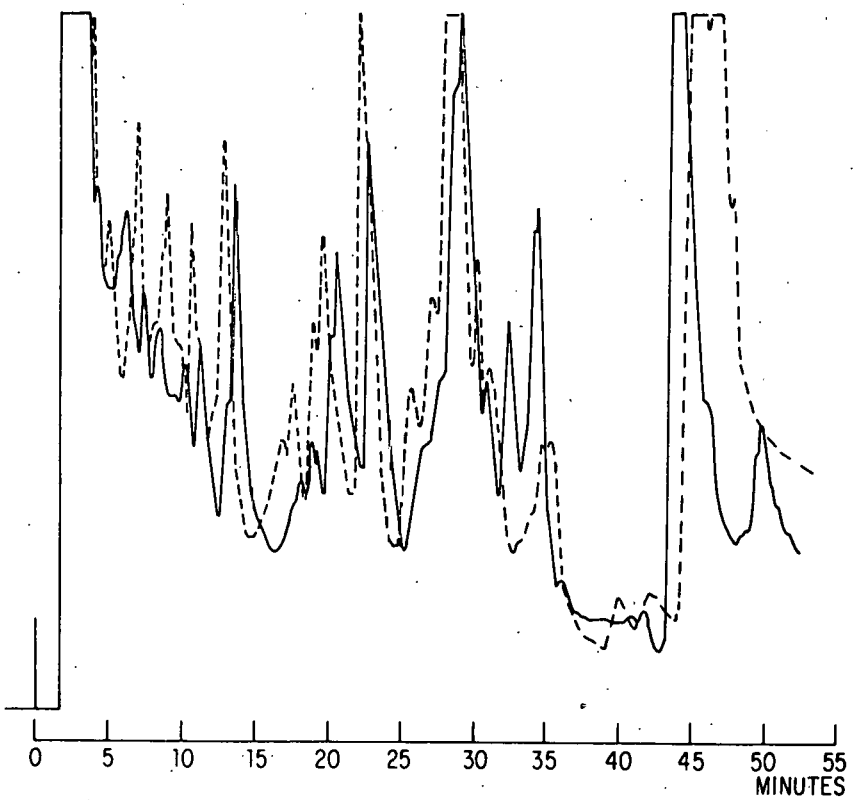

Fig. 1.15

Comparison of HPLC Chromatograms of 50 µL (Dashed) and 100 µL (Solid) HYGAS Oil Sample, 72/H/G/O/3, µBondapak CN Column, 2 mL/min Flow, Hexane for 16 min, Linear (Curve 6) Gradient, 0-1%, 1-5%, 5-100% THF in Hexane in 10 min, UV Detection at 254 nm, Curves Offset

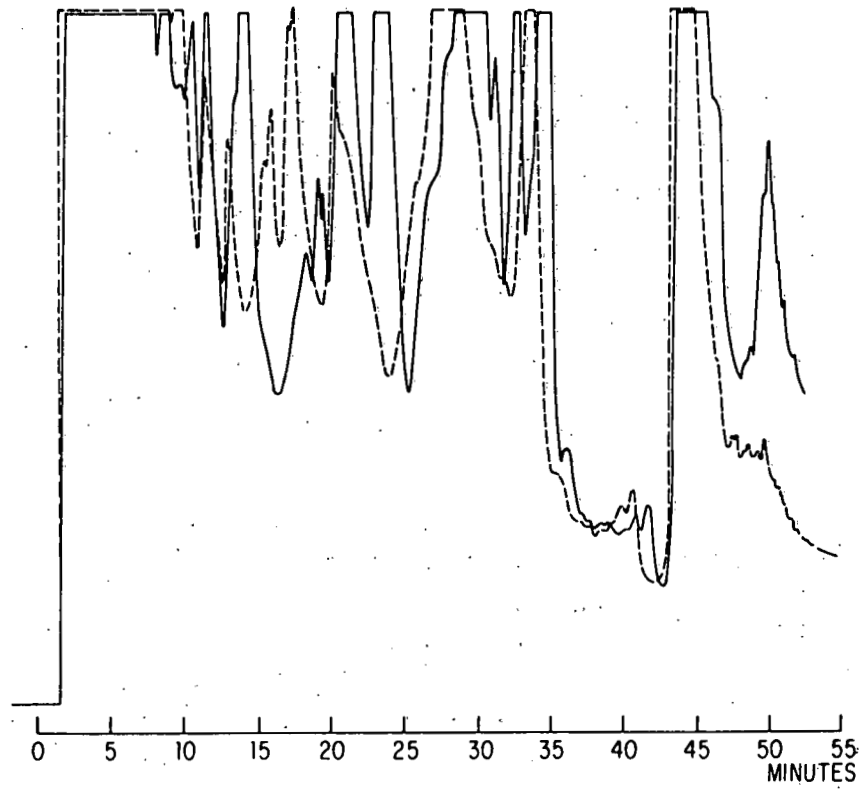

Fig. 1.16. Comparison of HPLC Chromatograms of 100 µL (Solid) and 200 µL (Dashed) HYGAS Oil Sample, 72/H/G/O/3, µBondapak CN Column, 2 mL/min Flow, Hexane for 16 min, Linear (Curve 6) Gradient, 0-1% in 10 min, 1-5% in 10 min, 5-100% THF in Hexane in 10 min, UV Detection at 254 nm, Curves Offset

Table 1.7. Measurement of Tailing Characteristics of Toluene as a Function of Peak Height and Time

Amount of Toluene Injected (µL)	Time (min)			
	Start of Peak	Downside 0.25 AU	Downside 0.10 AU	Downside 0.010 AU
2	1.7	2.2	--	2.7
20	1.7	2.4	—	4.7
100	1.7	3.2	—	NM
200	1.6	3.6	--	5.4
1000	1.6	5.0	6.5	T

NM Not measured
T Tailing

Table 1.8. Measurement of Ability of Gallic Acid, a Very Polar Compound with Several Adsorptive Sites, to Pass Through a μBondapak CN Column Programmed with a Linear 10-min Gradient of Varying Initial Concentrations of THF in Hexane to 100% THF

Gradient Start Concentration (Percent THF in Hexane)	Time (min) (Start of Peak)
100%[a]	1.7[b]
40%	2.3
30%	2.5
20%	5.1

[a] No gradient

[b] No holdup since it takes 1.7 min for a sample that is not adsorbed by the stationary phase to reach the detector

Table 1.9. Retention Times of Non-Polar and Polar Compounds on μBondapak CN (see Gradient Program below)

Compound	Time (min)
anthracene-d_{10}	2.5
2,6-dimethyl aniline	3.7
aniline-d_5	5.3
pyridine	6.2
2,4-lutidine	9.0
quinoline	9.1
benzyl alcohol	10.0
2,6-xylenol	10.7
phenol	21.3
1-naphthol	25.7
1-naphthalene acetic acid	33.2
benzyl amine	45.5

Gradient Program: 100% hexane for 16 min, linear gradient to 1% THF in hexane in 10 min, 1% to 5% THF in 10 min, and 5% to 100% THF in hexane in 10 min

that contains predominantly relatively non-polar compounds, since GC conditions can be tailor-made to each fraction. It would be particularly useful for identifying the higher PNAs.

2) μBondapak CN, used with the proper gradient program, is a satisfactory stationary phase for the general separation of HYGAS oil samples into a non-polar or weakly polar fraction, which contains the major component, toluene, and at least five other fractions varying in polarity from slightly polar to highly polar. μBondapak CN appears to be slightly better than μBondapak Phenyl in this separation.

Thus, the recommended method for a general separation of HYGAS oil samples into fractions is as follows:

1) Inject up to 100 μL of the HYGAS oil samples onto a Waters μBondapak CN column (3.9 mm ID × 30 cm) with a flow rate of 2 mL/min.

2) Run the following linear gradient:

   a) 0-16 min, 100% hexane,
   b) 16-26 min, 0% to 1% THF in hexane,
   c) 26-36 min, 1% to 5% THF in hexane,
   d) 36-46 min, 5% to 100% THF in hexane, and
   e) beyond 46 min, 100% THF.

With this gradient program, very polar compounds such as gallic acid will elute from the column.

For, a separation of the non-polar or weakly polar compounds of a HYGAS oil sample into fractions, the recommended method is as follows:

1. Inject sample into a Waters μBondapak NH_2 column (3.9 mm ID × 30 cm) and flow program from 1 to 4 mL/min with curve 10, an exponential-type curve.

2. Backwash after approximately 25 min to remove the polar compounds.

2 DERIVATIZATION OF POLAR HPLC FRACTIONS

2.1 INTRODUCTION

2.1.1 Objective

The objective of this part of the study was to determine which derivatizing agents are suitable for derivatizing the polar compounds typically found in HYGAS samples to make the compounds more amenable to identification by GC/MS.

2.1.2 Background

In preliminary analyses by GC/MS, it was found that HYGAS oil samples contain a variety of compounds, including toluene, the start-up and make-up oil, aromatic hydrocarbons, phenols, anilines, pyridines, thiophenes, benzonitriles, and PNAs. Direct analysis of the mixture by GC/MS is at best difficult for at least two reasons: (1) due to the large number (probably over 400) of compounds present in the mixture, many overlapping peaks occur, resulting in mass spectra that are often confusing; (2) capillary columns that give good separation of non-polar compounds are not adequate for the separation of polar compounds.

In Part I of this report, a HPLC method was developed in which complex mixtures of HYGAS oil samples could be separated into a number of fractions. However, many polar compounds in these fractions, such as phenols, anilines, and carboxylic acids are either not chromatographable by GC or give excessively broad peaks, frequently with excessive tailings as well. Therefore, in the past, identification of HYGAS, petroleum, and environmental samples has often been limited to the non-polar compounds, such as aliphatic and aromatic hydrocarbons, PNAs, thiophenes, and benzonitriles, and the polar compounds have been neglected.

Derivatization of the polar compounds appeared to be the simplest and most direct approach to making the polar compounds more amenable to identification by GC/MS. Of the numerous methods available for derivatizing polar compounds, only two, silylation and alkylation, were investigated in this study. Many silylating agents are available commercially (Pierce Chemical Co., Rockford, IL 61105). Some of these are:

For trimethylsilyl derivatives, trimethylchlorosilane, hexamethyldisilazane, N,O-bis(trimethylsilyl) acetamide (BSA), trimethylsilylimidazole, and trimethylsilyldiethylamine;

For dimethylsilyl derivatives, dimethylchlorosilane, tetramethyldisilazane, N,O-bis(dimethylsilyl) acetamide, and

For chloromethyldimethylsilyl derivatives suitable for electron capture detectors, chloromethyldimethylchlorosilane.

Of these silylating agents, N,O-bis(trimethylsilyl) acetamide (BSA) and Tri-Sil Concentrate, a 2:1 mixture of hexamethyldisilazane and trimethylchlorosilane, were chosen for study in this investigation on the basis of their high reactivity and wide range of reactivity. Of the various alkylating agents commercially available, only dimethylformamide dimethyl acetal (Methyl-8 Concentrate) was studied in this investigation.

2.1.3 Derivatization Method Development

It was anticipated that the fractions obtained from an HPLC run on a HYGAS oil sample could be evaporated under nitrogen to dryness. Each of these fractions could then be taken up in 50 µL of methylene chloride to which the derivatizing agent could be added. Alternatively, the fraction could be taken up in pyridine, which is known to be a good solvent for silylation. Thus, the procedure tested was to take the residue up in 50 µL of methylene chloride or pyridine, add 50 µL of the derivatizing agent, heat to 50-60°C for 5-10 min, and inject 3 µL into the GC. A second run was done in each case 20 hr later to determine if further derivatization had taken place. This procedure was used on 10 standards: three phenolic compounds, phenol, 2,4-xylenol, and 1-naphthol, three carboxylic acids, benzoic acid, phenoxyacetic acid, and 1-naphthalene acetic acid, three amines, aniline-d_5, 2,6-dimethyl aniline, and benzyl amine, and 1 alcohol, benzyl alcohol. (2,4-Xylenol, 2,6-dimethyl aniline, and, to a lesser extent, 1-naphthol have hindered reactive sites and are, therefore, excellent standards for testing the reactivity of the derivatizing agents.) The total ion count and a specific ion count associated with each of the derivatized standards was inspected to determine whether identification of the derivatized standard could be made. As a rule, when the total ion count of a peak falls below 3000 counts, identification of a compound becomes difficult.)

The various procedures were tested at 100 ng/µL concentration per standard (50 ng/µL in the derivatized solution and 150 ng/µL on-column based on a 3 µL injection). Procedures that appeared to be the most promising were then tested at 50, 20, and 10 ng/µL per standard in order to determine the lower limit of detection for each of the 10 standards.

No attempt was made to determine the actual yield of derivative for each standard.

2.2 EXPERIMENTAL PROCEDURES

2.2.1 Standard Solutions

Ten polar compounds were chosen for investigating the derivatization procedures. These compounds were obtained from the following sources (Table 2.1):

Table 2.1. Sources of Standards

Compound	Company	Specification	Catalog or Kit No.
Phenol	Polyscience	Qual	170BX
2,4-Xylenol	Polyscience	Qual	170BX
1-Naphthol	Aldrich	99 + %	N199-2
Benzoic acid	Aldrich	99%	10,947-9
Phenoxyacetic acid	Aldrich	98 + %	15,851-8
1-Naphthalene acetic acid	Aldrich	99%	N380-4
Aniline-2,3,4,5,6-d_5	Aldrich	99 + atom %	17,569-2
2,6-Dimethylaniline	Eastman	--	1736
Benzyl amine	Aldrich	99%	18,570-1
Benzyl alcohol	Aldrich	99 + %	B1,620-8

Polyscience Corp., 8366 Gross Point Road, Niles, IL 60648

Aldrich Chemical Co., 940 West Saint Paul Avenue, Milwaukee, WI 53233

Eastman Kodak Co., Rochester, N.Y. 14650

The standard solution was prepared as follows: 0.20 g of each of the phenolic compounds and carboxylic acids was placed in a 100-mL volumetric flask and methylene chloride (Burdick & Jackson Laboratories Inc., Muskegon, MI 49442, Pesticide Quality) was added to give 100 mL of a 2 mg/mL/compound solution, which was diluted several times to give a 200 ng/µL/compound solution. Similarly, a 200 ng/µL/compound solution was prepared of the amines and benzyl alcohol. The two solutions were combined to give a 100 ng/µL/compound solution from which 50, 20, and 10 ng/µL/compound solutions were prepared.

2.2.2 Derivatization of Standard Solutions

With Methylene Chloride as Solvent. To 50 µL of the standard solution, 50 µL of the derivatizing agent (Tri-Sil Concentrate No. 49005, BSA No. 38837, or Methyl-8 Concentrate No. 49355, products of the Pierce Chemical Co., P.O. Box 117, Rockford, IL 61105) was added in a vial, No. 5080-8712, obtained from the Hewlett-Packard, Route 41, Avondale, PA 19311. The vial was sealed with a cap, shaken for one minute, heated at 50-60°C for 5-10 minutes, and cooled to room temperature.

With Pyridine as Solvent. The standard solution (50 µL) was added to a vial and a stream of nitrogen was allowed to pass over the solution until all the methylene chloride had evaporated. Silylation grade pyridine, 50 µL, (No. 27530, Pierce Chemical Co.) was added to the vial along with 50 µL of the derivatizing agent. The vial was sealed with a cap, shaken for one minute, heated at 50-60°C for 5-10 min, and cooled to room temperature.

2.2.3 GC/MS of Derivatized Standard Solutions

Analyses of the derivatized standard solutions were performed on a Hewlett-Packard GC/MS equipped with a 50 m, OV-101 capillary column (No. 009-7980, Perkin-Elmer Corp., Norwalk, CT 06856). The GC/MS was a 5982A modified with a 5830 GC upgraded to a 5840 GC. The GC was equipped with a modified Hewlett-Packard split/splitless Grob-type injection system and splitless injection with 3 µL was used in the study. Temperature programming of 20-240°C at 2°/minute with 2 min hold at 20°C was employed. For pyridine solutions, the start temperature was 80°C. Mass spectra of each of the derivatives along with the retention time are shown in Appendix B. The data system was an HP 5934 consisting of a 21MX Computer, 5948A Data Subsystem (A/D and D/A Converters), 7900 Dual Disc Drive, and a Tektronix 4012 Display Terminal. Peripheral equipment included a Tektronix 4631 Hard Copy Unit and a Zeta 130-10 Incremental Plotter.

The parameters used for scanning were as follows: run time, 120 minutes; mass range, 40-400 AMU; A/D conversions, 1; thresholds, 5, 5; and mass offset, -0.2.

2.3 RESULTS AND DISCUSSION

2.3.1 Determination of the Best Procedure for Derivatization

In order to determine the best procedure for derivatization, a solution was prepared containing 10 standards at 100 ng/µL each. It consisted of three phenolic compounds, phenol, 2,4-xylenol, and 1-naphthol, three carboxylic acids, benzoic acid, phenoxyacetic acid, and 1-naphthalene acetic acid, three amines, aniline-d_5, 2,6-dimethyl aniline, and benzyl amine, and one alcohol, benzyl alcohol. (2,4-Xylenol and 2,6-dimethyl aniline with a highly hindered reactive hydroxy and amine and 1-naphthol with a slightly hindered reactive hydroxy were chosen because they would be expected to be difficult to derivatize.) The derivatizing agent, Tri-Sil Concentrate, BSA, or Methyl-8 Concentrate (50 µL), was added to 50 µL of each of the standards that were dissolved in either methylene chloride or pyridine. The mixture was heated to 50-60°C for 10 minutes and then analyzed by capillary column GC/MS immediately and 20 hr later. The following runs were made:

1. Tri-Sil Concentrate/methylene chloride at 0.5 hr
2. Tri-Sil Concentrate/methylene chloride at 20 hr
3. Tri-Sil Concentrate/pyridine at 0.5 hr
4. BSA/methylene chloride at 0.5 hr
5. BSA/methylene chloride at 20 hr
6. BSA/pyridine at 0.5 hr

7. Methyl-8 Concentrate/methylene chloride at 0.5 hr
8. Methyl-8 Concentrate/methylene chloride at 20 hr

(Runs of Tri-Sil Concentrate/pyridine and BSA/pyridine at 20 hr were not made because results from the 0.5-hr runs were not as good as the corresponding runs for Tri-Sil Concentrate/methylene chloride and BSA/methylene chloride.) The total ion count and selected ion count for these eight runs of each of the 10 standards can be found in Tables 2.2 and 2.3, respectively.

As shown in the tables, Tri-Sil Concentrate does effectively derivatize the phenolic compounds and benzyl alcohol but is ineffective in derivatizing the carboxylic acids or amines. BSA is effective in derivatizing the phenolic compounds, the amines, and benzyl alcohol but is ineffective in derivatizing the carboxylic acids. Methyl-8 Concentrate is effective in derivatizing the carboxylic acids and amines but gives only poor results with the phenolic compounds and apparently gives a non-chromatographable product with benzyl alcohol. However, with amines, the products were N,N-dimethyl formamidines rather than the expected methylated derivatives. These derivatives were easily identifiable by mass spectrometry and had very low limits of detection. It can also be seen that there is no distinct advantage in allowing the derivatized solution to stand at room temperature overnight. Relative ratings of these derivatization procedures for the four types of compounds are shown in Table 2.4.

2.3.2 Determination of Lower Limit of Detection

From the results in the preceding tables, it appears that two procedures for derivatization are required because the silylating agents do not derivatize carboxylic acids (at least, at these low concentrations) and Methyl-8 Concentrate is not useful for phenolic compounds or alcohols. It was decided therefore to investigate BSA/methylene chloride and Methyl-8 Concentrate further. Thus, runs in methylene chloride were made with the 10 standards at concentration levels of 100, 50, 20 and 10 ng/μL per standard spectra could be obtained. The total ion and selected ion counts for these experiments are shown in Table 2.5. From these results and by inspection of the mass spectra of the derivatized standards, estimated detection limits were determined as shown in Table 2.6. It can be seen that BSA is useful as a derivatizing agent for phenols and alcohols and Methyl-8 Concentrate for carboxylic acids and amines. Moreover, neither derivatizing agent by itself is acceptable for the whole range of polar standards.

With the use of derivatization, one has to ascertain whether a specific compound was or was not actually in the mixture before derivatization. In the case of silylation, no ambiguity exists, since trimethylsilyl compounds do not occur naturally. With the use of Methyl-8 Concentrate, however, the N,N-dimethyl formamidines do not pose a problem, but the methyl esters formed from the carboxylic acids can do so. In such cases, Tri-Deuter-8, the deuterated analog of Methyl-8 Concentrate, can be used.

The methods described herein can be said to be fairly foolproof, easy-to-perform methods for the analysis of polar compounds. For example, the detection limits could be decreased by working with smaller quantities of materials in cone-shaped vials; however, this method would involve somewhat

Table 2.2. Total Ion Count of Peaks of Ten Derivatized Polar Compounds (50 ng/μL/compound); Derivatizing Agents: Tri-Sil Concentrate, BSA, and Methyl-8 Concentrate

Compound	Total Ion Count of Peak (in Thousands)							
	Tri-Sil Concentrate/ Methylene Chloride (0.5 hr)	Tri-Sil Concentrate/ Methylene Chloride (20 hr)	Tri-Sil Concentrate/ Pyridine (0.5 hr)	BSA/ Methylene Chloride (0.5 hr)	BSA/ Methylene Chloride (20 hr)	BSA/ Pyridine (0.5 hr)	Methyl-8 Concentrate/ Methylene Chloride (0.5 hr)	Methyl-8 Concentrate/ Methylene Chloride (20 hr)
Phenol	97	94	55	127	100	54	8	8
2,4-Xylenol	87	79	49	68	76	49	4	5
1-Naphthol	69	64	59	49	67	46	4	I
Benzoic acid	T	T	T	T	T	T	39	40
Phenoxyacetic acid	--	--	--	--	--	--	18	25
1-Naphthalene acetic acid	--	--	--	--	--	--	14	14
Aniline-d_5	--	--	36	83	105	42	57	60
2,6-Dimethyl aniline	--	--	10	25	23	9	36	56
Benzyl amine	T	T	--	11	53	17	33	NM
Benzyl alcohol	103	98		86	100	60	--	--

T Trace

I Interfering peak prevented determination of total ion count

NM Not measurable

-- Not found

Table 2.3. Selected Ion Count of Peak of Ten Derivatized Polar Compounds (50 ng/μL/compound); Derivatizing Agents, Tri-Sil Concentrate, BSA, Methyl-8 Concentrate

Compound	Ion Used for Tri-Sil Derivative	Ion Used for Methyl-8 Derivative	Selected Ion Count of Peak: Tri-Sil Concentrate/ Methylene Chloride (0.5 hr)	Tri-Sil Concentrate/ Methylene Chloride (20 hr)	Tri-Sil Concentrate/ Pyridine (0.5 hr)	BSA/ Methylene Chloride (0.5 hr)	BSA/ Methylene Chloride (20 hr)	BSA/ Pyridine (0.5 hr)	Methyl-8 Concentrate/ Methylene Chloride (0.5 hr)	Methyl-8 Concentrate/ Methylene Chloride (20 hr)
Phenol	151	108	44159	41121	27570	38325	34209	22793	2690	2758
2,4-Xylenol	194	136	11347	10613	7100	8133	11049	5925	1299	6340
1-Naphthol	216	158	13665	12176	10556	8397	12410	8359	985	--
Benzoic acid	--	105	--	--	--	--	--	--	17381	17068
Phenoxyacetic acid	--	107	--	--	--	--	--	--	5181	6862
1-Naphthalene acetic acid	--	141	--	--	--	--	--	--	6913	6654
Aniline-d_5	155	153	--	--	16505	34684	50067	19254	10845	11929
2,6-Dimethyl aniline	178	132	--	--	2362	5941	6391	902	5461	10554
Benzyl amine	135	162	350	298	--	1702	14816	4751	5606	NM
Benzyl alcohol	135	--	22099	20640	7288	15487	19401	12008	--	--

NM Not measurable

-- Not found

Table 2.4. Relative Ratings (Poor, Fair, and Good) of Derivatization Methods Investigated

Class of Compound	Tri-Sil Concentrate/ Methylene Chloride (0.5 hr)	Tri-Sil Concentrate/ Methylene Chloride (20 hr)	Tri-Sil Concentrate/ Pyridine (0.5 hr)	BSA/ Methylene Chloride (0.5 hr)	BSA/ Methylene Chloride (20 hr)	BSA/ Pyridine (0.5 hr)	Methyl-8 Concentrate/ Methylene Chloride (0.5 hr)	Methyl-8 Concentrate/ Methylene Chloride (20 hr)
Phenols	GOOD	GOOD	GOOD	GOOD	GOOD	FAIR	FAIR	FAIR
Carboxylic Acids	--	--	--	--	--	--	FAIR TO GOOD	FAIR TO GOOD
Amines	--	--	POOR	POOR TO GOOD	FAIR TO GOOD	POOR TO GOOD	FAIR TO GOOD	FAIR TO GOOD
Alcohols	GOOD	GOOD	POOR	GOOD	GOOD	FAIR	--	--

Note: Methyl-8 Concentrate derivatives were rated somewhat higher because of easy identification and favorable peak shape.

Table 2.5. Total Ion Count and Selected Ion Count of Derivatized Polar Compounds as a Function of Concentration; Derivatizing Agents: BSA and Methyl-8 Concentrate

Compound	BSA 100 ng/µL	Methyl-8 100 ng/µL	BSA 50 ng/µL	Methyl-8 50 ng/µL	BSA 20 ng/µL	Methyl-8 20 ng/µL	BSA 10 ng/µL	Methyl-8 10 ng/µL
Phenol	126750(38325)	7612(2690)	50323(24360)	2252(638)	23485(9371)	1330(341)	16094(6616)	-- (191)
2,4-Xylenol	67823(8133)	4327(1299)	41548(5537)	-- (287)	16969(1957)	-- (190)	8735(871)	-- (85)
1-Naphthol	48574(8397)	3597(985)	34350(6222)	-- (48)	11531(2173)	-- (14)	6124(938)	-- --
Benzoic acid	-- --	38662(17381)	-- --	12644(5550)	-- --	5955(2792)	-- --	2854(1180)
Phenoxyacetic acid	-- --	17980(5181)	-- --	9925(2872)	-- --	3805(1203)	-- --	1409(413)
1-Naphthalene acetic acid	-- --	13838(6913)	-- --	6098(3266)	-- --	2056(1098)	-- --	1365(679)
Aniline-d_5	82936(34684)	56876(10845)	35599(16784)	23950(4323)	11170(5045)	10510(1340)	4085(1895)	4826(850)
2,6-Dimethyl aniline	24944(59411)	35903(5461)	NM (132)	8637(1736)	-- --	5765(1178)	-- --	2906(529)
Benzyl amine	7859(1702)	33288(5606)	-- (874)	17114(2698)	-- (181)	6767(1233)	-- (239)	2587(558)
Benzyl alcohol	85833(34684)	-- --	54163(10612)	-- --	18620(3833)	-- --	8696(1645)	-- --

(1) Ions used are shown in Table

NM Not measurable

Table 2.6. Estimated Minimum Concentration (Detection Limit) of Polar Compounds Required for Derivatization and Identification by Capillary Column GC/MS; Derivatizing Agents: BSA and Methyl-8 Concentrate[a]

Compound	Estimated Detection Limit (ng/μL) BSA	Methyl-8
Phenol	<10	50-100
2,4-Xylenol	<10	100
1-Naphthol	10	100
Benzoic acid	>	10-20
Phenoxyacetic acid	>	20
1-Naphthalene acetic acid	>	20
Amine-d_5	10	10
2,6-Dimethyl aniline	100	10
Benzyl amine	100	10
Benzyl alcohol	<10	>

[a]An estimate is based not only on a lower limit of 5000 counts for the total ion count of the peak, since mass spectra can typically be interpreted when there are at least 3000 to 5000 counts, but also on visual inspection of specific spectra of derivatives that have approximately 5000 counts

> Indicates greater than the highest concentration measured, that is, 100 ng/μL

intricate procedures that could possibly lead to errors due to contamination. It can be said further that by modifying the procedures or substituting other derivatizing agents, one might be able to achieve more sensitivity or more easily identifiable mass spectra. However, the methods described herein do work well and are fairly simple. The hindered phenols, 2,4-xylenol and 1-naphthol, and the hindered amine, 2,6-dimethyl aniline, also can be determined at fairly low levels.

2.3.3 Recommended Method

Based on the results achieved in this part of the study, it appears that:

1. No one silylating or alkylating agent is capable of derivatizing the whole spectrum of polar compounds.

2. The preferred silylating agent is BSA and the preferred alkylating agent is Methyl-8 Concentrate except where there is ambiguity as to the source of the derivatized products. In such cases, the deuterated analog of Methyl-8 Concentrate, Tri-Deuter-8, should be used.

3. There is no advantage in allowing the derivatized solution to stand for 20 hr.

Thus, the recommended method for derivatization of polar compounds from HYGAS oil samples is as follows:

1. Evaporate each fraction from the HPLC to dryness under a stream of nitrogen.

2. Take up the residue in 100 μL of methylene chloride.

3. Split the 100 μL solution into two 50 μL solutions and place in two vials sealable with caps.

4. Add 50 μL of BSA to one vial and 50 μL of Methyl-8 Concentrate (or Tri-Deuter-8) to the other vial.

5. Seal each vial with a cap and heat to 50-60°C for 5-10 min.

6. Perform capillary column (splitless) GC/MS analysis on each derivatized solution. (The starting temperature of the programmed run would be 20°C.)

The preceding method is for the polar HPLC fractions of HYGAS oil samples. However, for the initial nonpolar HPLC fraction of HYGAS oil samples, there is no need to derivatize. Moreover, this fraction (Fraction 1) contains predominantly toluene, which is difficult to remove. Therefore, the recommended method for analyzing this fraction is as follows:

1. Evaporate the nonpolar HPLC fraction with a stream of nitrogen to remove the low-boiling solvents used in the HPLC run to give a toluene solution of the nonpolar compounds.

2. Perform capillary column (splitless) GC/MS analysis of the toluene solution of the nonpolar compounds. (In this case, the starting temperature of the programmed run would be approximately 90°C.)

2.4 SUMMARY AND CONCLUSIONS

An investigation was undertaken to determine suitable agents for derivatizing the polar compounds typically found in HYGAS samples so that these compounds would be more amenable to identification by GC/MS. Of the silylating and alkylating agents investigated, no one by itself is capable of derivatizing the whole spectrum of compounds. The preferred silylating agent was BSA, which was effective for phenols and alcohols, and the preferred alkylating agent was Methyl-8 Concentrate, which was effective for carboxylic acids and amines. The lower limit of detection by capillary column GC/MS was in the range of less than 10-20 ng/μL of polar compound.

3 TESTING OF THE METHOD ON A HYGAS OIL SAMPLE

3.1 INTRODUCTION

In Part 1 of this report, an HPLC method was described for separating HYGAS oil samples into fractions. In Part 2, methods were presented for derivatizing the polar compounds, phenols, carboxylic acids, amines, and alcohols. In this part of the report, a HYGAS oil sample was separated into fractions by HPLC and some of the polar fractions were derivatized and analyzed by capillary column GC/MS to determine whether the separation and derivatization methods had simplified identification of the complex mixtures of HYGAS oil samples.

3.2 EXPERIMENTAL PROCEDURES

3.2.1 HYGAS Oil Sample

The HYGAS oil sample (72/H/G/O/3), whose description can be found in Appendix A, was filtered with a sample clarification kit (Waters Associates Inc., Milford, MA 01757) to remove unreacted coal.

3.2.2 Solvents

For the mobile phase in the HPLC run, Waters solvents were used. They were hexane (No. 84911) and THF (UV) (No. 94801). Where low concentrations of THF in hexane were used, such as 1 and 5%, the solvents were premixed because solvent gradients at low concentrations lead to their being mixed erratically. The methylene chloride used as a solvent for derivatization is the Burdick & Jackson pesticide quality (Burdick & Jackson Laboratories Inc., Muskegon, MI 49442).

3.2.3 Equipment

The HPLC equipment was that of Waters, Inc., consisting of two 6000A Solvent Delivery Systems, a 660 Solvent Programmer, U6K Universal Liquid Chromatograph Injector, 440 Absorbance Detector (UV), and a μBondapak CN (No. 84042) column. UV Detection was at 254 nm.

The flow rate of each pump was determined by measuring the volume of solvent at exhaust with a stop watch, after which adjustments were made to give the desired flow.

Analyses of the fractions were performed on a Hewlett-Packard GC/MS equipped with a 50-m OV-101 capillary column (No. 009-7980, Perkin-Elmer Corp., Norwalk, CT 06856). The GC/MS was a 5982A modified with a 5830 GC upgraded to a 5840 GC. The GC was equipped with a modified Hewlett-Packard split/splitless Grob-type injection system, and splitless injection with 3 μL was used in the study. Temperature programming, 20-240°C at 2°/min with 2-min hold at 20°C, was employed. Mass spectra of some of the compounds

found are shown in Appendix C. The data system was an HP 5934 consisting of a 21MX Computer, 5948A Data Subsystem (A/D and D/A Converters), 7900 Dual Disc Drive, and a Tektronix 4012 Display Terminal. Peripheral equipment included a Tektronix 4631 Hard Copy Unit and a Zeta 130-10 Incremental Plotter.

The parameters used for scanning were as follows: run time, 120 min; mass range, 40-450 AMU; A/D conversions, 1; thresholds, 5, 5; and mass offset, -0.2.

3.2.4 Determination of the Flow Time Between the UV Detector and Outlet of the HPLC

To determine the time lag between UV detection of a peak and the outlet of the HPLC, a solution of benzoic acid in THF was injected onto the μBondapak CN column and 10-sec fractions were taken after the initial appearance of the peak. The fractions were evaporated to dryness under a stream of nitrogen and allowed to stand at room temperature. The approximate start of a peak could then be determined by looking for the presence of benzoic acid. Having determined the approximate lag time, the experiment was repeated at 5- and 2-sec intervals. The lag time was found to be approximately 20 sec at a flow rate of 2 mL/min.

3.2.5 HPLC Separation of HYGAS Oil Sample into Fractions

To determine the approximate time at which fractions should be taken and make certain that conditions for separation into fractions were satisfactory, an initial HPLC run with 100 μL of HYGAS oil sample and a flow rate of 2 mL/min was undertaken under the following conditions:

0-16 min,	100% hexane, 0% THF
16-26 min,	0-1% THF in hexane, linear (curve 6) gradient
26-36 min,	1-5% THF in hexane, linear (curve 6) gradient
36-46 min,	5% THF in hexane to 100% THF, linear (curve 6) gradient
46-60 min,	100% THF, 0% hexane

The run was then repeated, after washing the column at length with THF under the same conditions, and fractions were collected as shown in Fig. 3.1 and as follows (with a time lag of 20 sec):

Fraction	Time (Min)
1	1.8-9.4
2	9.4-13.4
3	13.4-21.5
4	21.5-28.7
5	28.7-33.0
6	33.0-40.2
7	40.2-49.0

Each of the fractions was evaporated to dryness under a stream of nitrogen and, with the exception of Fraction 1, the nonpolar or weakly polar fraction, was taken up in approximately 200 μL of methylene chloride and

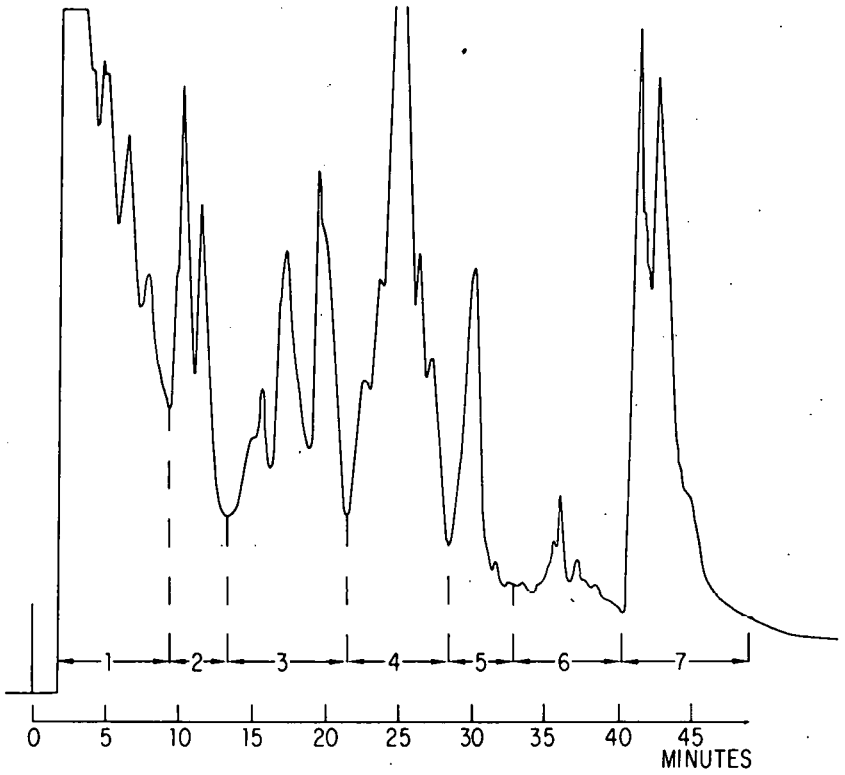

Fig. 3.1. HPLC Separation into Seven Fractions of HYGAS Oil Sample; Approximately 2.2 AUFS

split and placed into two vials (No. 5080-8712, Hewlett-Packard, Route 41, Avondale, PA 19311). The 100 µL solutions in each vial were then evaporated under a stream of nitrogen to 50 µL after which 50 µL of the derivatizing agent, BSA or Methyl-8 Concentrate, was added. The vial was sealed, shaken, heated to 50-60°C for 5-10 min, cooled, and 3 µL of solution was injected into the GC column. In the case of Fraction 1, the residue was taken up in 200 µL of methylene chloride, transferred to a vial, evaporated to 50 µL under a stream of nitrogen, and 3 µL was injected onto the GC column.

3.2.6 Mass Spectral Interpretation

Interpretation of the data was done by inspecting the mass spectrum of each peak or shoulder and by generating and inspecting massgrams. Mass spectra of selected compounds found in the HYGAS oil sample are shown in Appendix C.

3.3 RESULTS AND DISCUSSION

3.3.1 HPLC Separation of HYGAS Oil Sample into Fractions

A 100 µL sample of prefiltered HYGAS oil sample was injected into the HPLC with a µBondapak CN as the column with a flow rate of 2 mL/min. The

gradient program was as follows:

0-16 min,	100% hexane, 0% THF
16-26 min,	0-1% THF in hexane, linear gradient
26-36 min,	1-5% THF in hexane, linear gradient
36-46 min,	5% THF in hexane to 100% THF, linear gradient
46-60 min,	100% THF, 0% hexane

Seven fractions were collected at the following intervals, as shown in Fig. 3.1:

Fraction	Time (Min)
1	1.8-9.4
2	9.4-13.4
3	13.4-21.5
4	21.5-28.7
5	28.7-33.0
6	33.0-40.2
7	40.2-49.0

No attempt was made to collect a fraction before 1.8 min, which would contain predominantly alkanes.

3.3.2 Derivatization of the Fractions

In this limited study, Fractions 2, 3, and 4 were derivatized with BSA, a silylating agent, Fraction 3 with Methyl-8 Concentrate, an alkylating agent, and Fraction 4 with Tri-Deuter-8, an alkylating agent. Fraction 1, the nonpolar or weakly polar fraction, was not derivatized. Fractions 5, 6, and 7 were not investigated at this time.

3.3.3 Capillary Column GC/MS Investigation of the Fractions

A portion of a typical total ion chromatogram of one of the derivatized fractions is shown in Fig. 3.1. Peaks are sharp and resolution is good. Poor peak shape is due to overlapping of peaks. This particular fraction (Fig. 3.2) contains a variety of hydroxy aromatic compounds that would not be chromatographable under normal conditions without derivatization. It is noteworthy that, even with fractionation of the original HYGAS oil sample, the capillary column GC/MS total ion chromatogram is still complex, indicative of the several hundred compounds in the HYGAS oil sample.

In order to determine how well the separations had taken place, an analysis of the derivatized fractions was undertaken. The identification and total ion count (in thousands) of the BSA derivatized compounds in Fractions 2, 3, and 4 is shown in Tables 3.1-3.3. A summarized table (Table 3.4) permits comparisons of these fractions. The retention time ranges are shown in Fig. 3.3. Surprisingly, these fractions contain not only some alkylated phenols but also some higher hydroxy PNAs, which have not been reported previously. By careful inspection of the spectra and retention times for these three fractions, only a small overlap of compounds

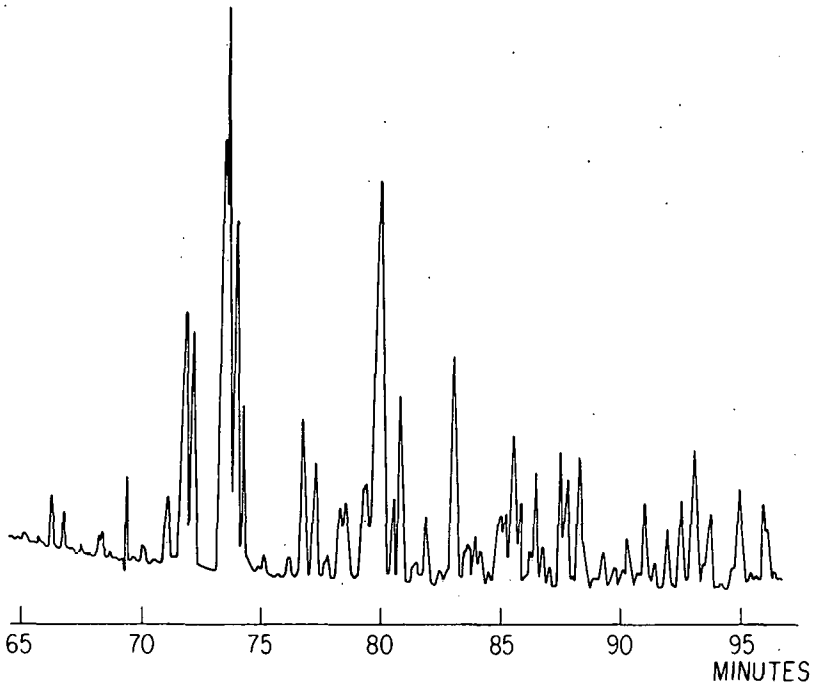

Fig. 3.2. Portion of Total Ion Chromatogram of Fraction 4, Derivatized with BSA

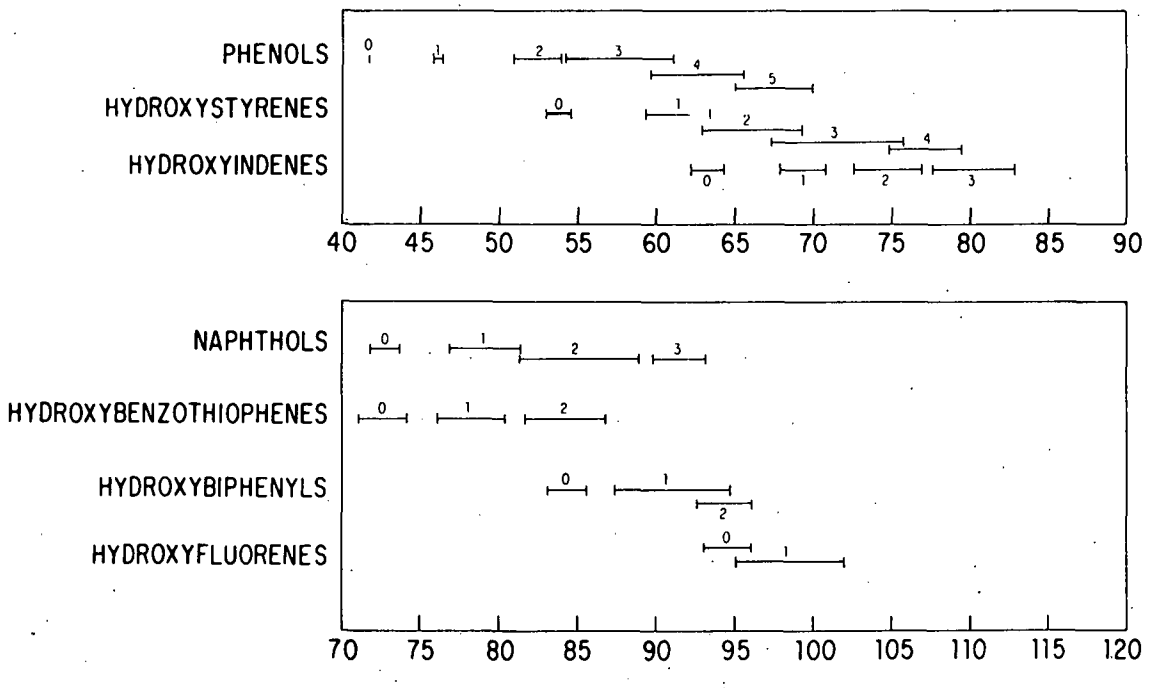

Fig. 3.3. Retention Time Ranges of Some Phenols and Hydroxy PNAs, Derivatized with BSA, in Fractions 2,3, and 4

Table 3.1. Tentative Identification and Total Ion Count (in thousands) of Compounds (as TMS ethers) in Fraction 2

Retention (min)	Phenols				Hydroxystyrenes				Hydroxyindenes		Hydroxybenzothiophenes	Hydroxybiphenyls
	C_2	C_3	C_4	C_5	C_1	C_2	C_3	C_4	C_2	C_3	C_2	C_3
49.2	T											
50.2	25											
51.2	47											
52.7	18											
54.1		2										
54.4		5										
55.3		34										
55.5		19										
55.7		T										
56.8		59										
57.8		10										
58.1		69										
59.9			T									
60.1			19									
60.4			20									
60.9		13										
61.5					27							
61.9			6									
62.4			28									
62.7			5									
62.9						12						
63.1			T									
63.6						6						
64.1						11						
64.9						T						
65.1				T								
65.6			T									
65.7				T								
66.7						29						
67.9						24						
68.3						35						
68.5							T					
68.7				5								
69.2						25						
69.4							6					
69.9							7					
70.1							13					
70.5							3					
70.9							3					
71.1							5					
71.3							8					
71.5							6					
71.7							2					
72.8							7					
73.1							6					
73.8									T			
74.5							7					
74.8							9					
75.2									T			
75.8							4					
76.2								8				
76.8								6				
77.6										6		
78.6										T		
80.7										T		
81.3										T		
81.9											T	
82.3											T	
83.1										4		
86.3										T		
87.3										T		
90.0												T

T Trace

Table 3.2. Tentative Identification and Total Ion Count (in thousands) of Compounds (as TMS ethers) in Fraction 3

Retention (min)	Phenols					Hydroxy-styrenes				Hydroxy-indenes				Naphthols			Hydroxybenzo-thiophenes		Hydroxy-biphenyls
	C_1	C_2	C_3	C_4	C_5	C_1	C_2	C_3	C_4	C_0	C_1	C_2	C_3	C_1	C_2	C_3	C_1	C_2	C_1
46.6(2)	130																		
47.1	72																		
50.8		T																	
51.5(2)		172																	
51.9		279																	
52.6(2)		90																	
54.0		136																	
54.5			18																
55.9			20																
56.9			249																
57.1			40																
58.1			33																
58.5			30																
58.9			26																
59.3						T													
59.6				20															
59.9			T																
61.0			18																
61.3(2)				47															
61.7						39													
61.9				40															
62.2										13									
62.7										6									
63.0				T															
63.3				T															
63.5				56(E)		56(E)													
63.8							6												
64.2							10												
64.5				8															
65.4							28												
65.8							20												
66.0							24												
66.3					15														
66.7							T												
67.3								10											
67.7					T														
67.9											T								
68.4								T											
68.6											T								
68.7											T								
68.8											T								
68.9								T											
69.1											T								
69.4							64												
69.8											5								
70.1											7								
70.3											T								
70.7								T											
71.0								14											
71.2								15											
71.4								T											
72.2								T											
72.7								T											
72.9								T											
73.1								T											
73.3								16											
73.5													T						
73.8								6											
74.8									T										
75.0									T										
75.2													T						
75.3													T						
76.7																		T	
76.9													T						
77.7																		T	
77.9									T										
78.2														27					
78.5																		11	
78.9									T										
79.9														20					
80.4													T						
81.2															11				
81.9															13				
83.6															9(E)			5(E)	
83.9																		7	
84.1															9(E)			5(E)	
84.3															9				
84.6																		T	
84.9															8(E)			4(E)	
85.7															12				
86.0															T				
87.1															T				
87.5															T				
87.8															T				
88.5																			11
88.7																5			
88.9															T				
89.3																T			
89.5																			5
91.8																5			
93.3																			10
94.6																			T
94.8																			T

T Trace

(E) Estimated due to overlapping peaks

Table 3.3. Tentative Identification and Total Ion Count (in thousands) of Compounds (as TMS ethers) in Fraction 4

Retention (min)	Phenols			Hydroxystyrenes					Hydroxyindenes		Naphthols				Hydroxybenzothiophenes				Hydroxybiphenyls				Hydroxyfluorenes	
	C_0	C_1	C_2	C_0	C_1	C_2	C_3	C_4	C_0	C_1	C_0	C_1	C_2	C_3	C_0	C_1	C_2	C_3	C_0	C_1	C_2	C_3	C_0	C_1
41.7	T																							
45.8		T																						
46.2		T																						
50.9			T																					
51.2			T																					
51.9			T																					
53.0				11																				
53.4			T																					
54.6				T																				
59.7					6																			
61.3					5																			
61.8					6																			
62.6										T														
63.4					T																			
64.1										14														
64.3										16														
65.2						T																		
65.7						T																		
66.2						7																		
67.0						T																		
67.3						T																		
68.3						4																		
68.5						4																		
70.1										6														
71.1															19									
71.8											89													
72.2															43									
73.7											279													
74.0															67									
74.2															23									
75.1							3																	
76.2																5								
76.8												22(E)				22(E)								
77.2																28								
77.7																5								
78.2												25												
78.6																22								
79.3												39												
80.0												186												
80.4																10								
80.8												38												
81.3												T												
81.5																	T							
81.8																	11							
82.4																	T							
82.7																	T							
83.0																			56					
83.2																	T							
83.4													6											
83.6																	6							
83.8																	7							
84.5								T																
84.8													T											
85.0																	T							
85.2													T											
85.6													25(E)						15(E)					
85.8													7											
86.0																	T							
86.2													5											
86.4													17											
86.7																	6							
87.0													3											
87.4(2)																				22				
87.7													20											
88.3																				26				
88.5													8											
89.3																				5				
89.8																		3						
90.1														T										
90.3																				10				
91.0																				13				
91.9																				12				
92.5																					18			
93.0																				11(E)	11(E)			11(E)
93.5																					T			
93.7																								15
94.9																					13(E)			13(E)
96.1																					9(E)	9(E)		9(E)
99.7																								T
100.1																								T
101.0																								T

T Trace

(E) Estimated due to overlapping peaks

Table 3.4 Summary of Tables 3.1, 3.2, and 3.3 Allowing Comparisons of Total Ion Count (in thousands) of Classes of Compounds Versus Fraction

Type of Compound	Fraction 2	Fraction 3	Fraction 4
Phenols			
C_0	-	-	2(1)
C_1	-	202(2)	4(2)
C_2	92(4)	669(5)	8(4)
C_3	213(9)	419(9)	-
C_4	84(8)	255(7)	-
C_5	9(3)	17(2)	-
Hydroxystyrenes			
C_0	-	-	13(2)
C_1	27(1)	97(3)	19(4)
C_2	144(8)	154(7)	19(7)
C_3	80(15)	77(13)	3(1)
C_4	14(2)	8(4)	2(1)
Hydroxyindenes			
C_0	-	19(2)	32(3)
C_1	-	24(8)	6(1)
C_2	4(2)	8(4)	-
C_3	20(7)	2(1)	-
Naphthols			
C_0	-		368(2)
C_1	-	47(2)	277(6)
C_2	-	73(12)	95(10)
C_3	-	12(3)	2(1)
Hydroxybenzothiophenes			
C_0	-	-	152(4)
C_1		15(3)	92(6)
C_2	4(2)	23(5)	42(10)
C_3	-	-	3(1)
Hydroxybiphenyls			
C_0	-	-	71(2)
C_1	-	30(5)	101(7)
C_2	-	-	53(5)
C_3	2(1)	-	9(1)
Hydroxyfluorenes			
C_0	-	-	48(4)
C_1	-	-	6(3)

was found in certain instances, that is, compounds appearing in two adjacent fractions. By inspection of the total ion chromatograms and massgrams, there appears to be over three hundred of these phenolic-like compounds! This estimation does not include the higher hydroxy PNAs for which the chromatographic conditions were not suitable.

It is interesting to note that, as expected, the more highly alkylated compounds appear in the earlier fractions, since they are relatively more nonpolar than the less highly alkylated compounds. Fraction 2 contains predominantly the more alkylated phenols and hydroxystyrenes; Fraction 3 contains large quantities of partially alkylated phenols, hydroxystyrenes, hydroxyindenes, and naphthols; and Fraction 4 contains the parent hydroxy aromatic compounds along with some partially alkylated derivatives.

The presence of a variety of alkylated phenolic-like compounds in Fraction 3 (Table 3.5) was verified in the sample derivatized with Methyl-8 Concentrate. Some C_2 and C_3-pyridines were found as well. Pyridine and picolines could not be identified because the by-products of the derivatization interfere with the detection of these compounds. (This condition applies to silylation with BSA.) No anilines or carboxylic acids were found in Fraction 3; these compounds probably occur in later fractions.

Verification of the presence of a variety of phenolic-like PNAs in Fraction 4 was found in the Tri-Deuter-8 derivatized sample (Table 3.6). However, by-products of the derivatization interfere with the determination of lower boiling compounds.

As expected, Fraction 1 contains a variety of the weakly polar PNAs as shown in Table 3.7. Alkyl benzenes were missing, apparently because of workup conditions. (Evaporation of the sample to 100 µL of toluene, rather than to dryness, would probably prevent the loss of the alkyl benzenes.) The higher PNAs were also missing, due to the chromatographic conditions.

3.3.4 Problems with the Analysis and Modifications that Might Lead to Better Analysis

Although only a limited study of the HYGAS oil sample was undertaken, a few minor problems seem to be associated with the procedures outlined in parts 1 and 2 of this report. These problems are due in part to the complexity of HYGAS oil samples wherein there is a wide range of boiling points and polarities of compounds in the mixture.

With respect to Fraction 1, evaporation of toluene results in the loss of the lower alkyl aromatics. (With a higher temperature program or shorter column, the higher PNAs would elute from the column.) In regard to the other fractions, a split of each fraction into three parts would allow derivatization with BSA and Methyl-8 Concentrate, along with the possibility of injecting the sample "as is" to detect the underivatized pyridines and sulfides. A higher temperature program also would permit identification of the higher hydroxy PNAs. Finally, the total ion chromatogram of Fraction 4 contains too many overlapping peaks so that further separation by slowing down the gradient is warranted.

Table 3.5. A Partial Listing of Tentative Identifications of Compounds in the Methyl-8 Concentrated Derivatized Fraction 3

Retention Time (Minutes)	Tentative Identification[a]
28.1	Anisole
28.4	Lutidine
34.3	Methyl anisole
35.1	Methyl anisole
39.4	Hydroxystyrene, methyl ether
40.9	C_2-Anisole
41.6	C_2-Anisole
41.8	C_2-Anisole
42.6	C_2-Anisole
44.2	C_2-Anisole
45.7	C_3-Anisole
46.3	C_3-Anisole
48.1	C_3-Anisole
48.4	C_3-Anisole
48.7	C_3-Anisole
50.1	C_3-Anisole
50.3	C_3-Anisole
52.5	C_4-Anisole
53.6	C_4-Anisole
54.0	Methyl hydroxystyrene, methyl ether
54.2	Methyl hydroxystyrene, methyl ether
54.5	C_4-Anisole
54.8	C_4-Anisole
55.0	Methyl hydroxystyrene, methyl ether
57.8	C_2-Hydroxystyrene, methyl ether
58.1	C_2-Hydroxystyrene, methyl ether
61.3	C_5-Anisole
62.1	C_5-Anisole
62.7	C_2-Hydroxystyrene, methyl ether
64.9	C_3-Hydroxystyrene, methyl ether
65.1	C_3-Hydroxystyrene, methyl ether
65.6	C_3-Hydroxystyrene, methyl ether
66.2	C_3-Hydroxystyrene, methyl ether
72.7	Methyl methoxynaphthalene
73.2	Methyl methoxynaphthalene
78.6	C_2-Methoxynaphthalene
79.1	C_2-Methoxynaphthalene
79.4	C_2-Methoxynaphthalene
80.3	C_2-Methoxynaphthalene
81.0	C_2-Methoxynaphthalene

[a]This represents only a partial listing of compounds in the Methyl-8 Concentrate derivatized Fraction 3.

Table 3.6. A Partial Listing of Tentative Identification of Compounds in the Tri-Deuter-8 Derivatized Fraction 4

Retention Time (Minutes)	Tentative Identification[a]
68.7	Hydroxybenzothiophene, methyl-d_3 ether
73.8	Methyl hydroxybenzothiophene, methyl-d_3 ether
74.0	Methyl naphthol, methyl-d_3 ether
75.1	Methyl naphthol, methyl-d_3 ether
78.1	Hydroxybiphenyl, methyl-d_3 ether
79.2	Hydroxybiphenyl, methyl-d_3 ether
82.0	C_2-Naphthol, methyl-d_3 ether
83.6	C_1-Hydroxybiphenyl, methyl-d_3 ether
83.9	C_1-Hydroxybiphenyl, methyl-d_3 ether
85.0	C_1-Hydroxybiphenyl, methyl-d_3 ether
86.7	C_1-Hydroxybiphenyl, methyl-d_3 ether
87.0	C_1-Hydroxybiphenyl, methyl-d_3 ether
87.5	C_1-Hydroxybiphenyl, methyl-d_3 ether
89.0	C_2-Hydroxybiphenyl, methyl-d_3 ether
91.8	C_2-Hydroxybiphenyl, methyl-d_3 ether
92.7	C_2-Hydroxybiphenyl, methyl-d_3 ether

[a]This represents only a partial listing of compounds in the Tri-Deuter-8 derivatized Fraction 4.

3.3.5 Recommended Modifications for the Analytical Method

Although the modifications alluded to in the previous section may make the analysis of HYGAS oil samples unduly complicated, it must be remembered that HYGAS oil samples contain such a wide variety of compounds that analysis must involve several procedures. The major problems in the present analytical scheme are:

1. Analysis of higher boiling PNAs is not possible with the present temperature program or chromatographic conditions.

2. Under the preparative conditions used for Fraction 1, certain lower boiling aromatic compounds are lost.

3. Certain lower boiling pyridines and sulfides cannot be detected due to derivatization by-products.

Thus, the modifications or additions to the procedures outlined in parts 1 and 2 of this report are:

1. Run all fractions, including those derivatized, on both a 50-meter OV-101 column and a 20-meter OV-101 or similar column.

Table 3.7. A Partial Listing of Tentative Identifications of Compounds in Fraction 1

Retention (min)	Tentative Identification[a]	Retention (min)	Tentative Identification[a]
55.1	Methyl naphthalene	84.1	C_3-Biphenyl
56.3	Methyl naphthalene	84.6	C_2-Acenaphthene
61.0	Biphenyl	84.9	C_2-Acenaphthene
61.3	C_2-Benzothiophene	86.5	Phenanthrene
61.7	C_2-Naphthalene	81.0	Anthracene
62.0	C_2-Benzothiophene	91.0	Methyl dibenzothiophene
62.4	C_2-Benzothiophene		
62.4	C_2-Naphthalene	92.3	Methyl phenanthrene/ anthracene
62.4	C_2-Naphthalene		
63.5	C_2-Naphthalene	92.6	Methyl phenanthrene/ anthracene
63.7	C_2-Naphthalene		
64.9	C_2-Naphthalene	94.0	Methyl phenanthrene/ anthracene
65.8	C_2-Naphthalene		
65.8	C_2-Naphthalene	96.2	Aceanthrene
67.6	Acenaphthene	101.5	Pyrene
67.8	Methyl biphenyl		
68.3	Methyl biphenyl		
68.7	C_3-Naphthalene		
68.9	C_3-Benzothiophene		
69.1	C_3-Naphthalene		
69.5	C_3-Naphthalene		
69.9	C_3-Naphthalene		
70.4	Methyl biphenyl		
70.7	C_3-Naphthalene		
71.6	C_3-Naphthalene		
71.8	C_3-Naphthalene		
72.6	C_3-Naphthalene		
72.8	C_3-Naphthalene		
74.1	C_3-Naphthalene		
74.3	Fluorene		
74.6	Methyl acenaphthene		
76.6	C_2-Biphenyl		
77.5	C_2-Biphenyl		
78.0	C_2-Biphenyl		
79.1	Dibenzothiophene		
80.9	Methyl fluorene		
81.6	Methyl fluorene		
82.0	Methyl fluorene		
83.0	C_3-Biphenyl		
83.2	C_3-Biphenyl		

[a]This group represents only a partial listing of compounds in underivatized Fraction 1

2. Evaporate Fraction 1 to 100 μL of toluene solvent rather than to dryness.

3. Prepare a split of three rather than two of the polar fractions and analyze an underivatized sample for each fraction.

3.4 SUMMARY AND CONCLUSIONS

A preliminary study of the methods for analysis of complex oil samples as described in parts 1 and 2 of this report, namely, HPLC separation into fractions and derivatization of polar fractions, was undertaken on an authentic HYGAS oil sample to determine whether the method would make HYGAS oil samples more amenable to analysis by capillary column GC/MS. It was found that:

1. HPLC does separate, based on polarity, the complex mixtures of HYGAS oil samples into less complex mixtures.

2. Derivatization of the polar fractions does enhance the identification of compounds by capillary column GC/MS.

3. Small modifications or additions of the method will be required for analysis of pyridines, sulfides, and other underivatized polar compounds that are highly volatile, due to interferences from by-products of the derivatization reactions.

4. Additional capillary column GC/MS identifications under slightly different conditions will be required for analysis of the higher boiling PNAs and hydroxy PNAs.

A wide variety of previously unreported hydroxy PNAs were found in the HYGAS oil sample.

ACKNOWLEDGMENTS

The author acknowledges the useful discussions with Bill Dark of Waters Associates, Inc. Wyman Harrison of Argonne and Professor Larry T. Taylor of Virginia Polytechnic Institute and State University reviewed the manuscript.

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2. Das, B.J. and G.H. Thomas, 1978, *Fluorescence Detection in High Performance Liquid Chromatographic Determination of Polycyclic Aromatic Hydrocarbons*, Anal. Chem., v. 50, p. 967-973.

3. Dark, W.A., and W.H. McFadden and D.L. Bradford, 1977, *Fractionation of Coal Liquids by HPLC with Structural Characterization by LC-MS*, J. Chrom. Sc., v. 15, p. 454-460.

4. Dark, W.A. and W.H. McFadden, *The Role of HPLC in the Separation and Characterization of Coal Liquefaction Products*, J. Chrom. Sc., v. 16, p. 289-293.

5. Galya, L.G. and J.C. Suatoni, *Rapid SARA Separations by HPLC*, Pittsburgh Conference, 1979, paper 292.

6. Farcasiu, M., *Fractionation and Structural Characterization of Coal Liquids*, Fuel, v. 56, p. 9-14.

APPENDIX A

ANL Bulk Sample Log-In Record

ANL BULK SAMPLE LOG-IN RECORD

SAMPLE I.D. NO. 72/H/G/O/3

Pilot Plant: HYGAS

Run No.: 72

Date Collection: 25 May 78

Time Collected: 1150 hr

Transport to ANL

Person: Sather

Time: 2:30

Date: 25 May 78

Description: "F Code 1053 4040"
Oil Slurry Auto
DT3012
1-1 gal. bottle

Comments:

The sample was taken during a steady-state period of test run 72 from the pilot plant oil-char slurry feed stream which is the recirculating oil stream to slurry the coal prior to injection into the reactor. Initially, this stream contains commercial-grade toluene, which is gradually replaced during a test run with product oil.

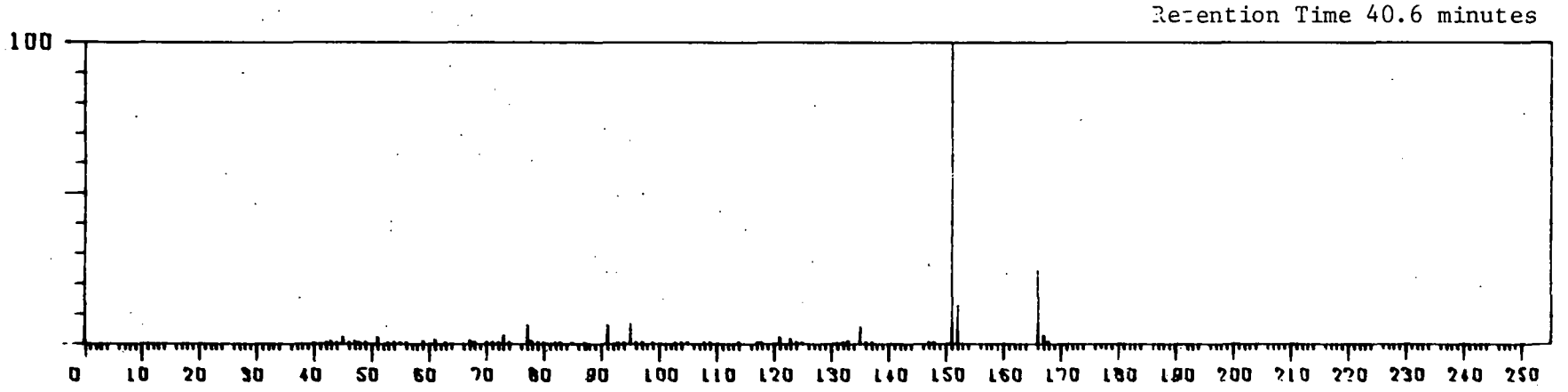
Special Comments:

500 psi run

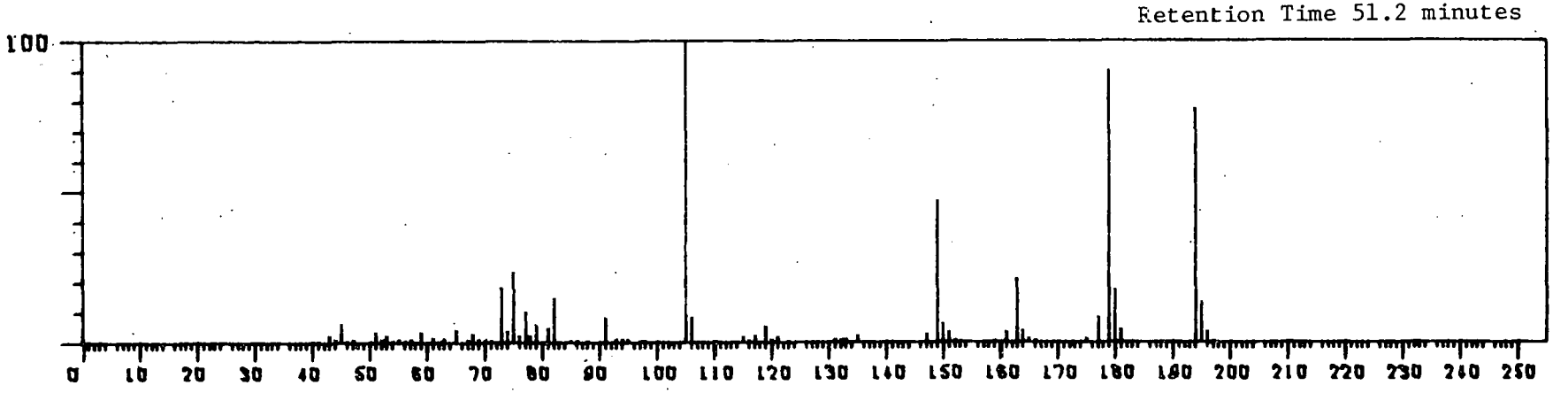
Wyman Harrison
Signature

APPENDIX B

Mass Spectra of Derivatized Standards

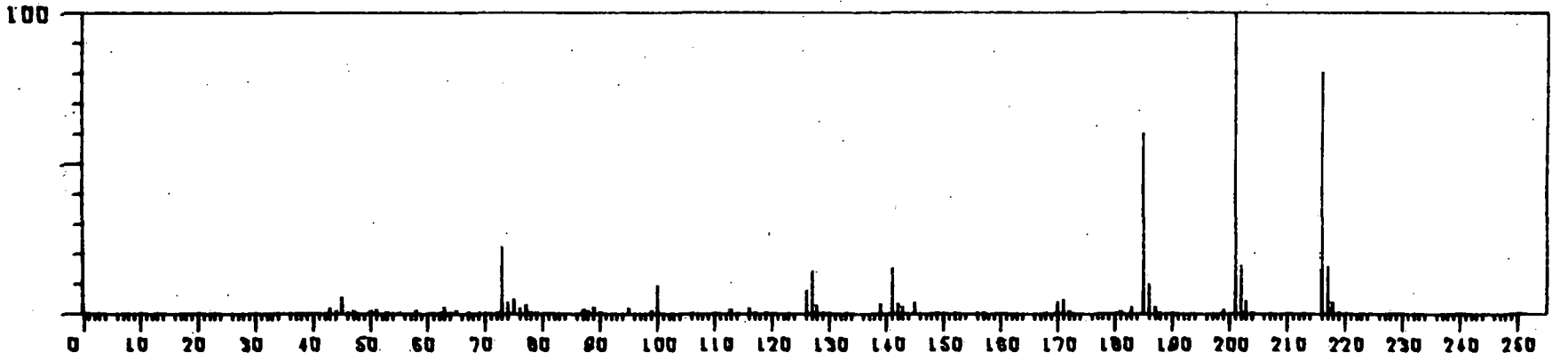


Mass Spectrum of Phenol, Trimethylsilyl Ether, TMS Derivative of Phenol



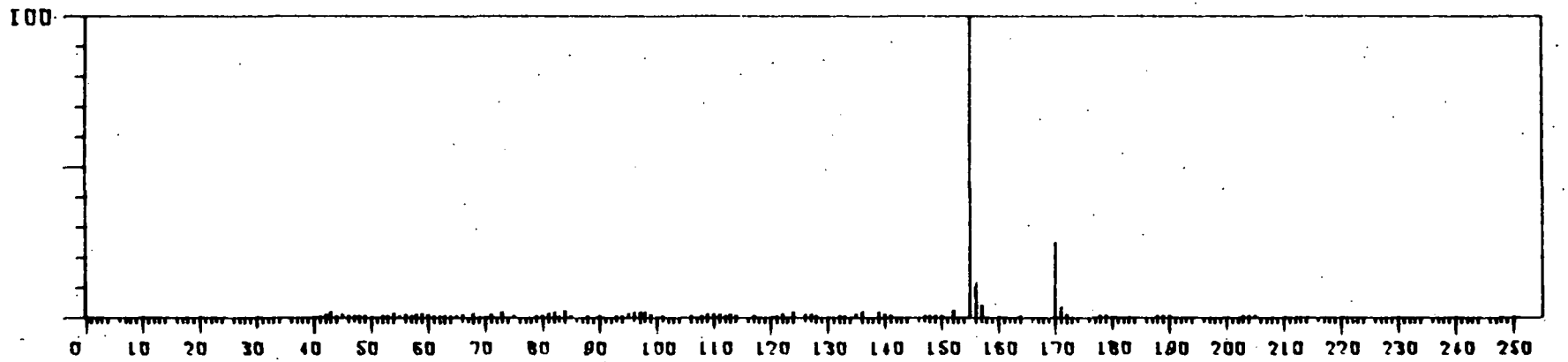
Mass Spectrum of 2,4-Xylenol, Trimethylsilyl Ether, TMS Derivative of 2,4-Xylenol

Retention Time 71.5 minutes



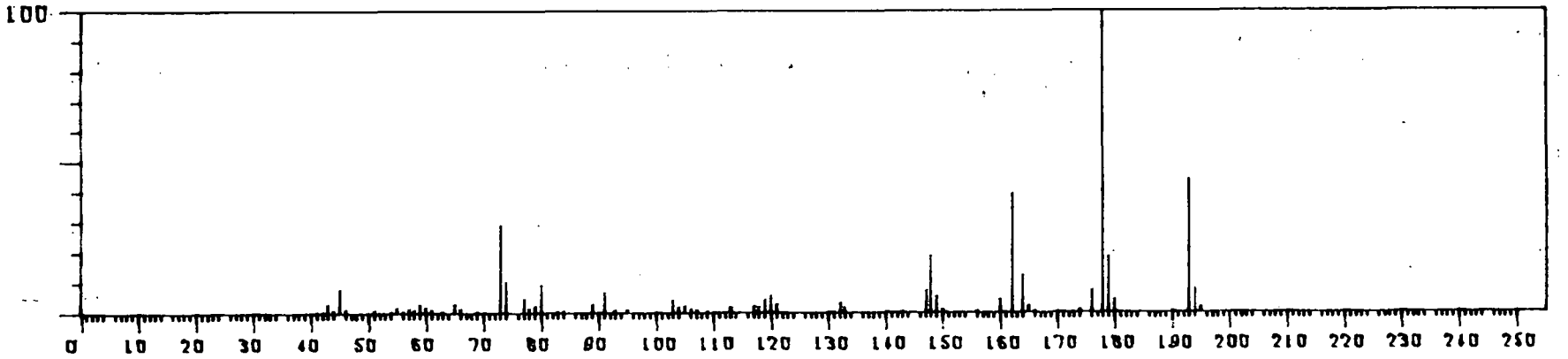
Mass Spectrum of 1-Naphthol, Trimethylsilyl Ether, TMS Derivative of 1-Naphthol

Retention Time 49.7 minutes



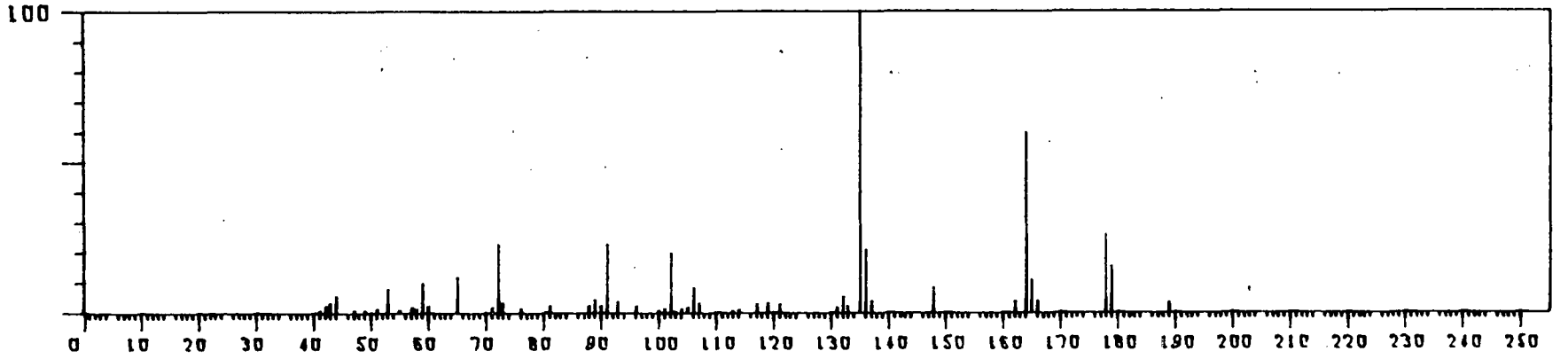
Mass Spectrum of N-(Trimethylsilyl) Aniline-d_5, TMS Derivative of Aniline-d_5

Retention Time 56.5 minutes



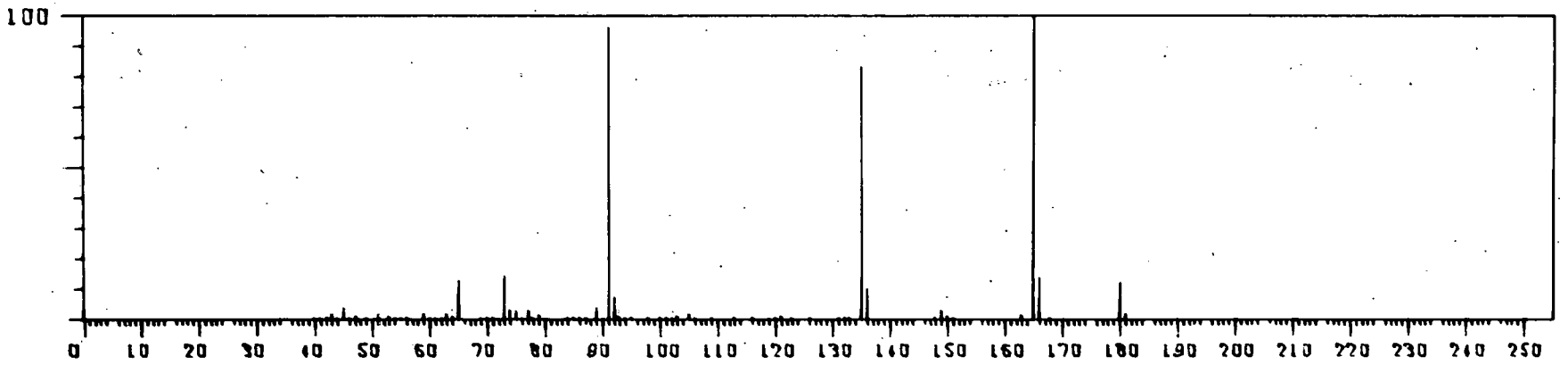
Mass Spectrum of N-(Trimethylsilyl) 2,6-Dimethyl Aniline, TMS Derivative of 2,6-Dimethyl Aniline

Retention Time 50.5 minutes



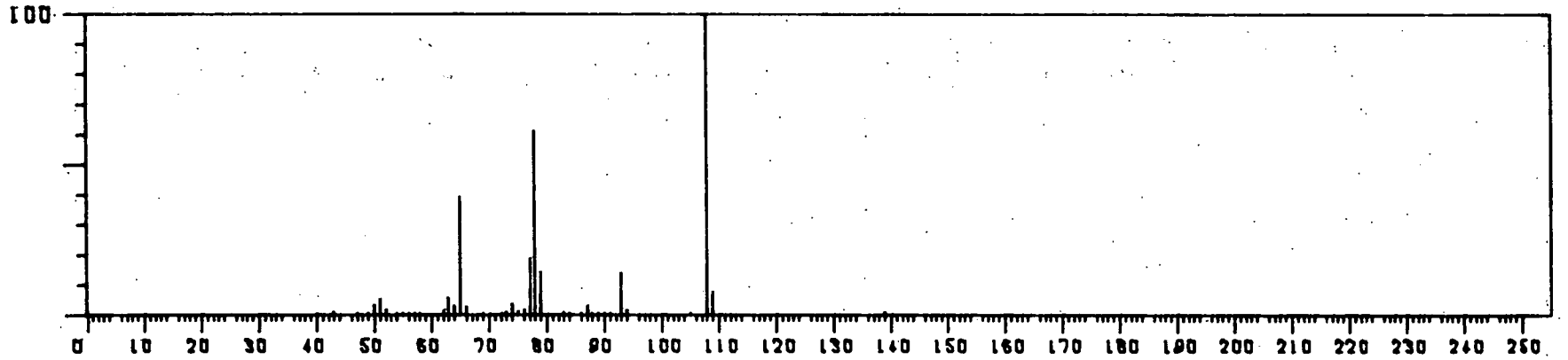
Mass Spectrum of N-(Trimethylsilyl) Benzyl Amine, TMS Derivative of Benzyl Amine

Retention Time 46.4 minutes



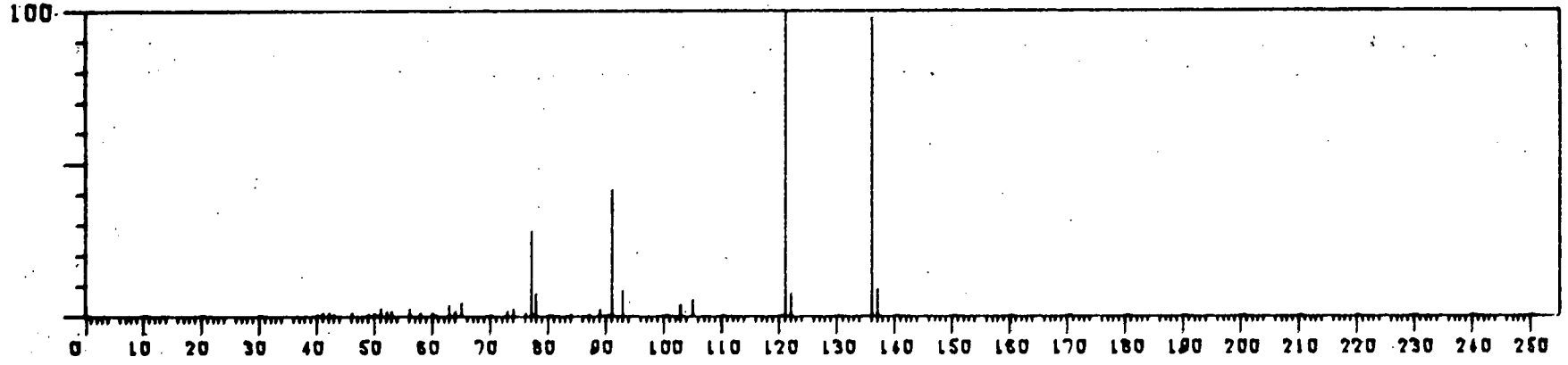
Mass Spectrum of Benzyl Alcohol, Trimethylsilyl Ether, TMS Derivative of Benzyl Alcohol

Retention Time 27.4 minutes



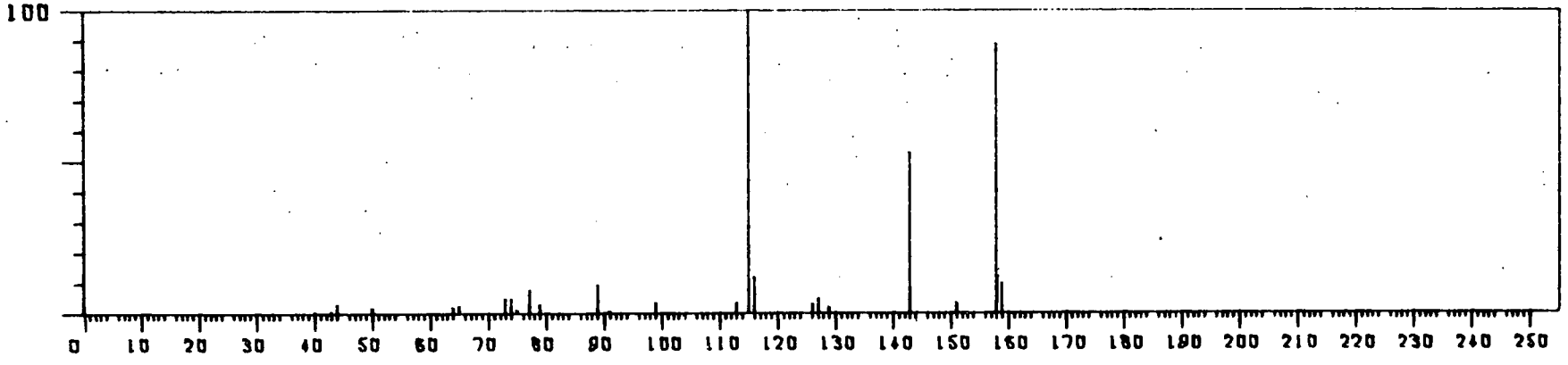
Mass Spectrum of Methoxybenzene, Methyl-8 Derivative of Phenol

Retention Time 41.2 minutes



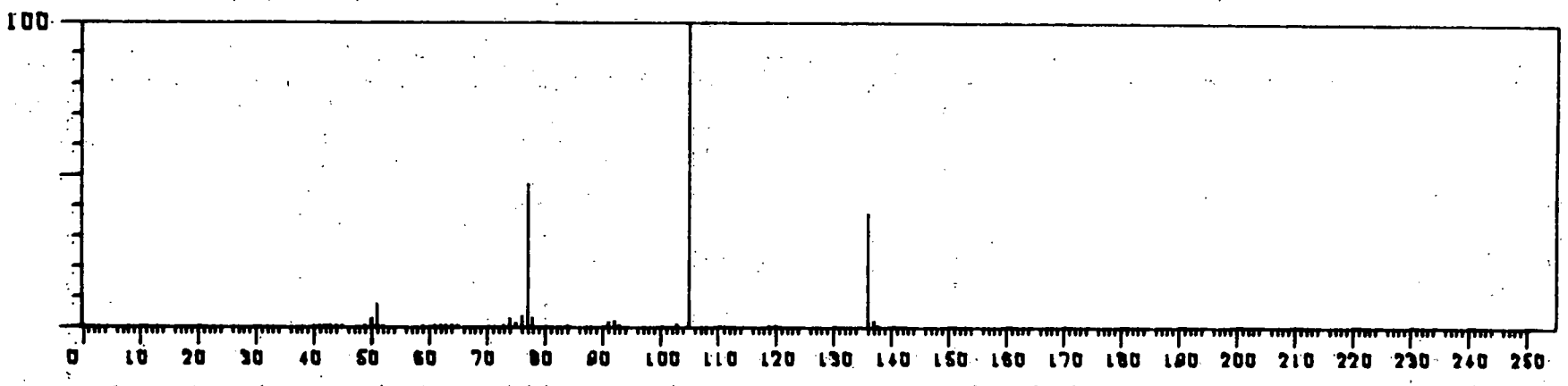
Mass Spectrum of 1-Methoxy-2,4-Dimethyl Benzene, Methyl-8 Derivative of 2,4-Xylenol

Retention Time 66.1 minutes



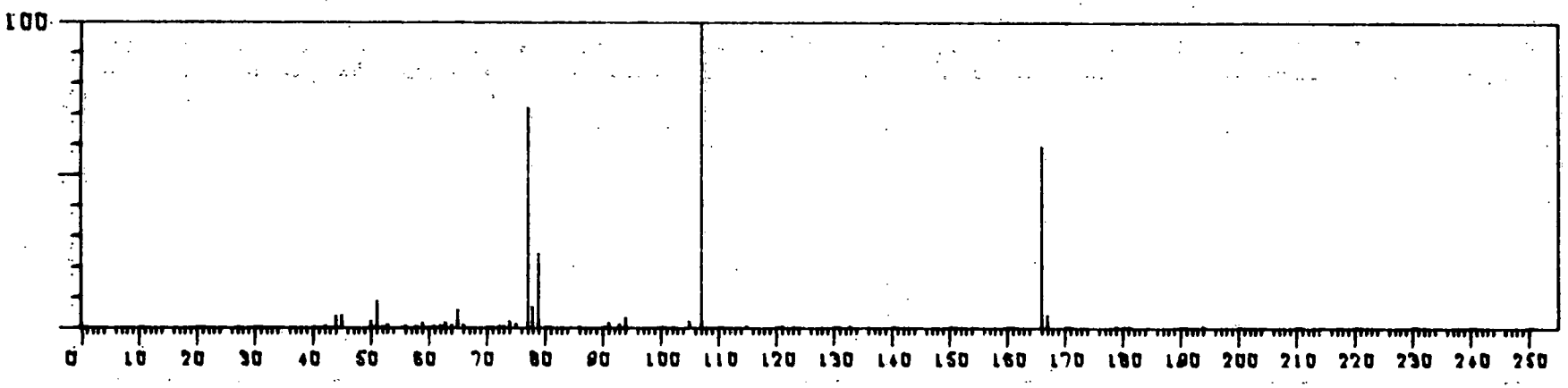
Mass Spectrum of 1-Methoxy Naphthalene, Methyl-8 Derivative of 1-Naphthol

Retention Time 40.8 minutes



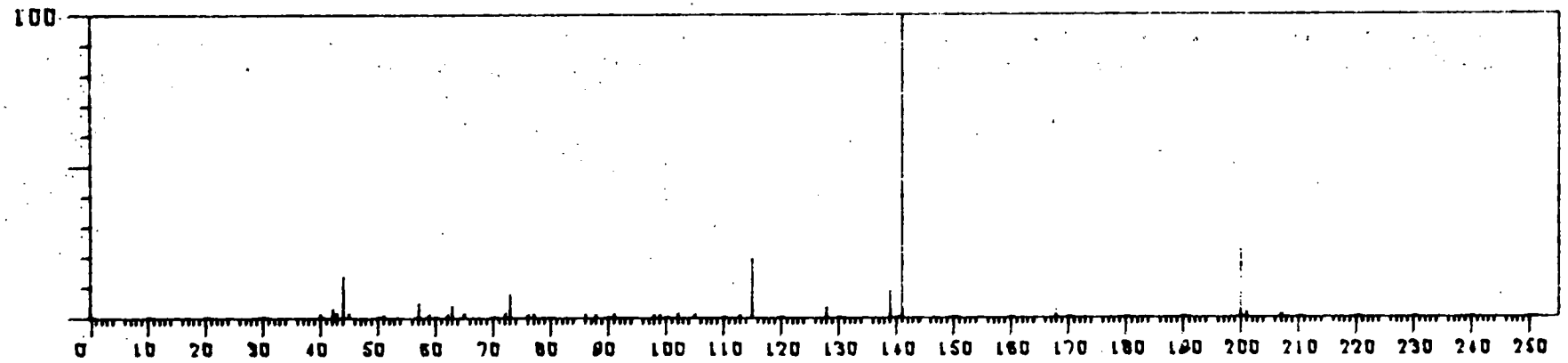
Mass Spectrum of Methyl Benzoate, Methyl-8 Derivative of Benzoic Acid

Retention Time 57.6 minutes



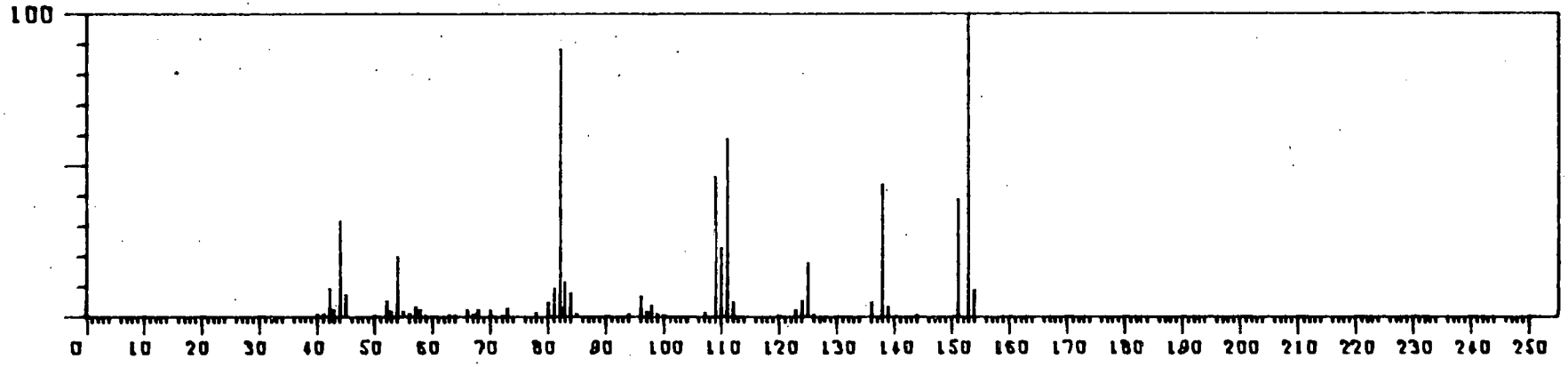
Mass Spectrum of Phenoxyacetic Acid, Methyl Ester, Methyl-8 Derivative of Phenoxyacetic Acid

Retention Time 82.2 minutes



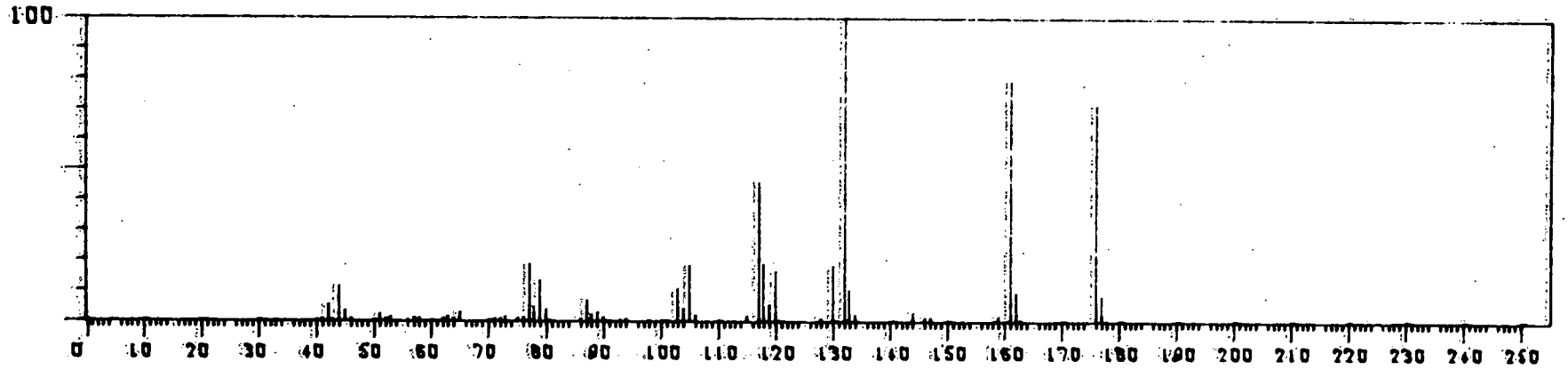
Mass Spectrum of 1-Naphthalene Acetic Acid, Methyl Ester, Methyl-8 Derivative of 1-Naphthalene Acetic Acid

Retention Time 61.7 minutes



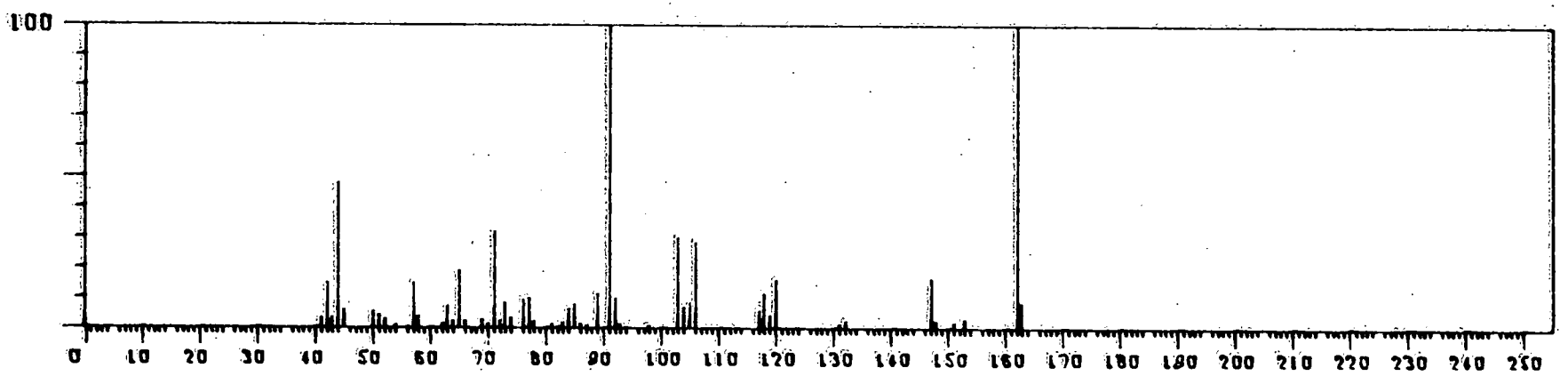
Mass Spectrum of N,N-Dimethyl-N'-Phenyl-d_5 Formamidine, Methyl-8 Derivative of Aniline-d_5

Retention Time 67.0 minutes



Mass Spectrum of N,N-Dimethyl-N'-(2,6-Dimethylphenyl) Formamidine, Methyl-8 Derivative of 2,6-Dimethyl Aniline

Retention Time 62.7 minutes



Mass Spectrum of N,N-Dimethyl-N'-(Benzyl) Formamidine, Methyl-8 Derivative of Benzyl Amine

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APPENDIX C

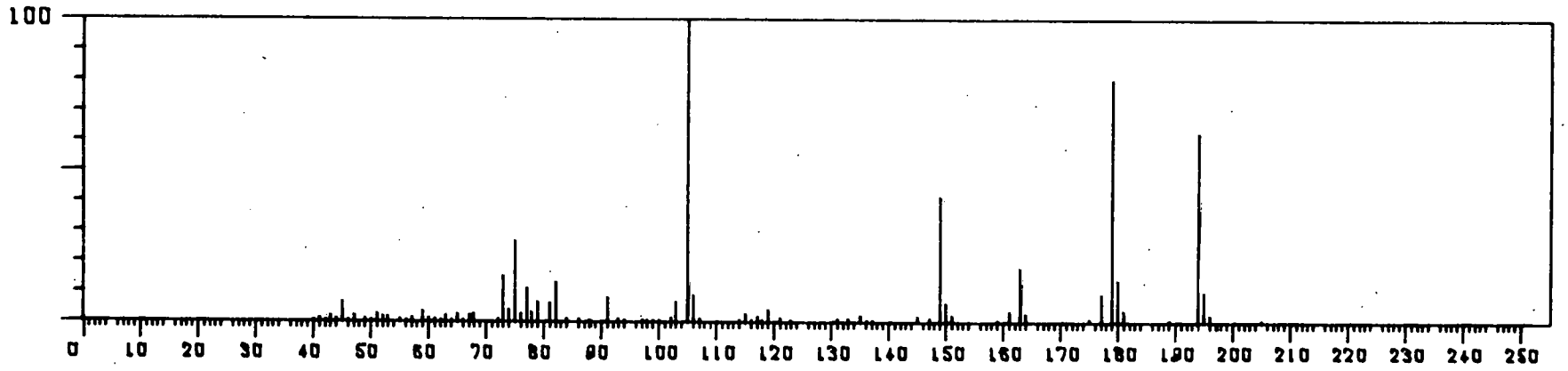
REPRESENTATIVE MASS SPECTRA OF COMPOUNDS IN FRACTIONS 1,2,3, AND 4; TENTATIVE IDENTIFICATIONS

APPENDIX C (Contd.)

Retention Time (Minutes)	Fraction	Compound	Page
69.4	3	C_2-Hydroxystyrene, TMS ether	88
69.8	3	Methyl hydroxyindene, TMS ether	88
71.0	3	C_3-Hydroxystyrene, TMS ether	89
71.2	3	C_3-Hydroxystyrene, TMS ether	89
73.8	3	C_3-Hydroxystyrene, TMS ether	90
74.8	3	C_4-Hydroxystyrene, TMS ether	90
76.9	3	C_2-Hydroxyindene, TMS ether	91
78.5	3	Methyl hydroxybenzothiophene, TMS ether	91
53.0	4	Hydroxystyrene, TMS ether	92
59.7	4	C_1-Hydroxystyrene, TMS ether	92
61.8	4	C_1-Hydroxystyrene, TMS ether	93
64.1	4	Hydroxyindene, TMS ether	93
64.3	4	Hydroxyindene, TMS ether	94
66.2	4	C_2-Hydroxystyrene, TMS ether	94
70.1	4	Methyl hydroxyindene, TMS ether	95
71.1	4	Hydroxy benzothiophene, TMS ether	95
71.8	4	Naphthol, TMS ether	96
72.2	4	Hydroxybenzothiophene, TMS ether	96
74.0	4	Hydroxybenzothiophene, TMS ether	97
76.2	4	Methyl hydroxybenzothiophene, TMS ether	97
77.2	4	Methyl hydroxybenzothiophene, TMS ether	98
79.3	4	Methyl naphthol, TMS ether	98
80.0	4	Methyl naphthol, TMS ether	99
80.4	4	Methyl hydroxybenzothiophene, TMS ether	99
80.8	4	Methyl naphthol, TMS ether	100
81.8	4	C_2-Hydroxybenzothiophene, TMS ether	100
83.0	4	Hydroxybiphenyl, TMS ether	101
85.8	4	C_2-Naphthol, TMS ether	101
86.4	4	C_2-Naphthol, TMS ether	102
87.0	4	C_2-Naphthol, TMS ether	102
87.4	4	Methyl hydroxybiphenyl, TMS ether	103
87.7	4	C_2-Naphthol, TMS ether	104
88.3	4	Methyl hydroxybiphenyl, TMS ether	105
91.9	4	Methyl hydroxybiphenyl, TMS ether	106
92.5	4	C_2-Hydroxybiphenyl, TMS ether	107
93.7	4	Hydroxyfluorene, TMS ether	108
28.1	3	Anisole	109
28.4	3	C_2-Pyridine	109
35.1	3	Methyl anisole	110
39.4	3	Hydroxystyrene, methyl ether	110
40.9	3	C_2-Anisole	111
41.6	3	C_2-Anisole	111
41.8	3	C_2-Anisole	112
42.6	3	C_2-Anisole	112
44.2	3	C_2-Anisole	113
48.1	3	C_3-Anisole	113
48.4	3	C_3-Anisole	114

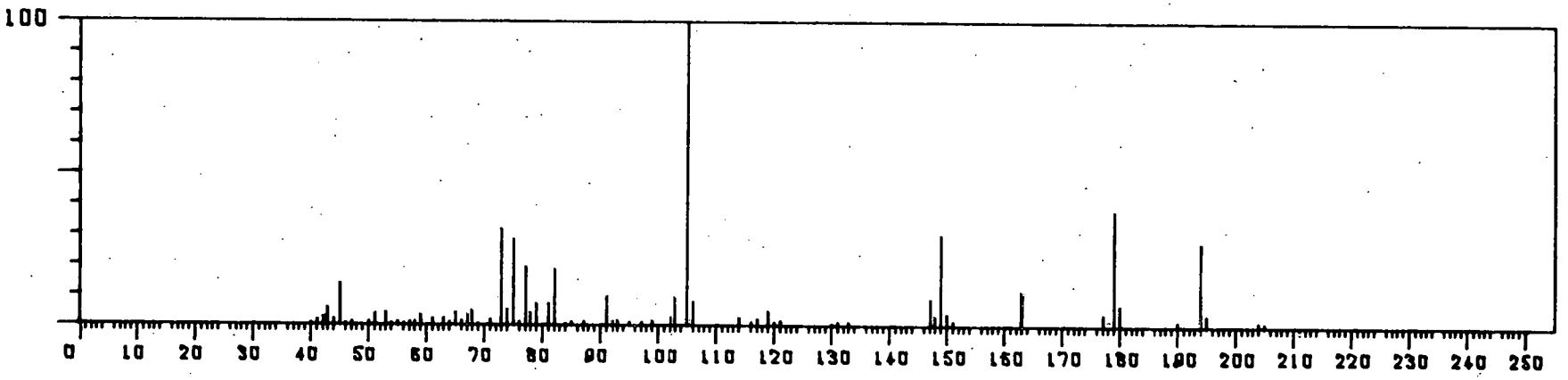
APPENDIX C (Contd.)

Retention Time (Minutes)	Fraction	Compound	Page
48.7	3	C_3-Anisole	114
50.1	3	C_3-Anisole	115
50.3	3	C_3-Anisole	115
52.5	3	C_4-Anisole	116
54.5	3	C_4-Anisole	116
54.8	3	C_4-Anisole	117
55.0	3	Methyl hydroxystyrene, methyl ether	117
58.1	3	C_2-Hydroxystyrene, methyl ether	118
68.7	4	Hydroxybenzothiophene, methyl-d_3 ether	118
75.1	4	Methyl naphthol, methyl-d_3 ether	119
78.2	4	Hydroxybiphenyl, methyl-d_3 ether	119
79.3	4	Hydroxybiphenyl, methyl-d_3 ether	120
83.8	4	C_1-Hydroxybiphenyl, methyl-d_3 ether	120
85.1	4	C_1-Hydroxybiphenyl, methyl-d_3 ether	121
89.0	4	C_2-Hydroxybiphenyl, methyl-d_3 ether	121
91.8	4	C_2-Hydroxybiphenyl, methyl-d_3 ether	122
55.2	1	Methyl naphthalene	122
63.5	1	C_2-Naphthalene	123
70.4	1	Methyl biphenyl	123
70.9	1	C_3-Naphthalene	124
72.7	1	C_3-Naphthalene	124
74.5	1	Fluorene	125
76.6	1	C_2-Acenaphthene	125
77.6	1	C_2-Acenaphthene	126
83.3	1	C_3-Acenaphthene	126
84.2	1	C_3-Acenaphthene	127
84.7	1	C_2-Biphenyl	127
86.5	1	Phenanthrene	128
87.0	1	Anthracene	128
96.2	1	Aceanthrene/Acephenanthrene	129
101.6	1	Pyrene	129



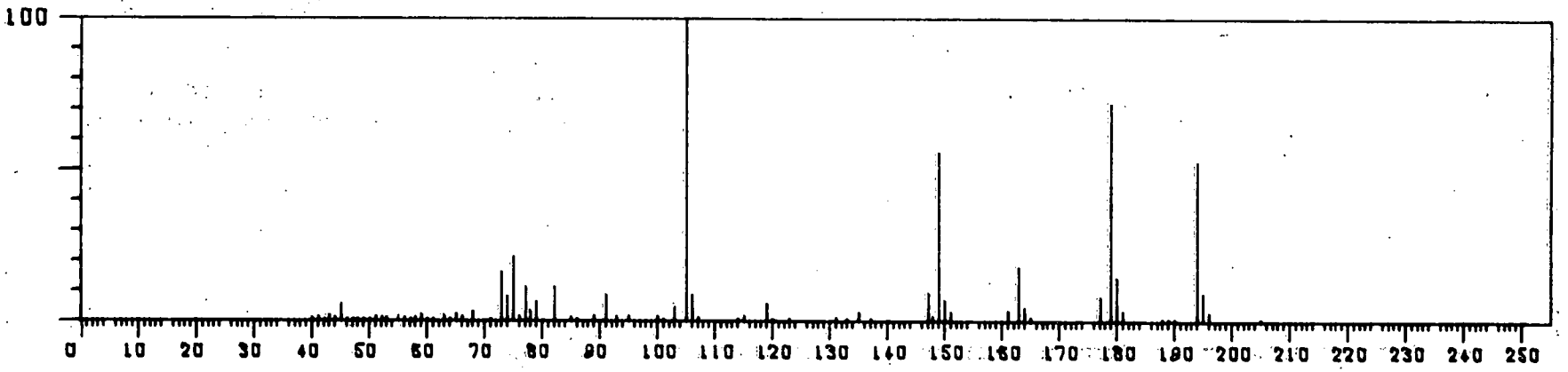
C_2-Phenol, TMS ether

Retention Time 50.2



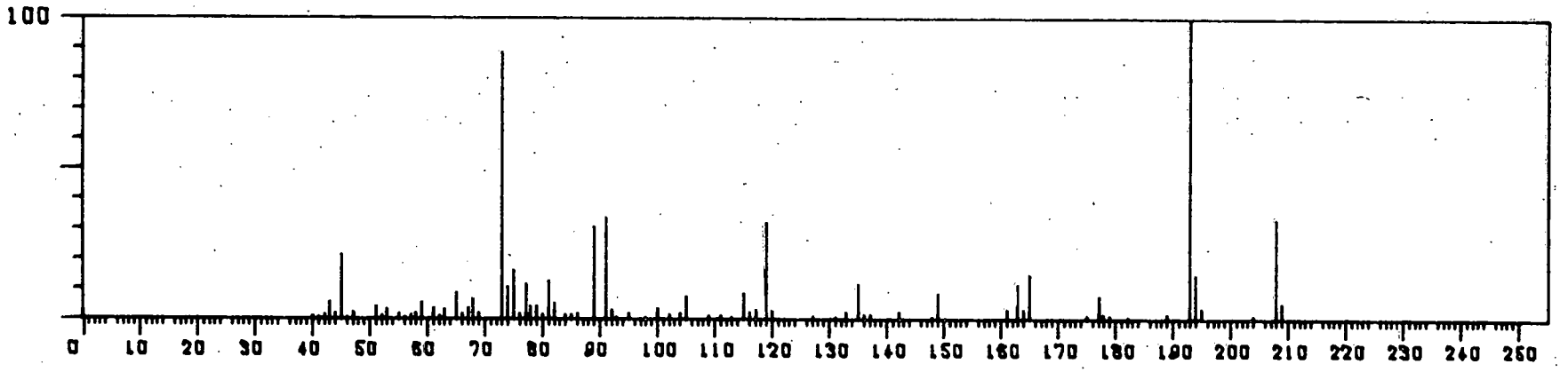
C_2-Phenol, TMS ether

Retention Time 51.2



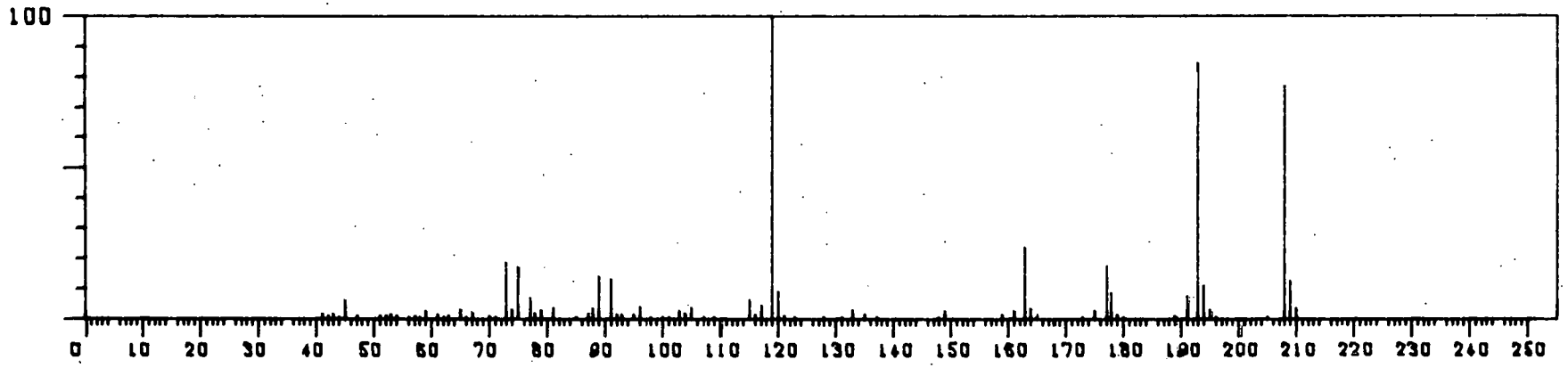
C_2-Phenol, TMS ether

Retention Time 52.7



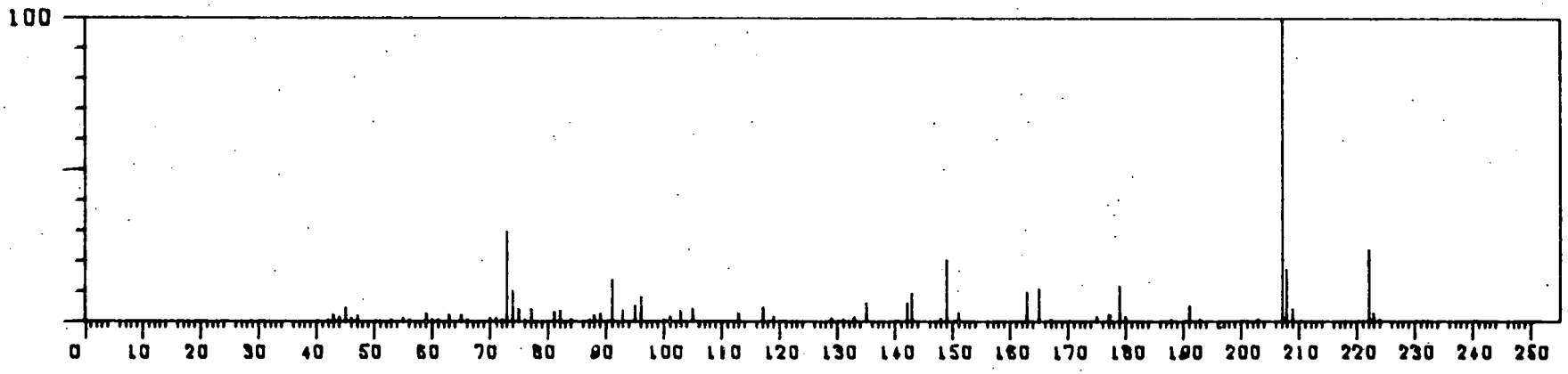
C_3-Phenol, TMS ether

Retention Time 56.8



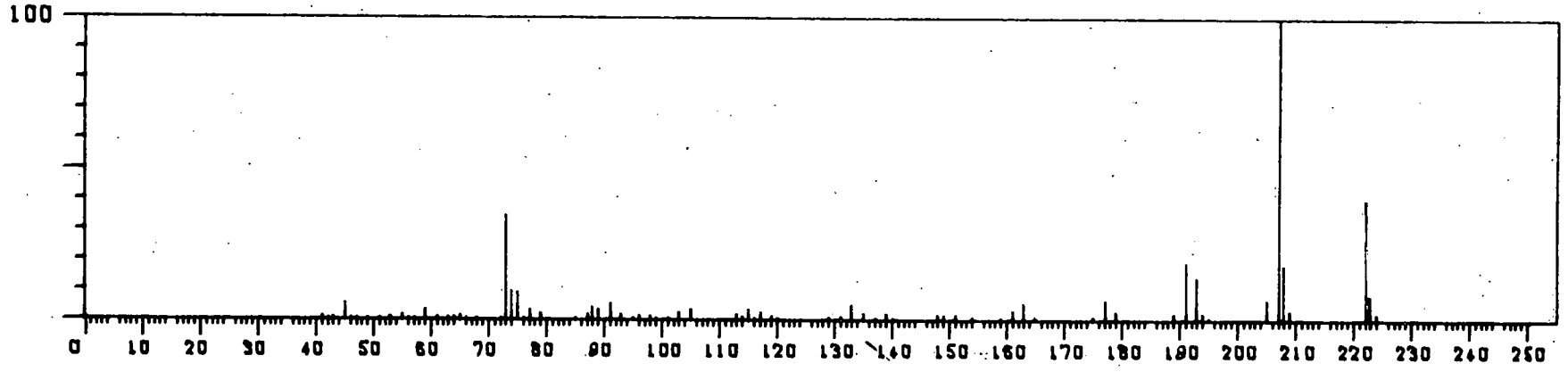
C_3-Phenol, TMS ether

Retention Time 58.1



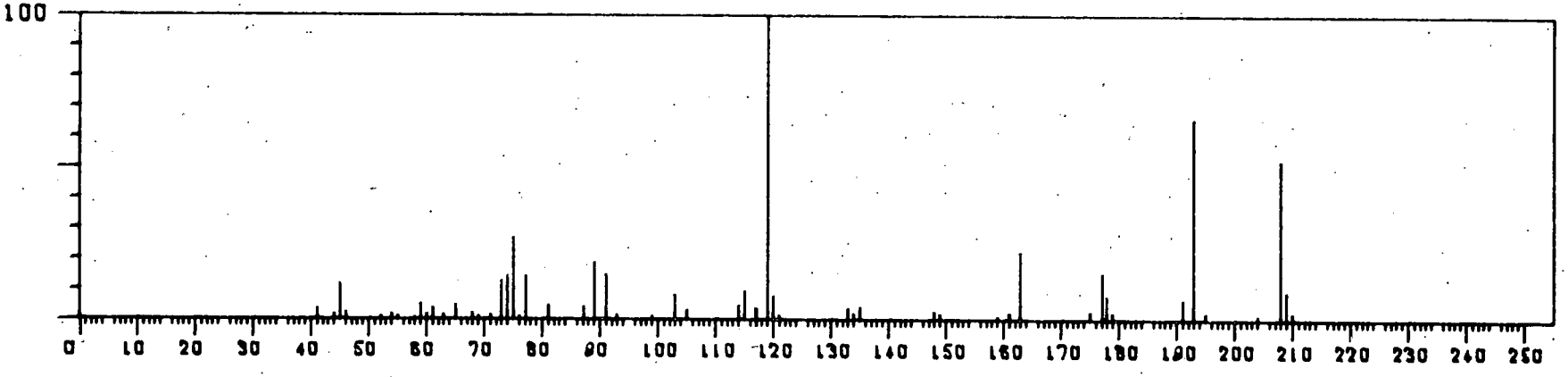
C_4-Phenol, TMS ether

Retention Time 60.1



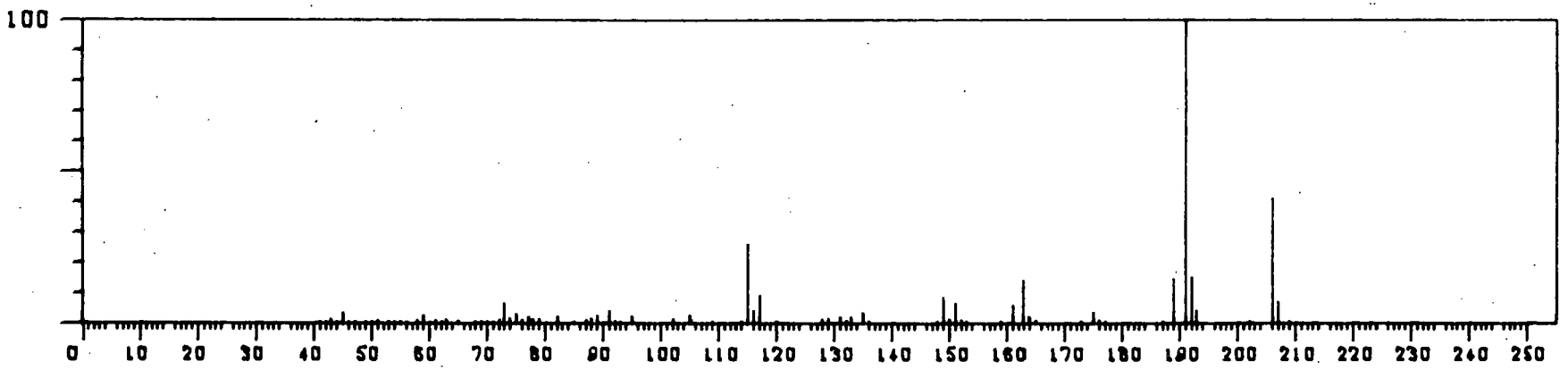
C_4-Phenol, TMS ether

Retention Time 60.4



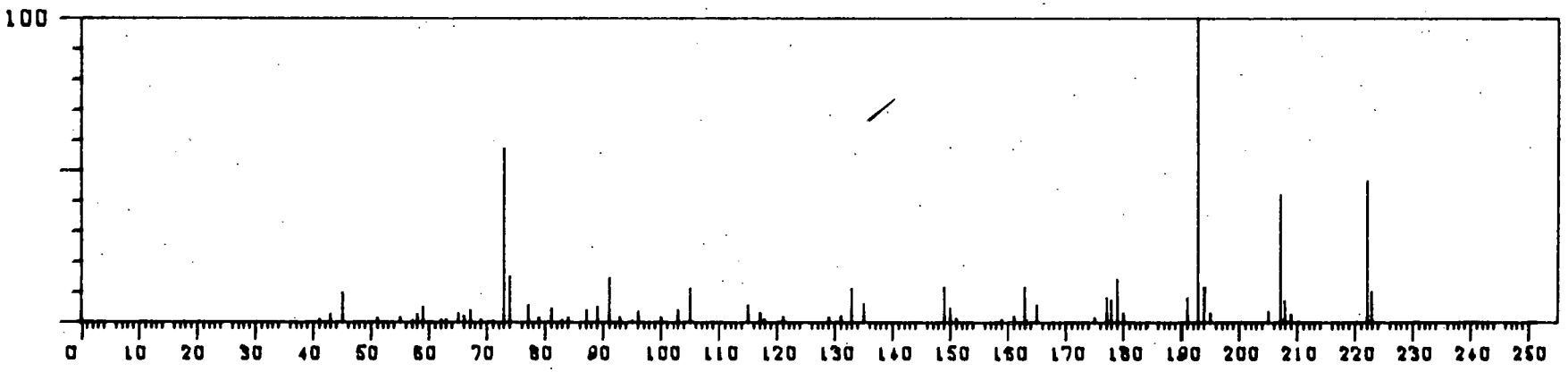
C_3-Phenol, TMS ether

Retention Time 60.9



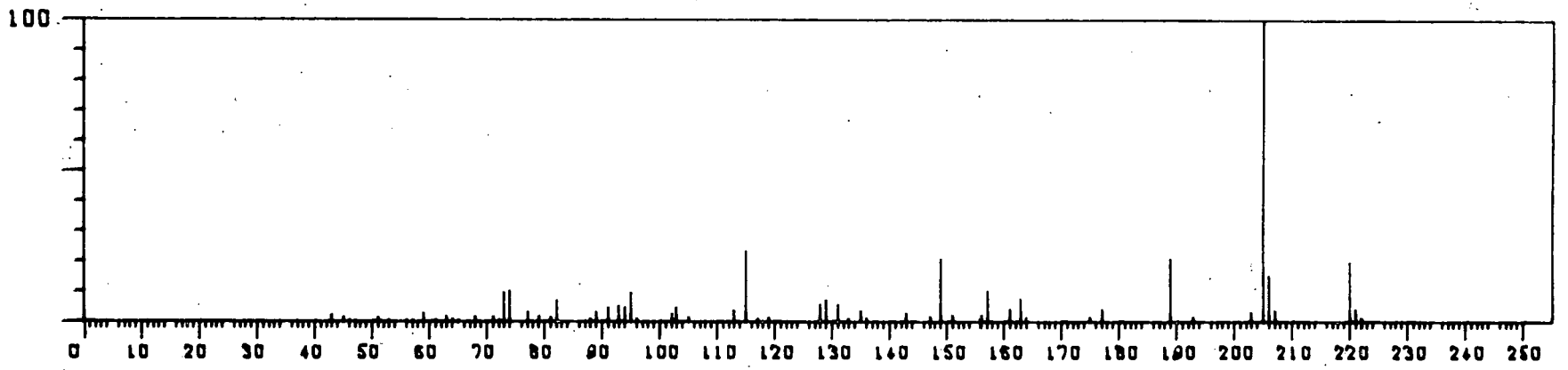
C_1-Hydroxystyrene, TMS ether

Retention Time 61.5



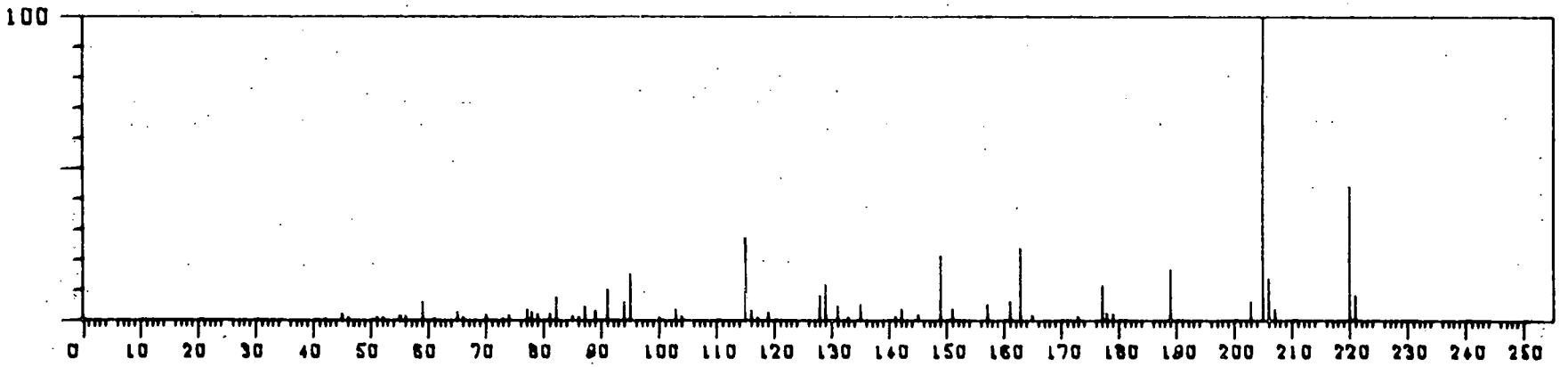
C_4-Phenol, TMS ether

Retention Time 62.4



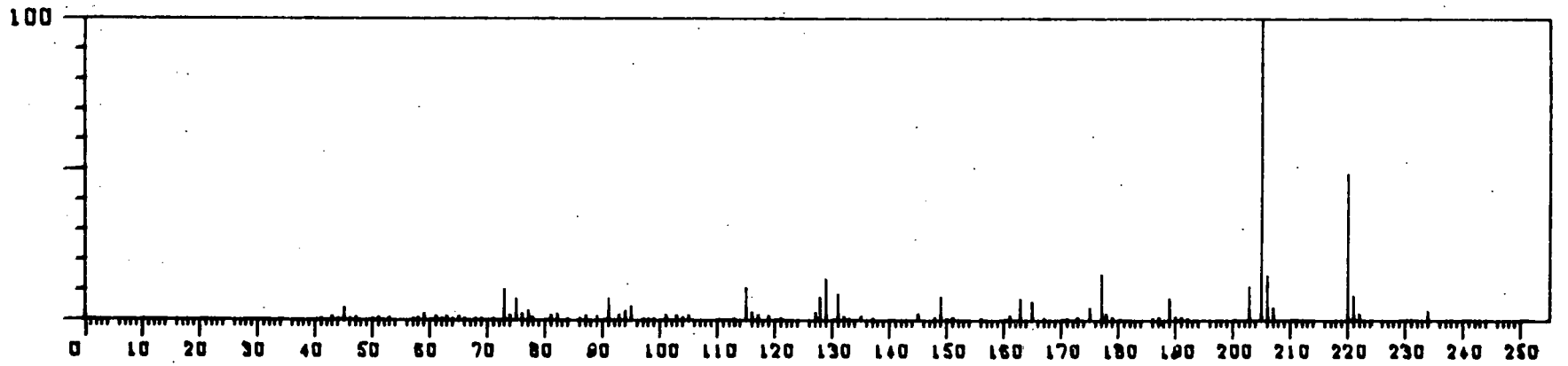
C_2-Hydroxystyrene, TMS ether

Retention Time 62.9



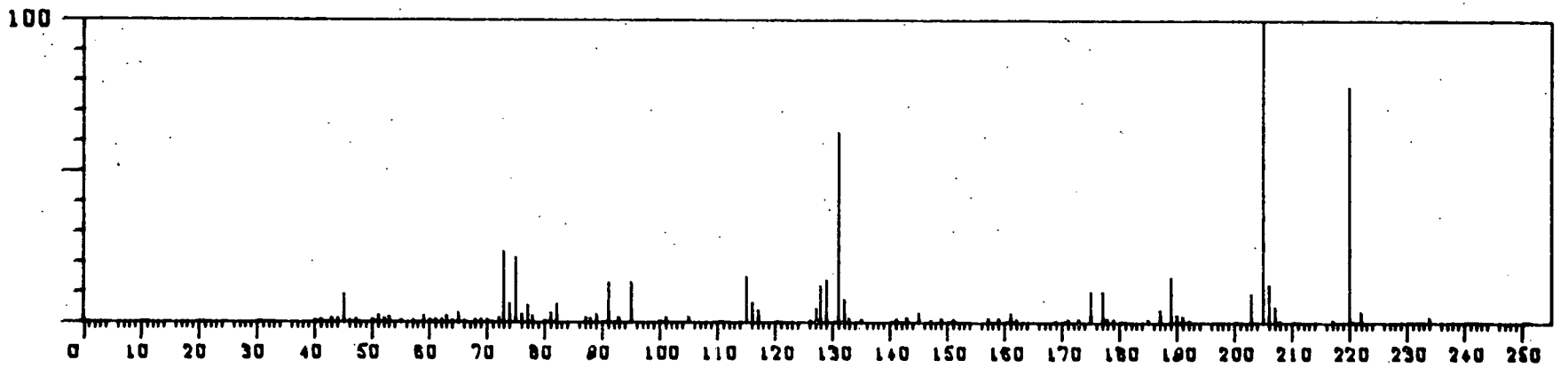
C_2-Hydroxystyrene, TMS ether

Retention Time 64.1



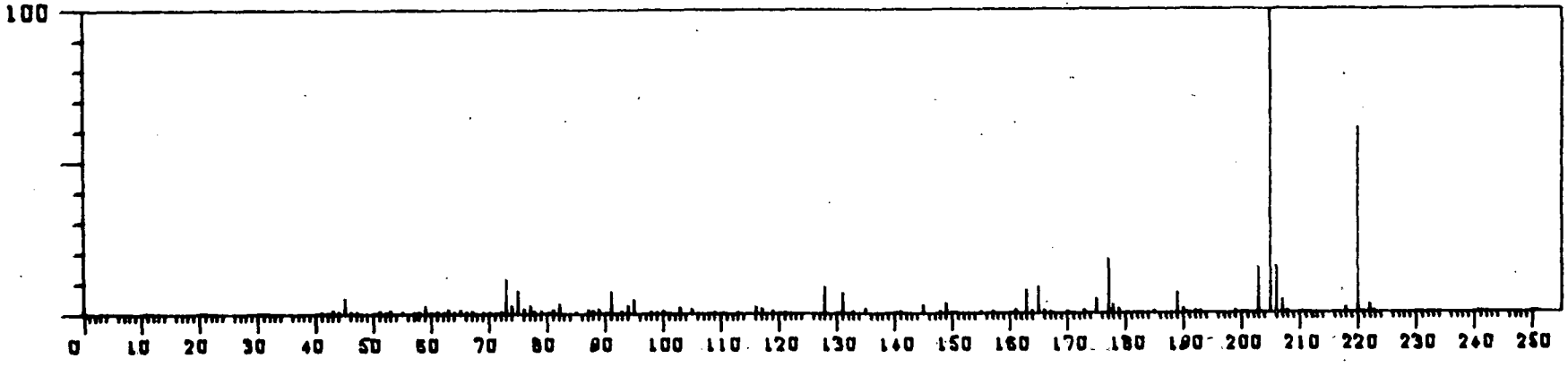
C_2-Hydroxystyrene, TMS ether

Retention Time 66.7



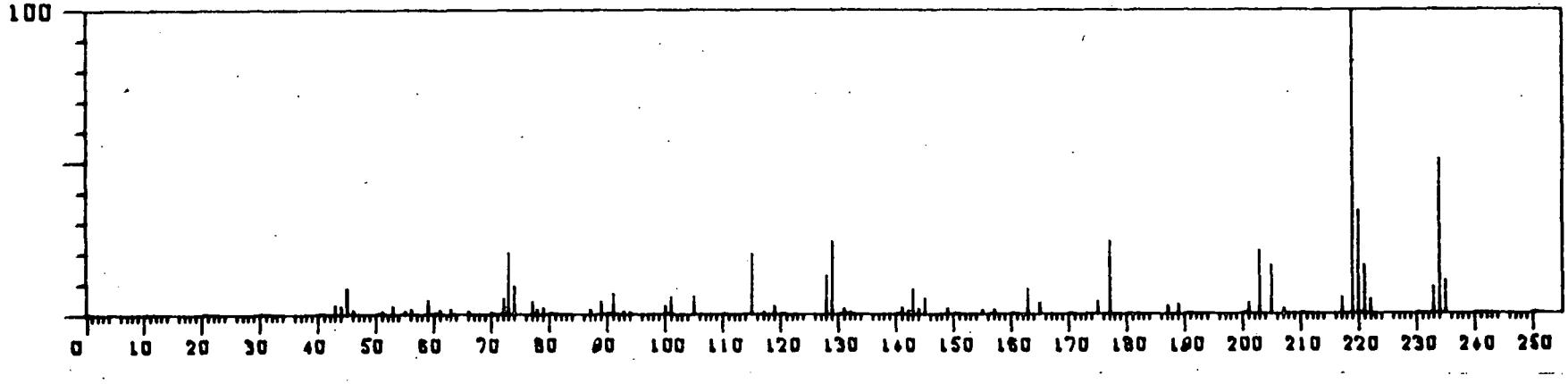
C_2-Hydroxystyrene, TMS ether

Retention Time 67.9



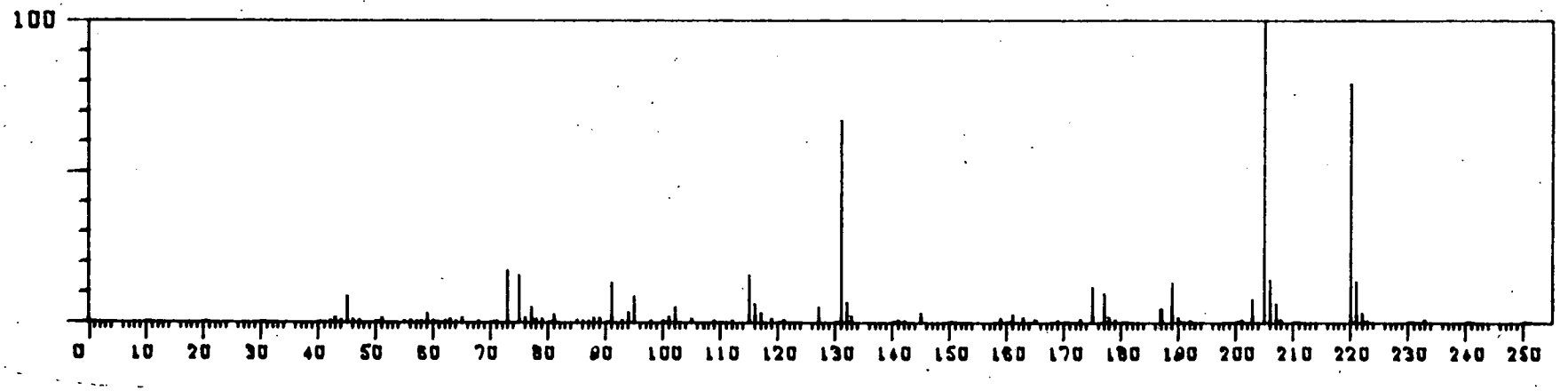
C_2-Hydroxystyrene, TMS ether

Retention Time 68.3



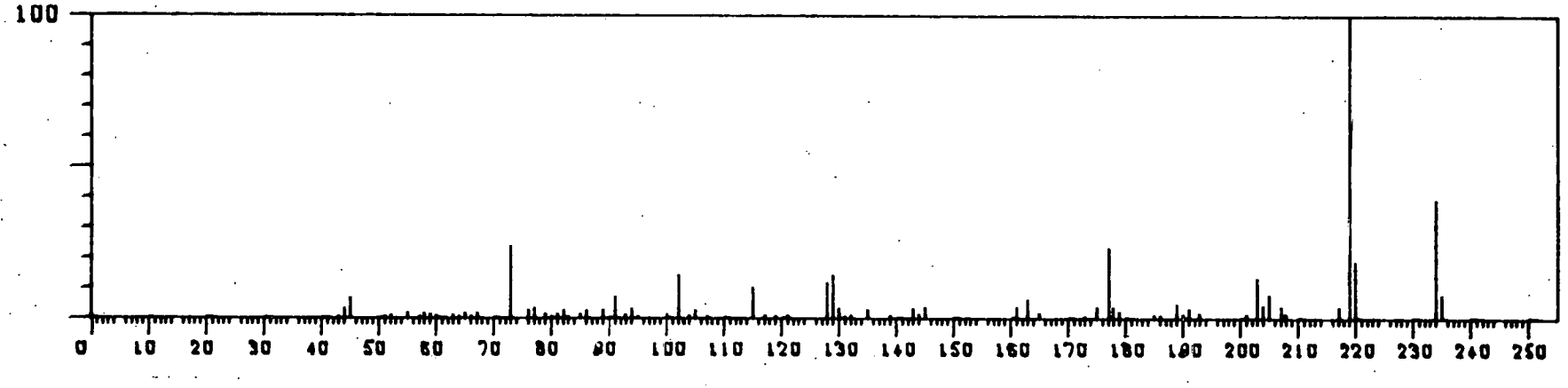
C_3-Hydroxystyrene, TMS ether

Retention Time 69.0



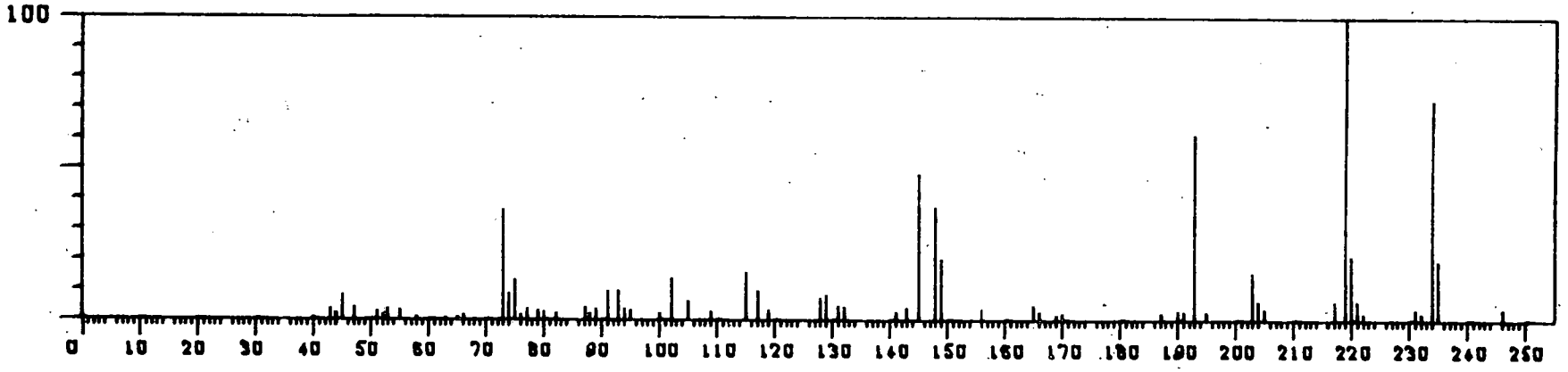
C_2-Hydroxystyrene, TMS ether

Retention Time 69.2



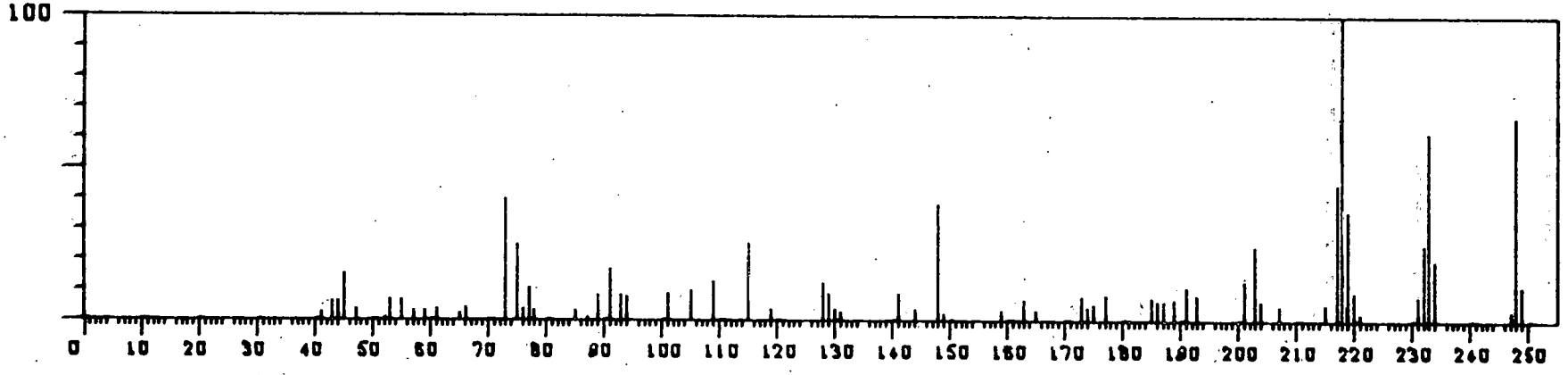
C_3-Hydroxystyrene, TMS ether

Retention Time 70.1



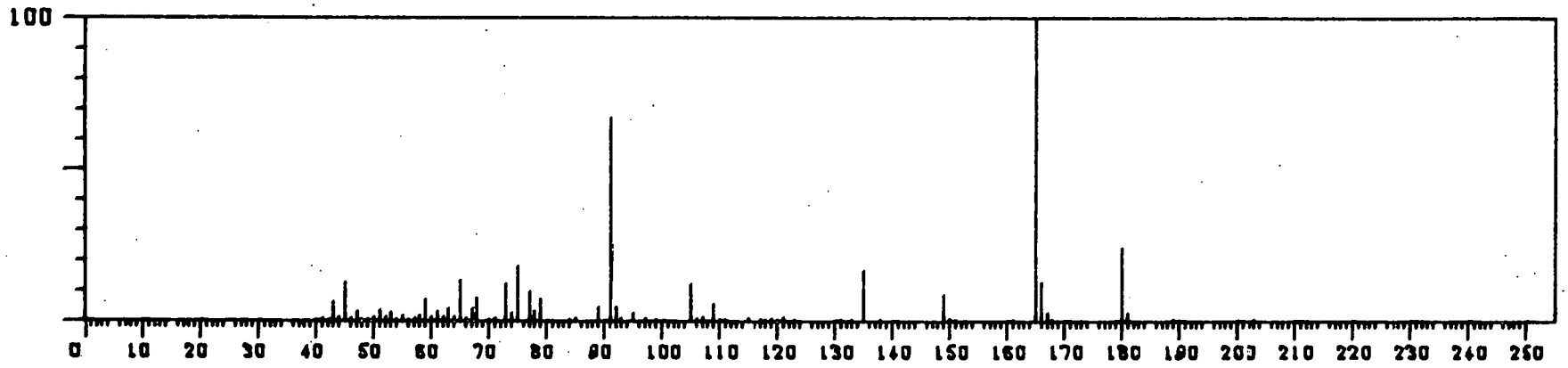
C_3-Hydroxystyrene, TMS ether

Retention Time 74.5



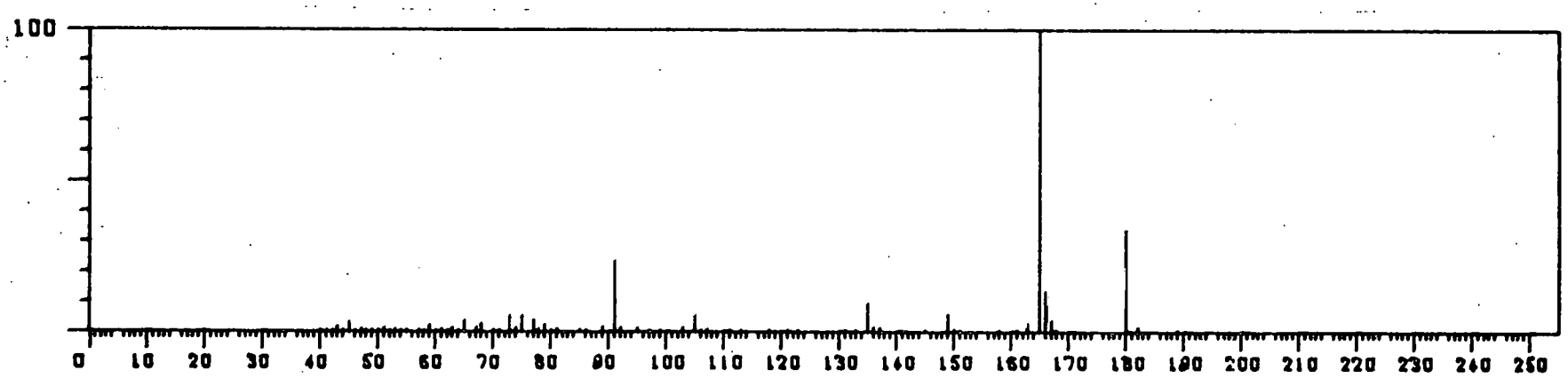
C_4-Hydroxystyrene, TMS ether

Retention Time 76.2



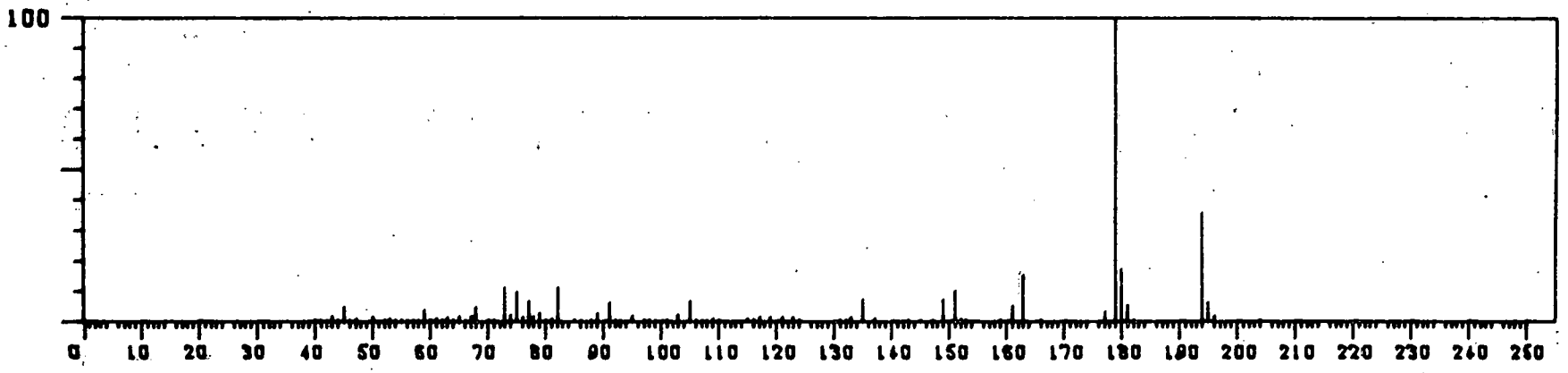
Cresol, TMS ether

Retention Time 46.6



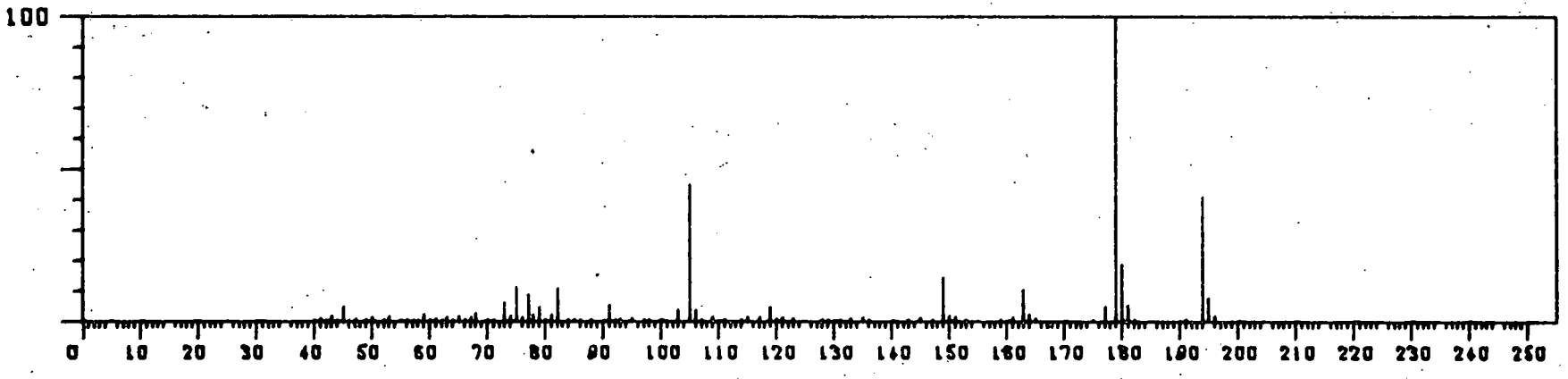
Cresol, TMS ether

Retention Time 47.1



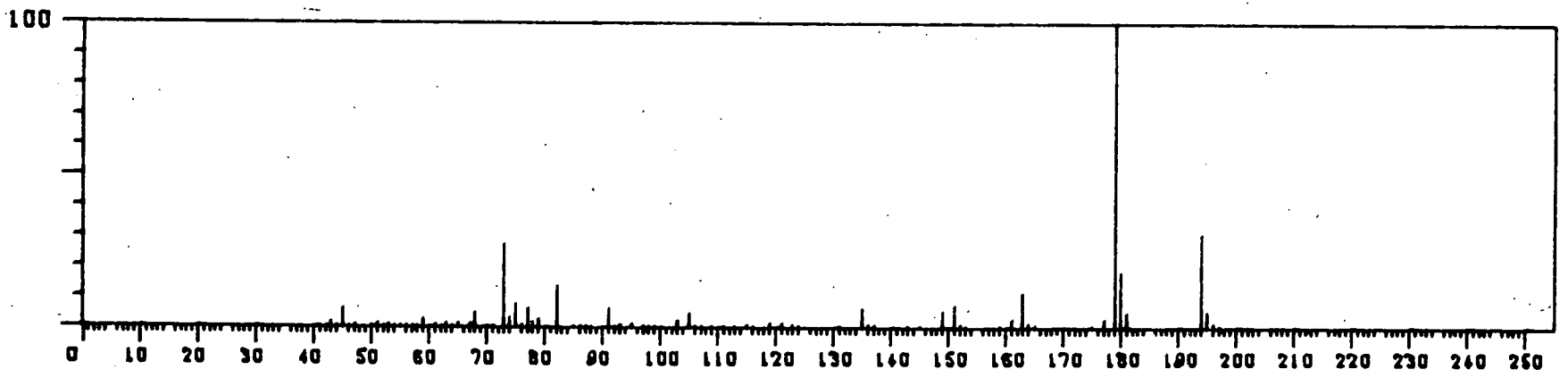
C_2-Phenol, TMS ether

Retention Time 51.5



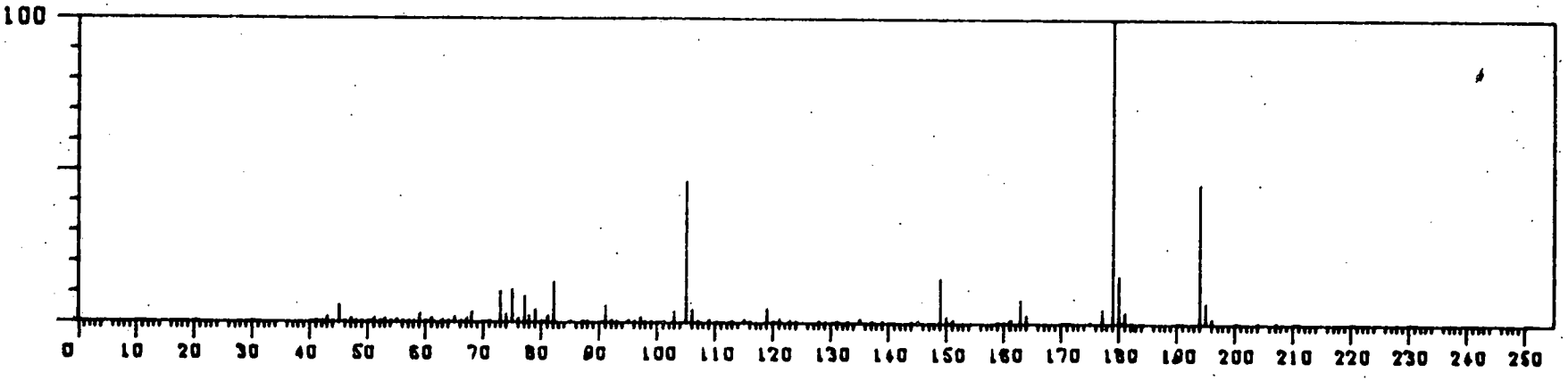
C_2-Phenol, TMS ether

Retention Time 51.9



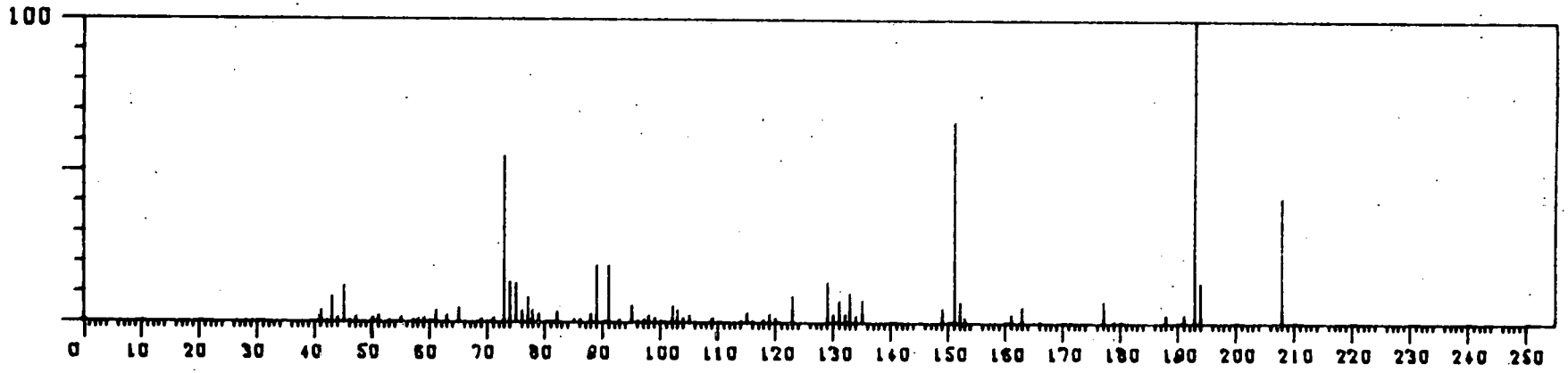
C_2-Phenol, TMS ether

Retention Time 52.6



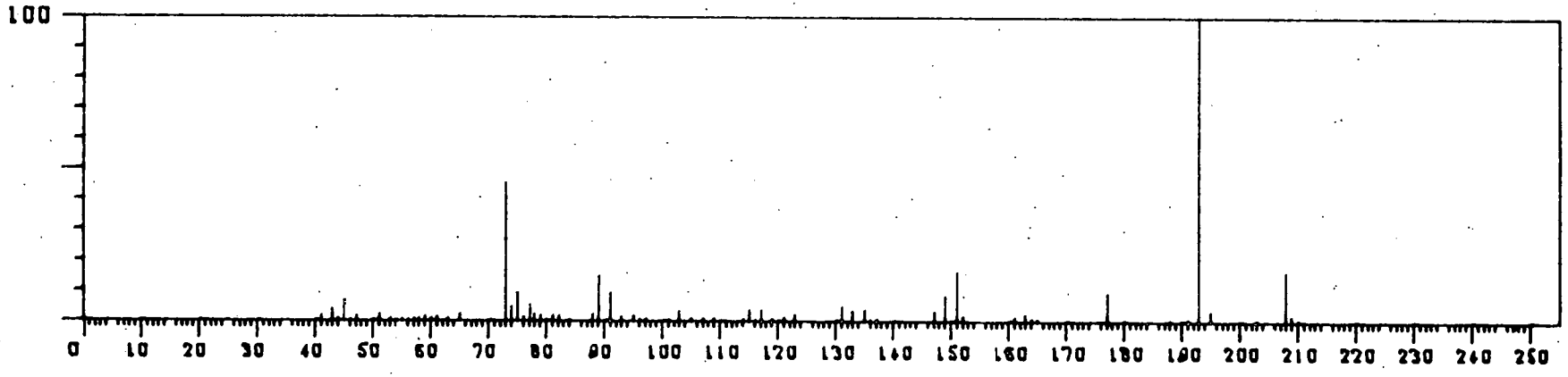
C_2-Phenol, TMS ether

Retention Time 54.0



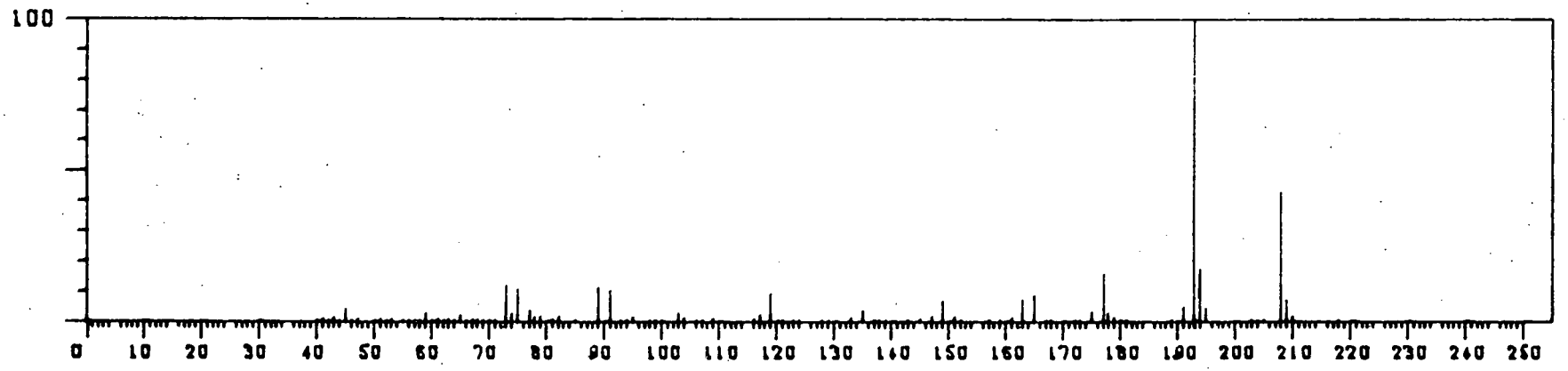
C_3-Phenol, TMS ether

Retention Time 54.5



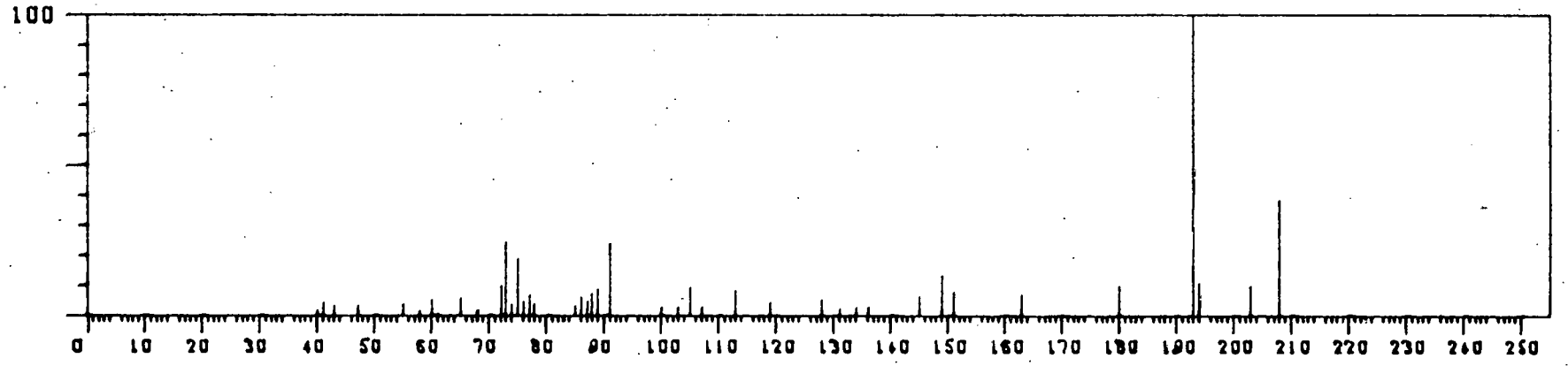
C_3-Phenol, TMS ether

Retention Time 55.9



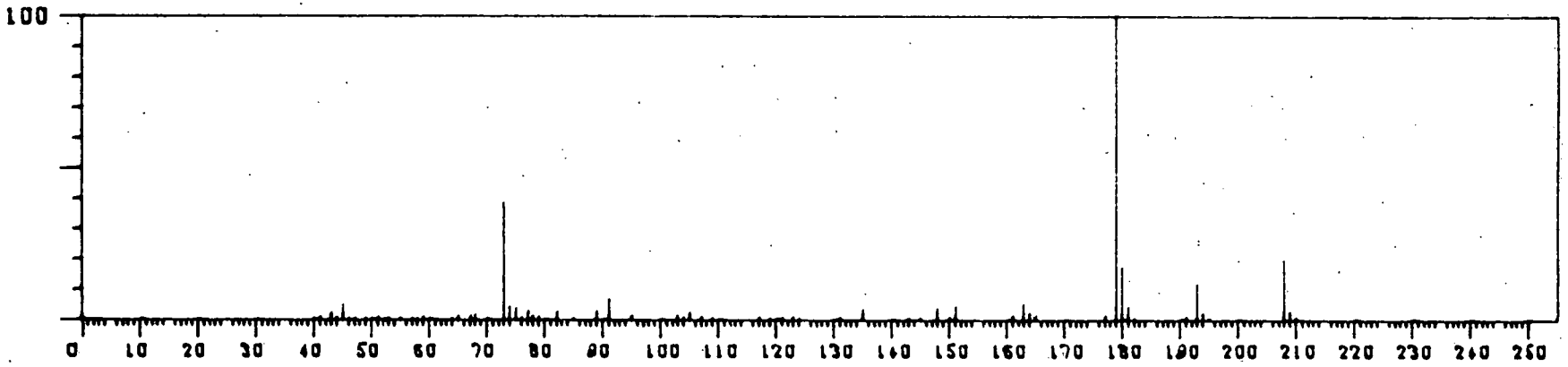
C_3-Phenol, TMS ether

Retention Time 56.9



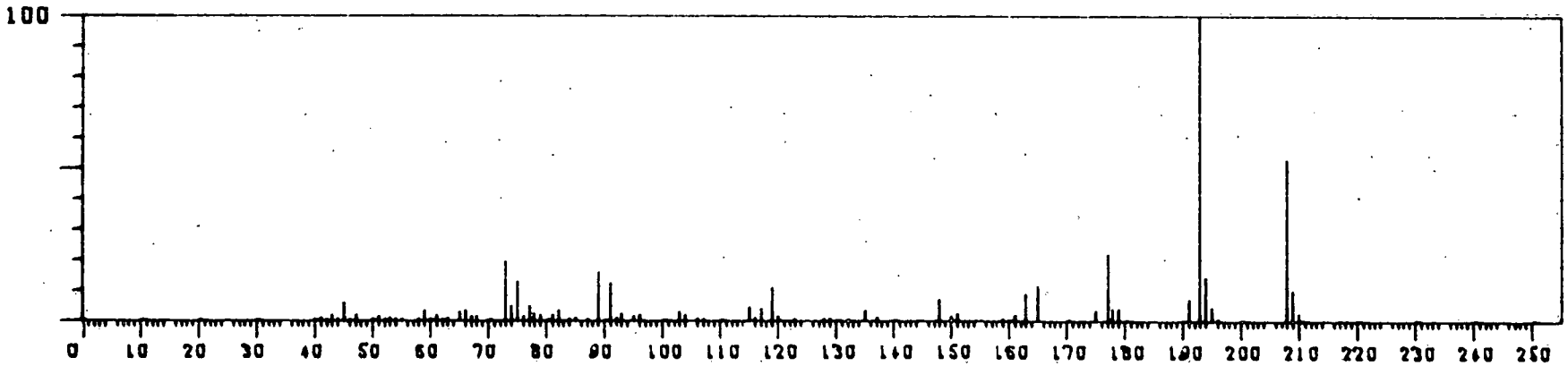
C_3-Phenol, TMS ether

Retention Time 57.1



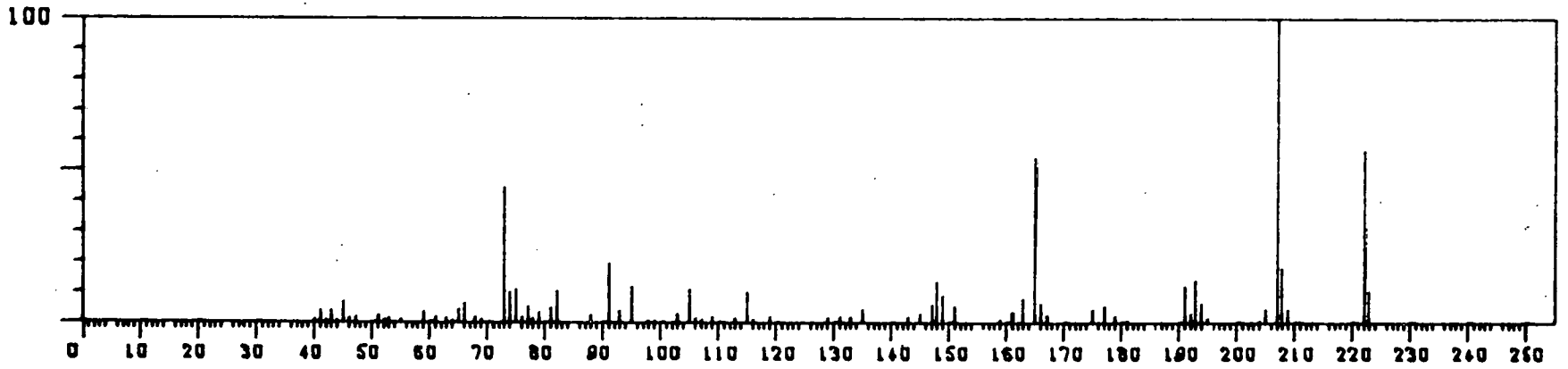
C_3-Phenol, TMS ether

Retention Time 58.1



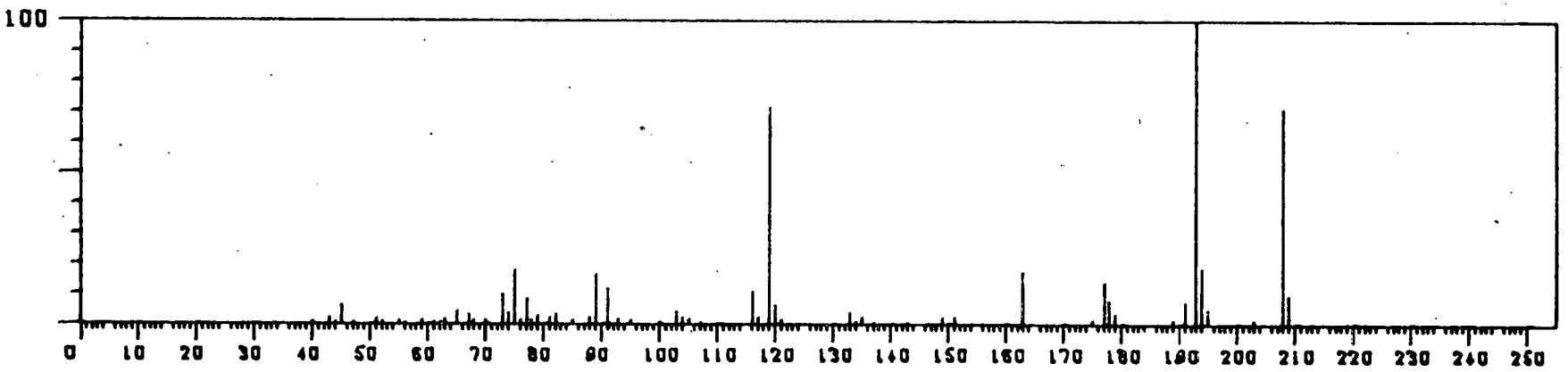
C_3-Phenol, TMS ether

Retention Time 58.5



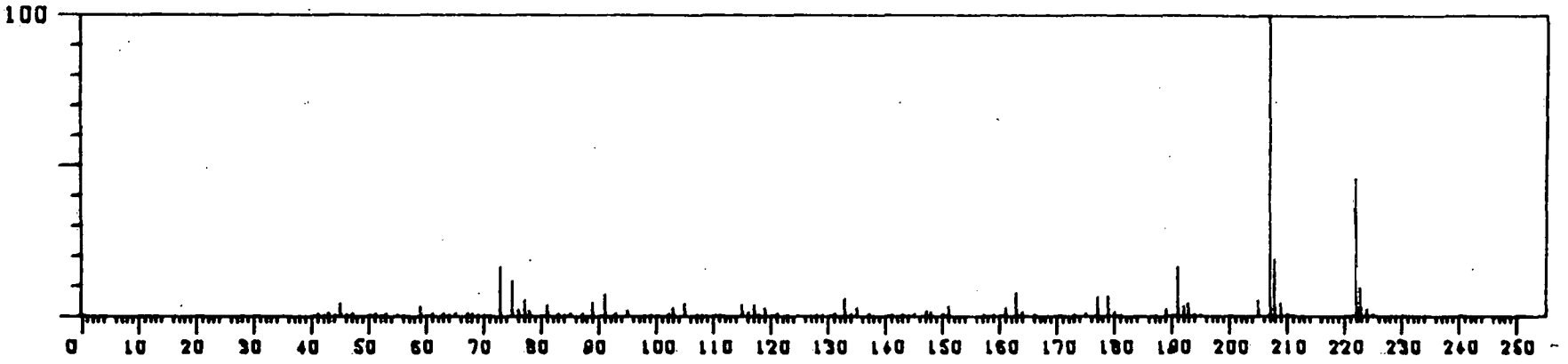
C_4-Phenol, TMS ether

Retention Time 59.6



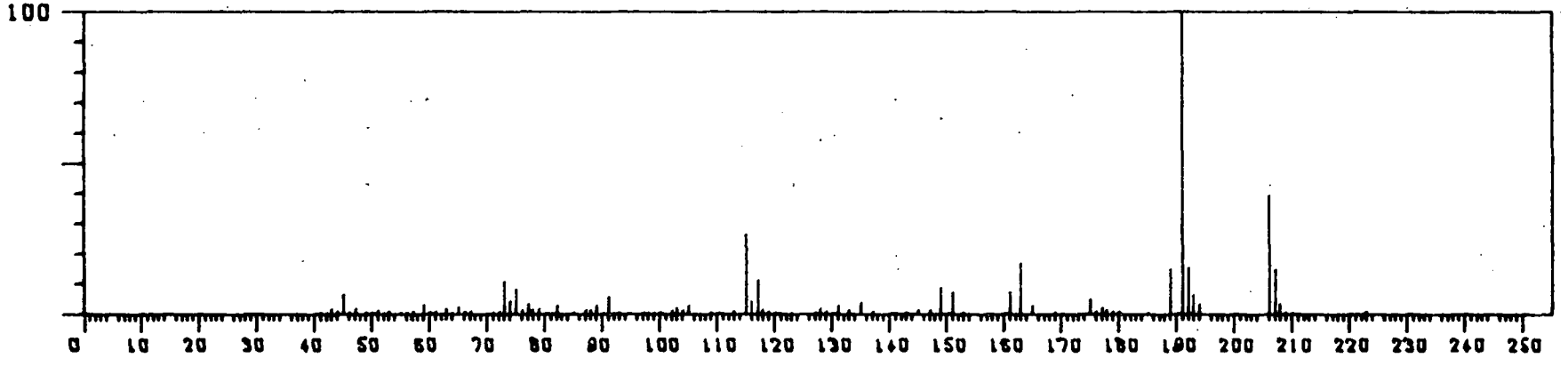
C_3-Phenol, TMS ether

Retention Time 61.0



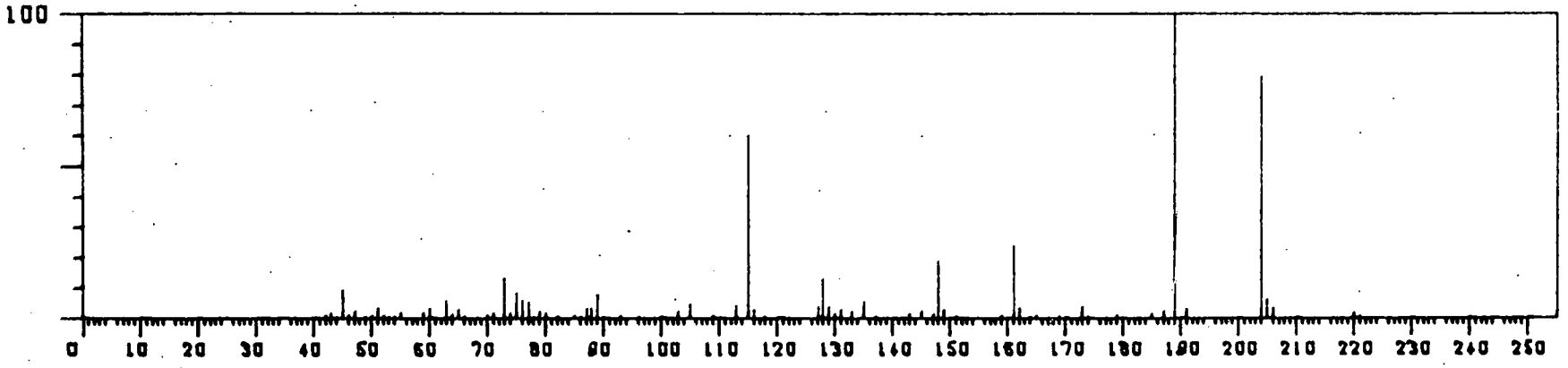
C_4-Phenol, TMS ether

Retention Time 61.3



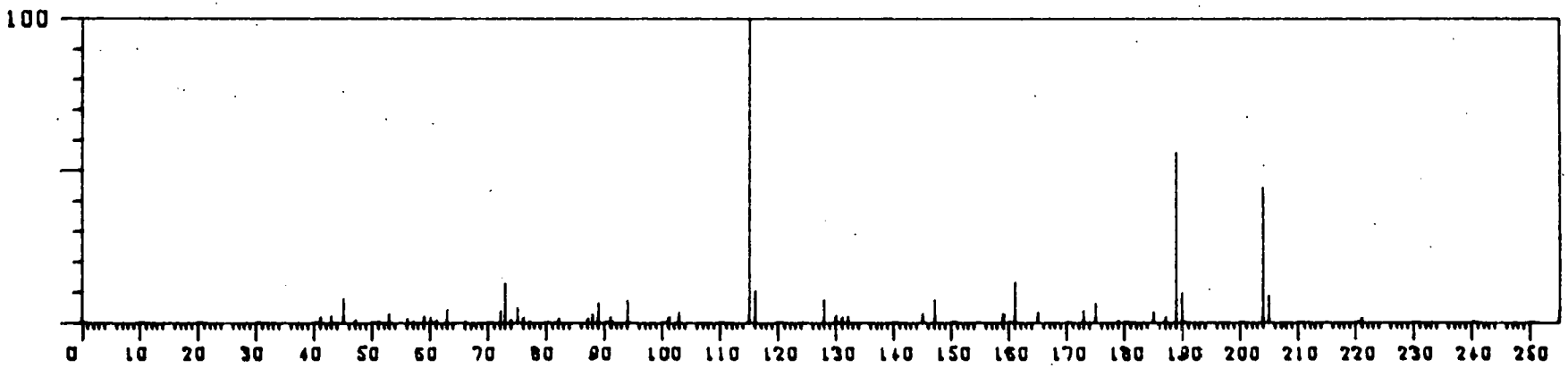
C_1-Hydroxystyrene, TMS ether

Retention Time 61.7



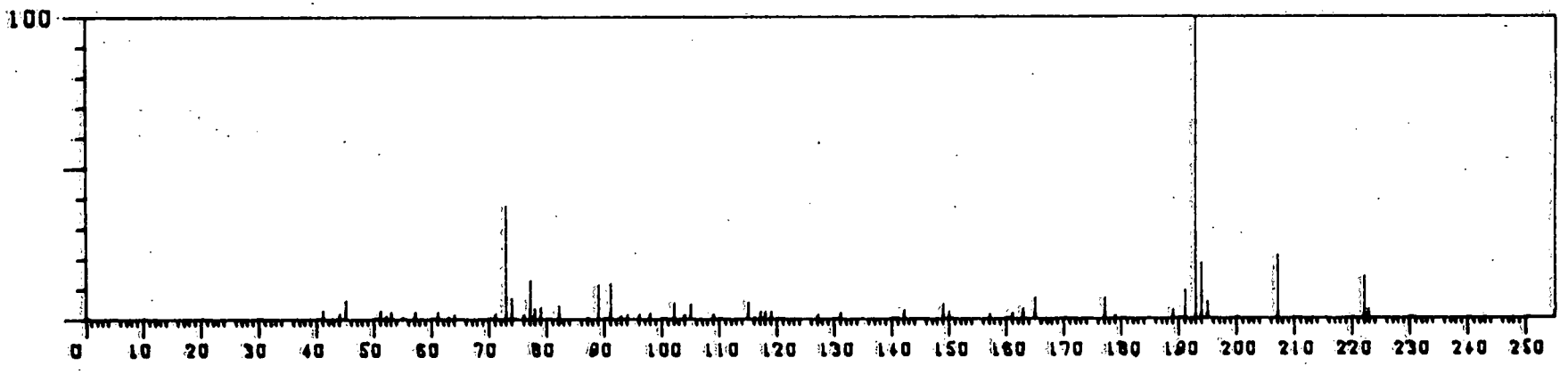
Hydroxyindene, TMS ether

Retention Time 62.2



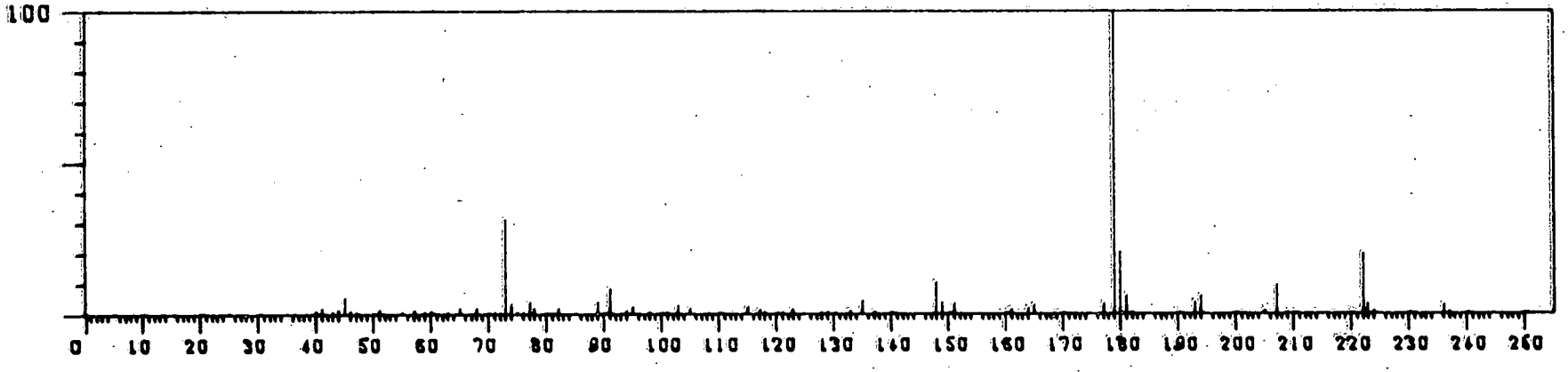
Hydroxyindene, TMS ether

Retention Time 62.7



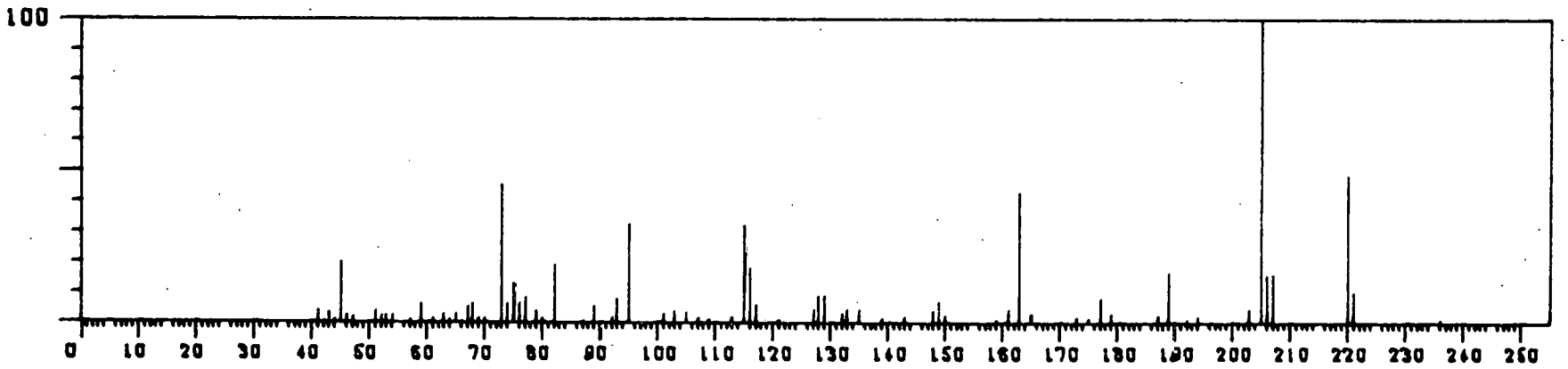
C_4-Phenol, TMS ether

Retention Time 64.2



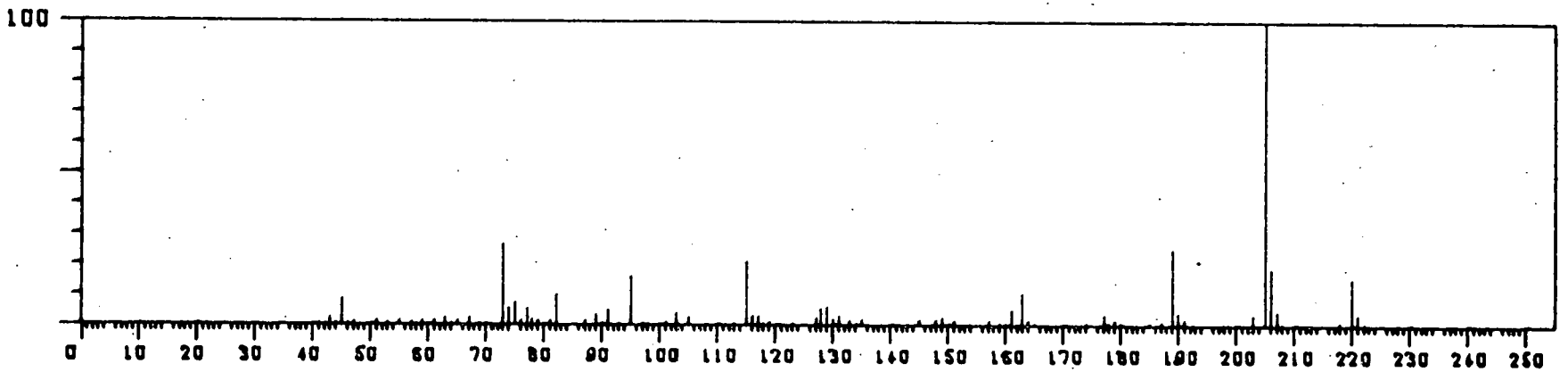
C4-Phenol, TMS ether

Retention Time 64.5



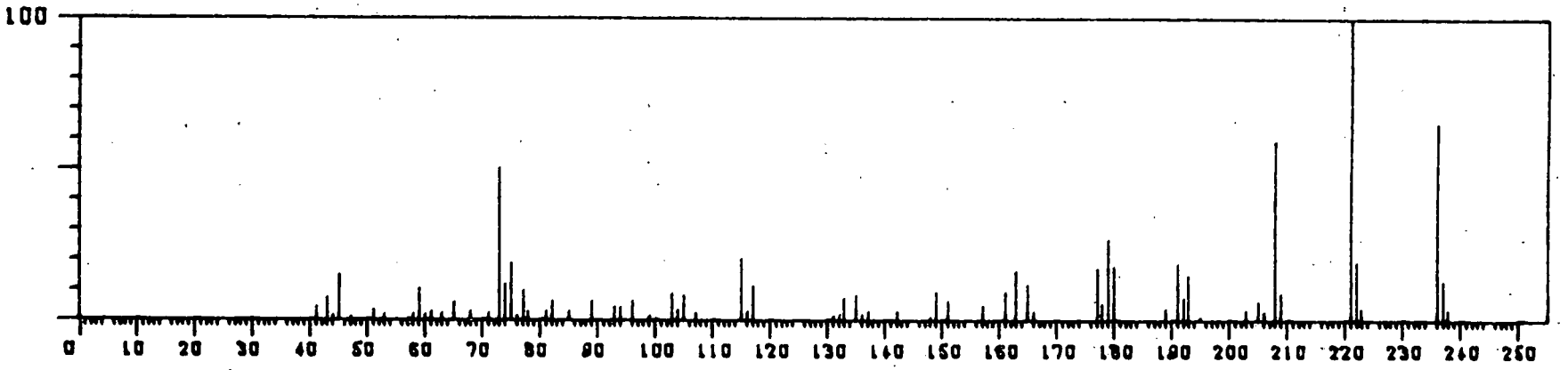
C_2-Hydroxystyrene, TMS ether

Retention Time 65.4



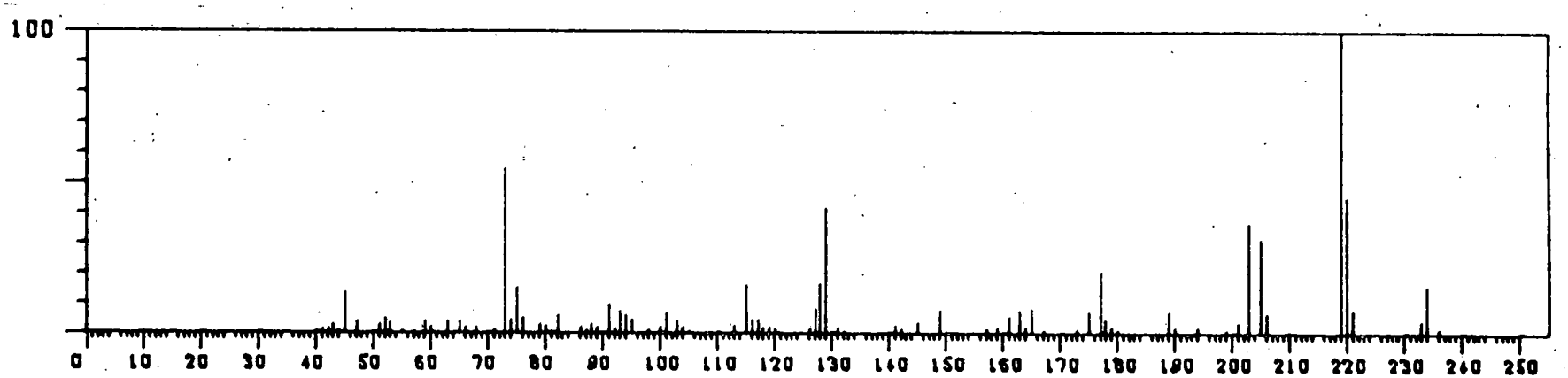
C_2-Hydroxystyrene, TMS ether

Retention Time 66.0



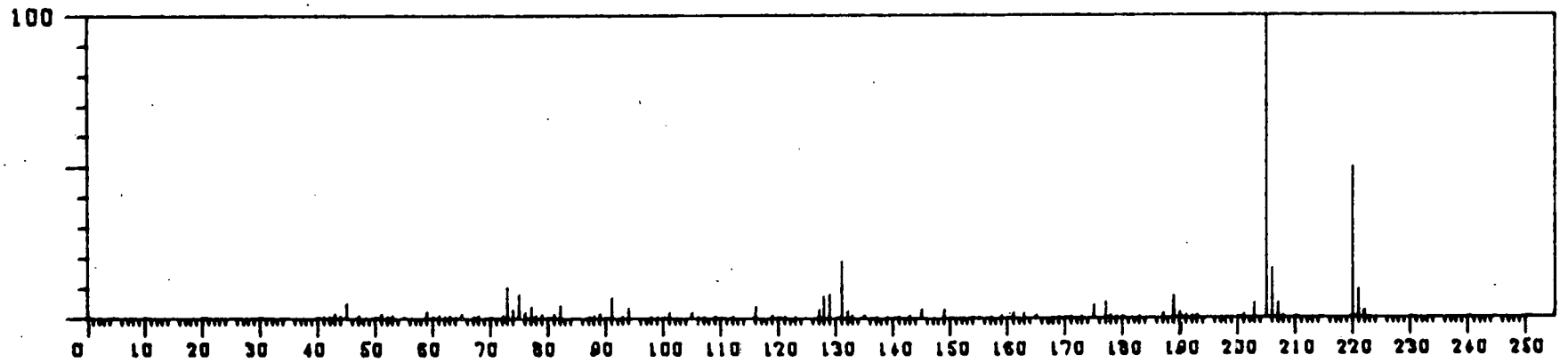
C_5-Phenol, TMS ether

Retention Time 66.3



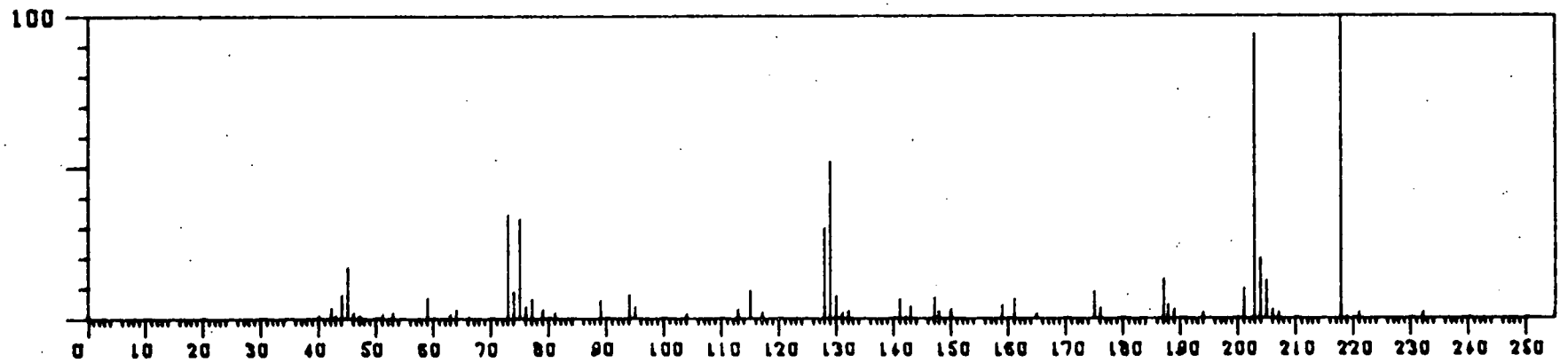
C_3-Hydroxystyrene, TMS ether

Retention Time 67.3



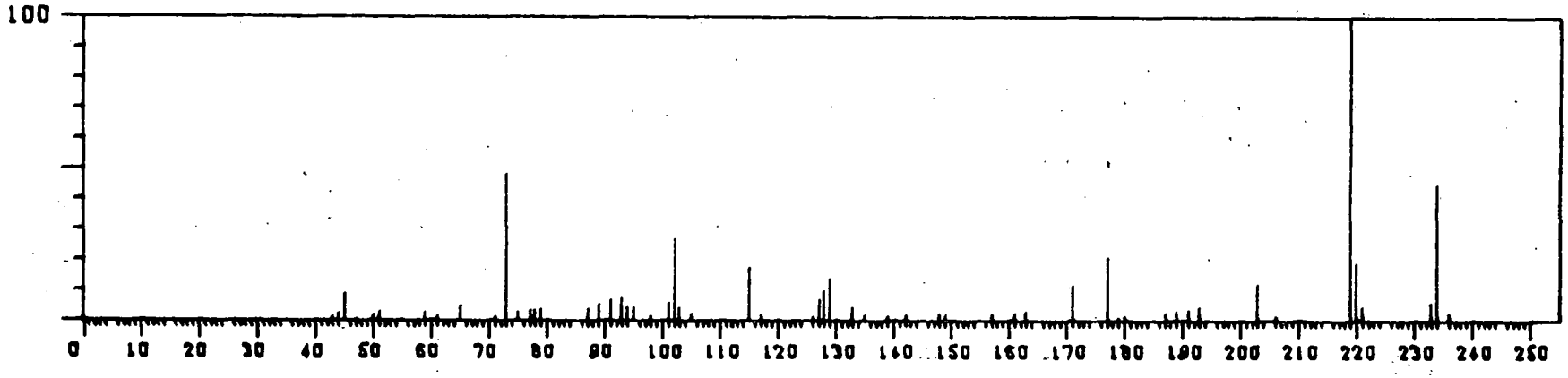
C_2-Hydroxystyrene, TMS ether

Retention Time 69.4



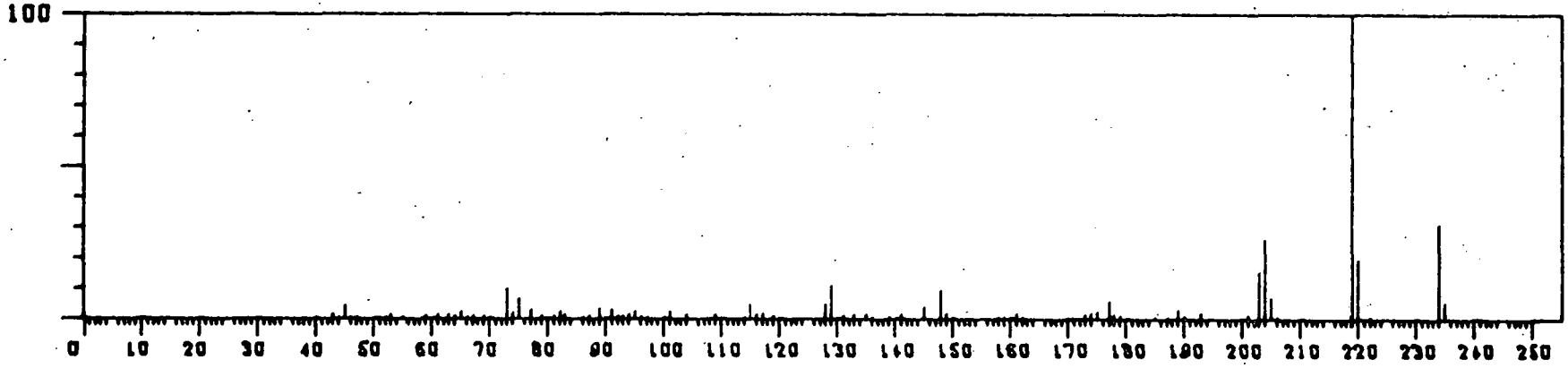
Methyl hydroxyindene, TMS ether

Retention Time 69.8



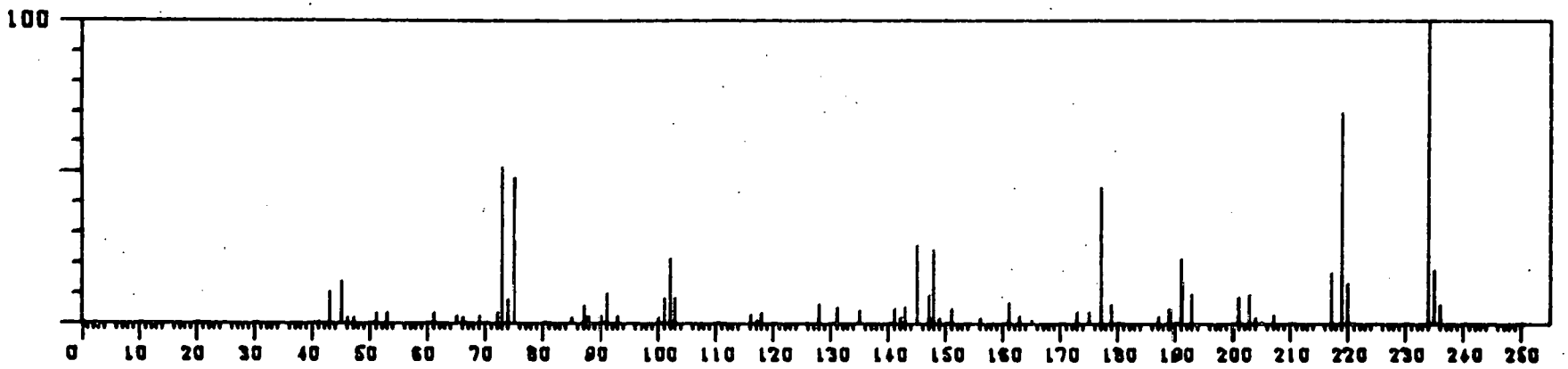
C_3-Hydroxystyrene, TMS ether

Retention Time 71.0



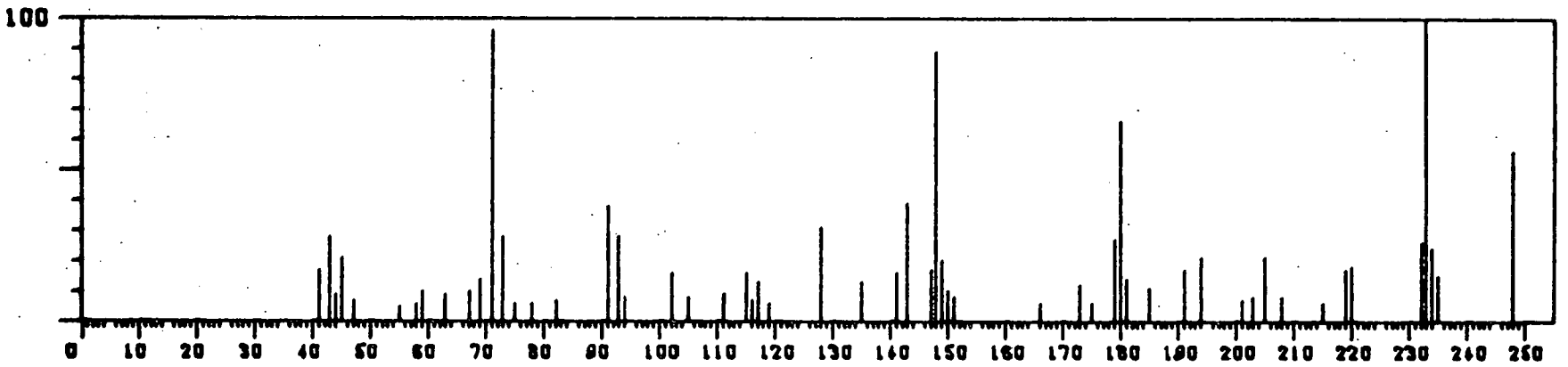
C_3-Hydroxystyrene, TMS ether

Retention Time 71.2



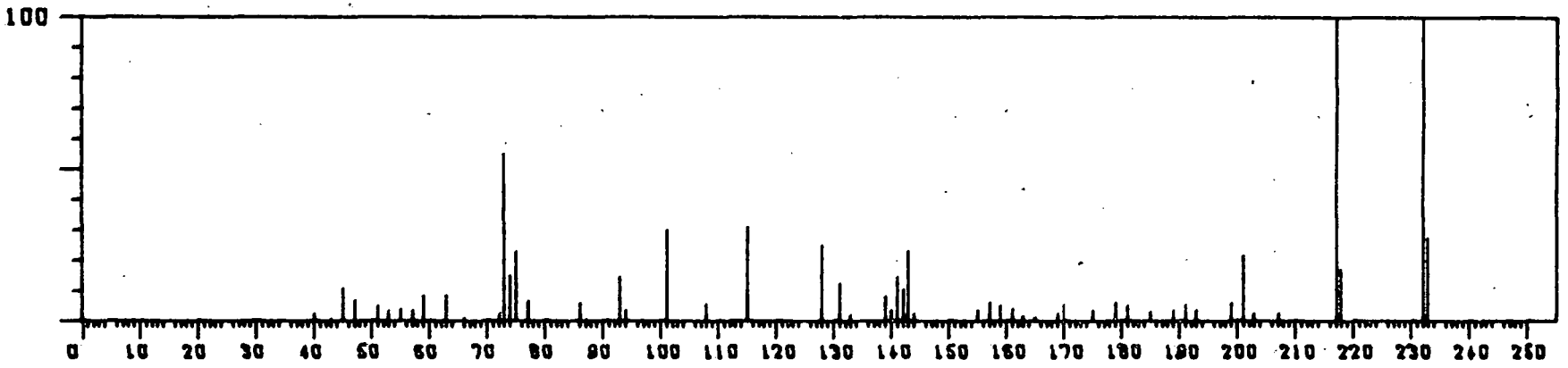
C_3-Hydroxystyrene, TMS ether

Retention Time 73.8



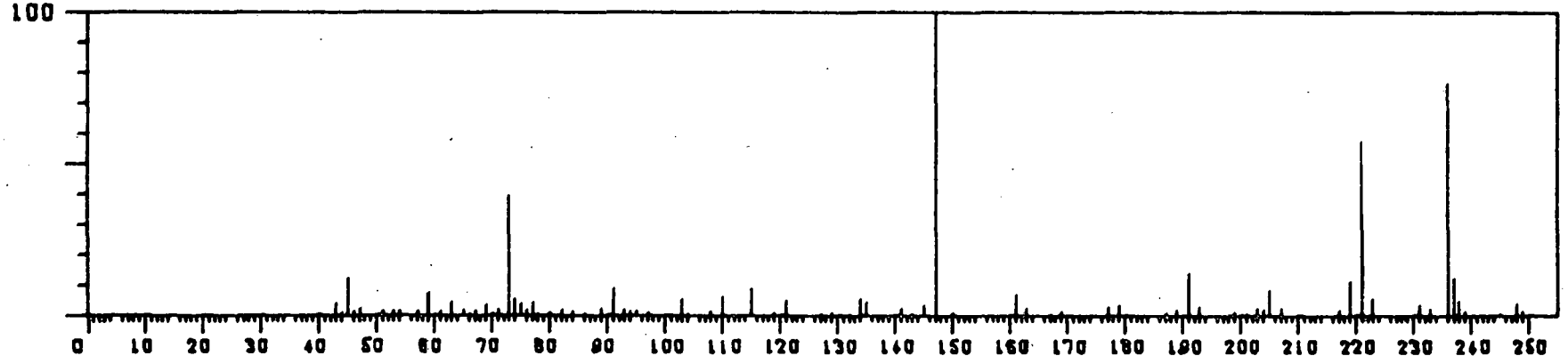
C_4-Hydroxystyrene, TMS ether

Retention Time 74.8



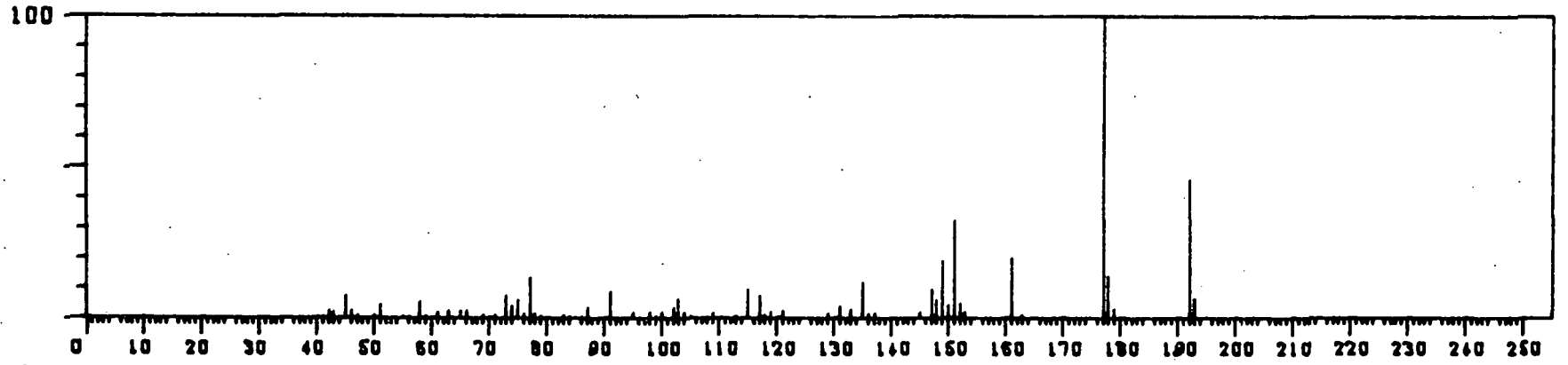
C_2-Hydroxyindene, TMS ether

Retention Time 76.9



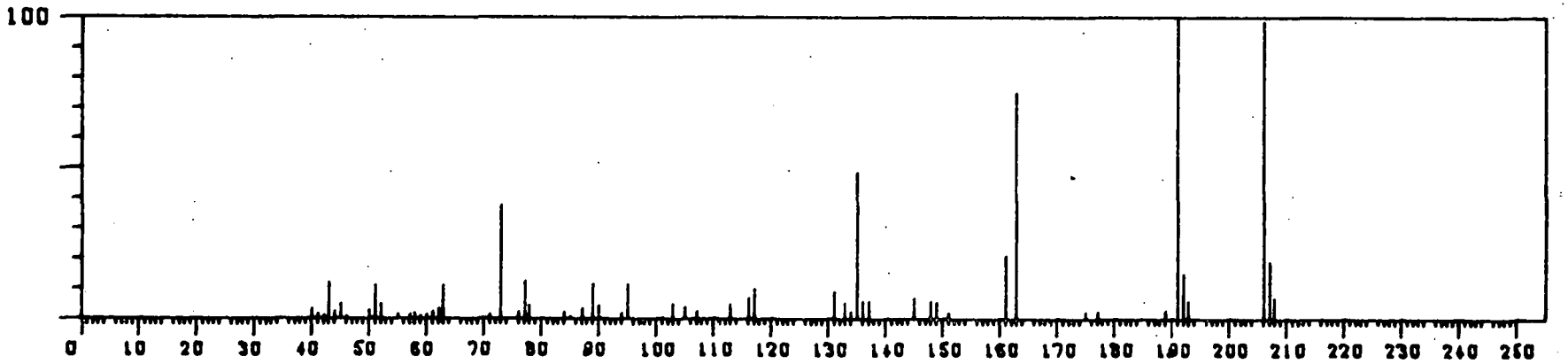
Methyl hydroxybenzothiophene, TMS ether

Retention Time 78.5



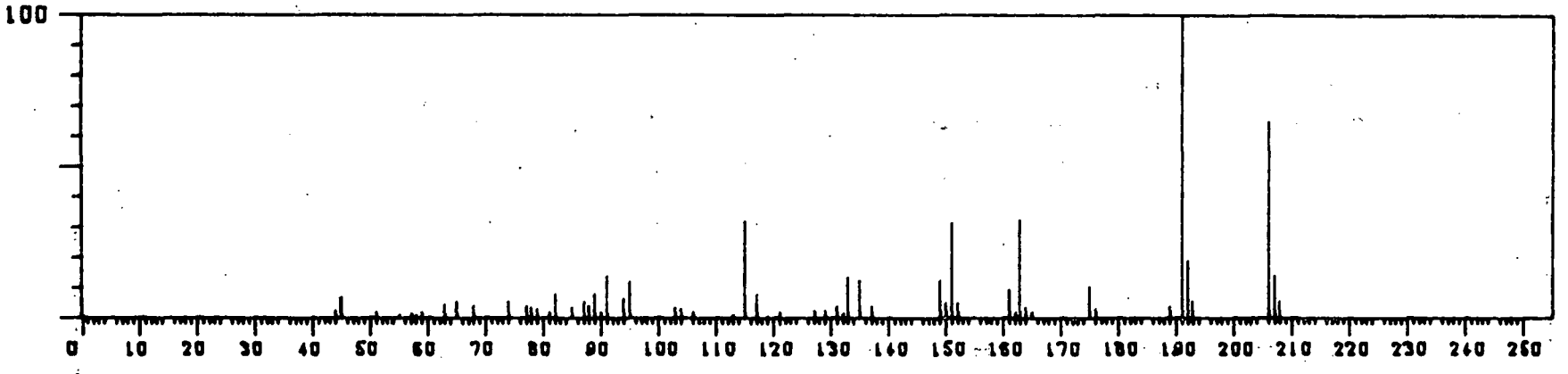
Hydroxystyrene, TMS ether

Retention Time 53.0



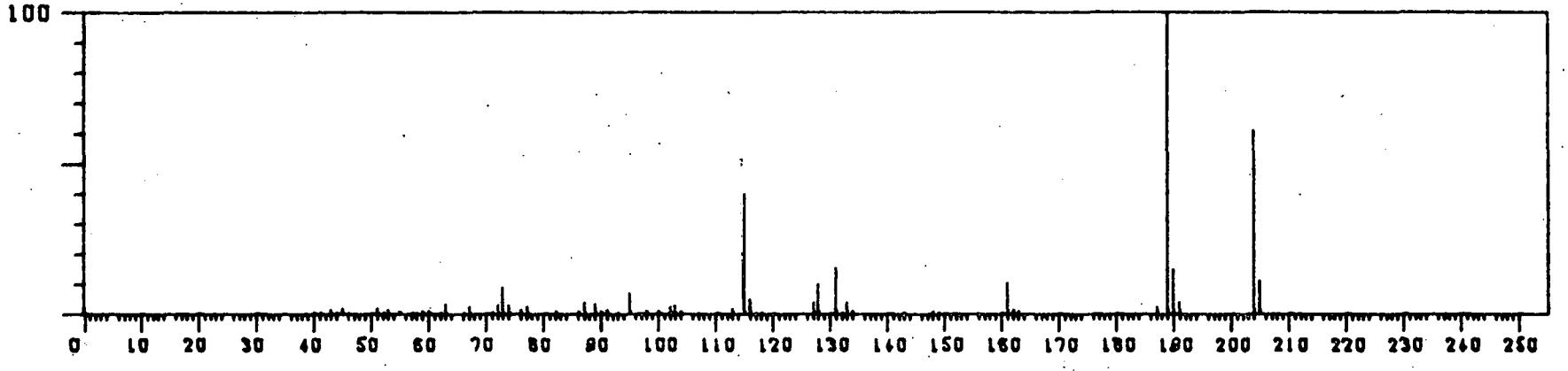
C_1-Hydroxystyrene, TMS ether

Retention Time 59.7



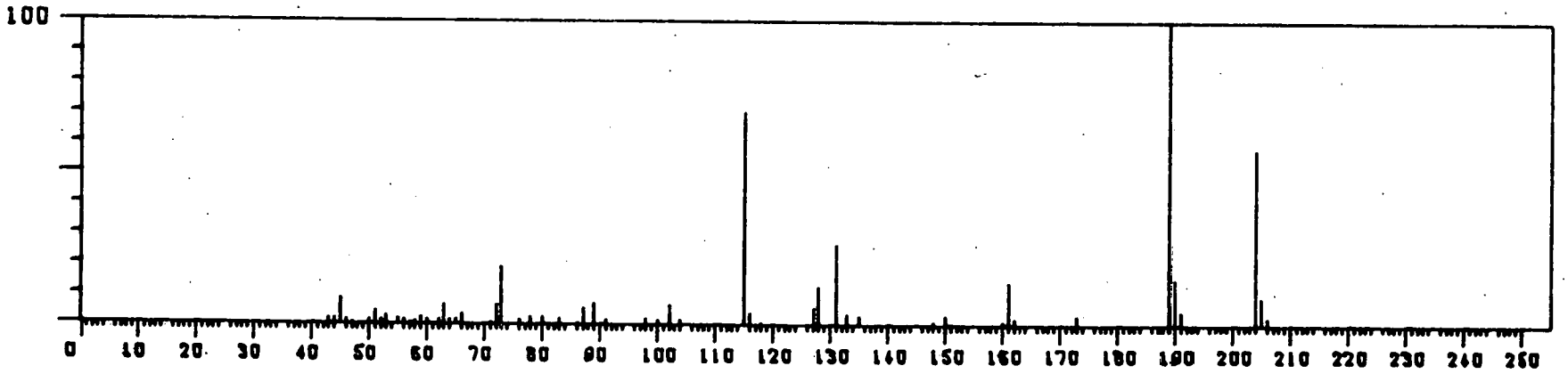
C_1-Hydroxystyrene, TMS ether

Retention Time 61.8



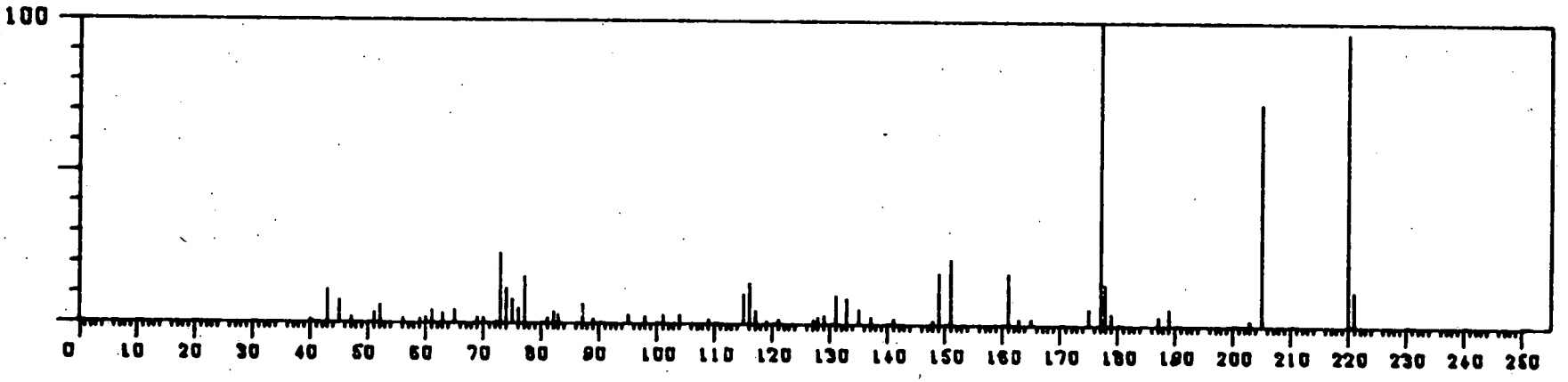
Hydroxyindene, TMS ether

Retention Time 64.1



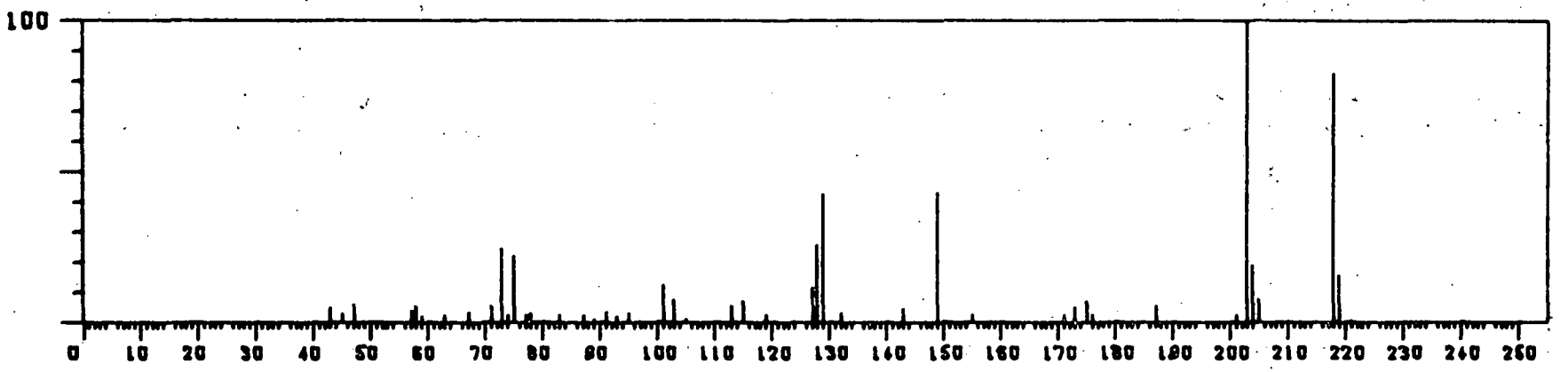
Hydroxyindene, TMS ether

Retention Time 64.3



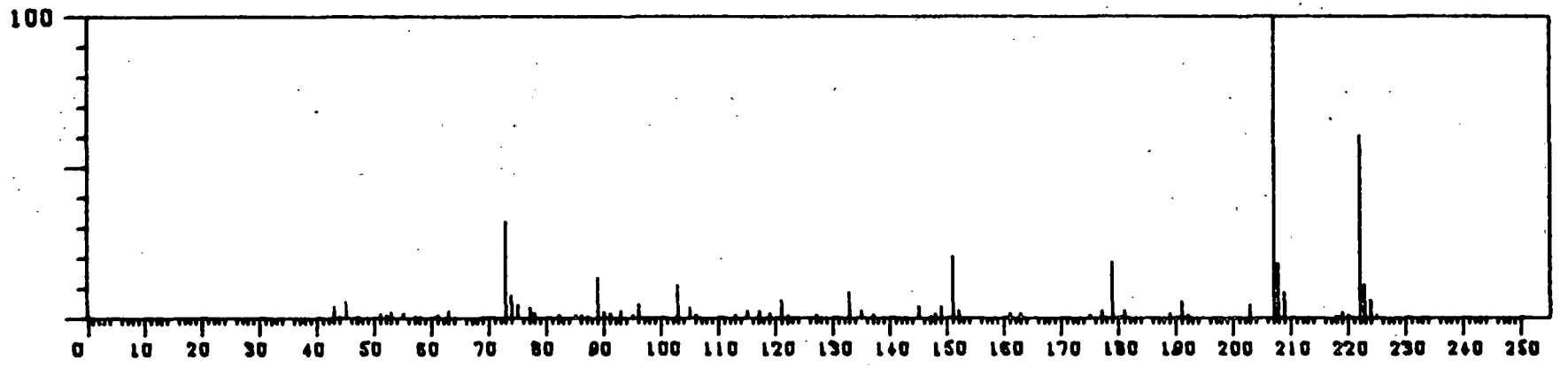
C_2-Hydroxystyrene, TMS ether

Retention Time 66.2



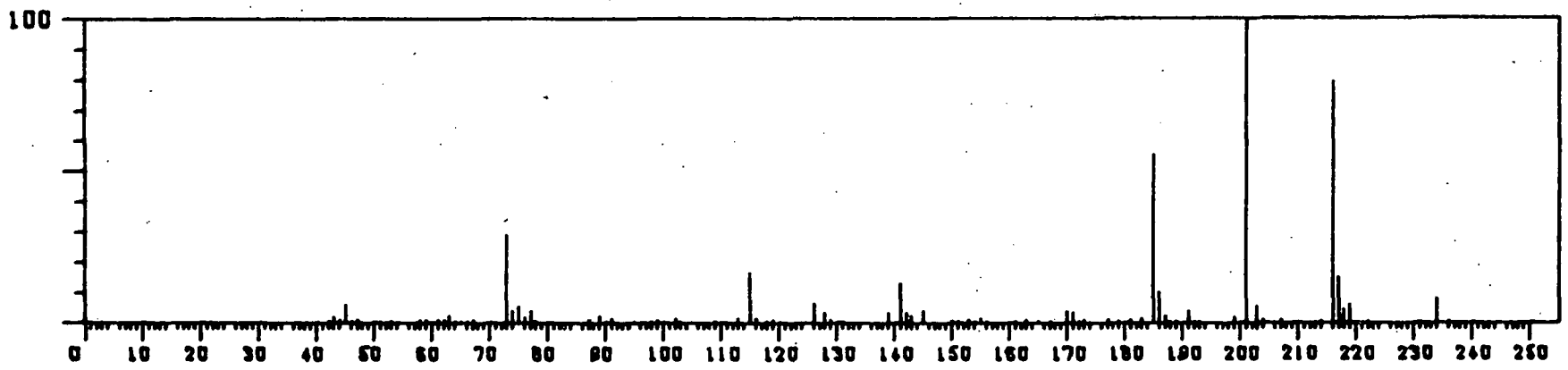
Methyl hydroxyindene, TMS ether

Retention Time 70.1



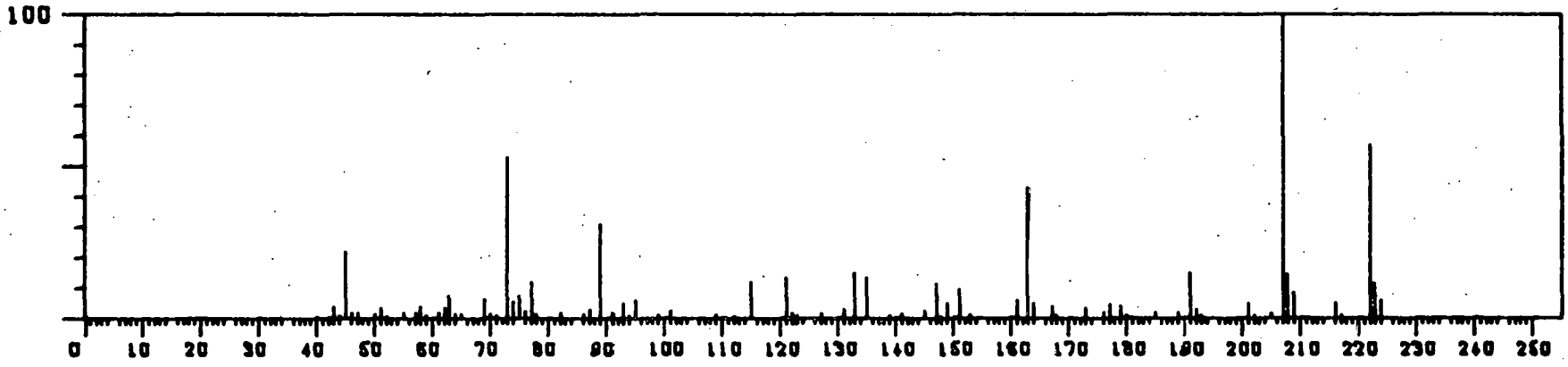
Hydroxybenzothiophene, TMS ether

Retention Time 71.1



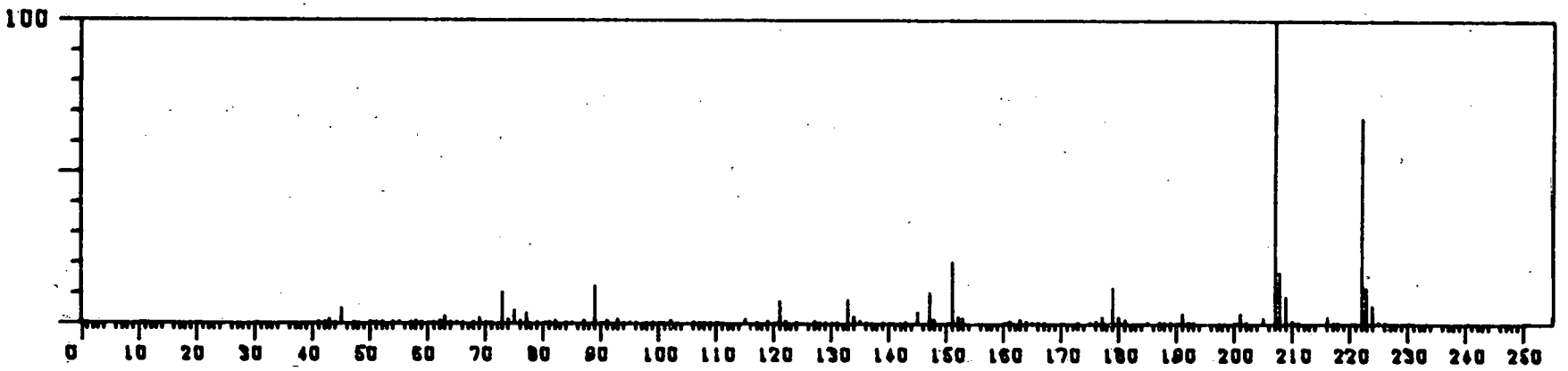
Naphthol, TMS ether

Retention Time 71.8



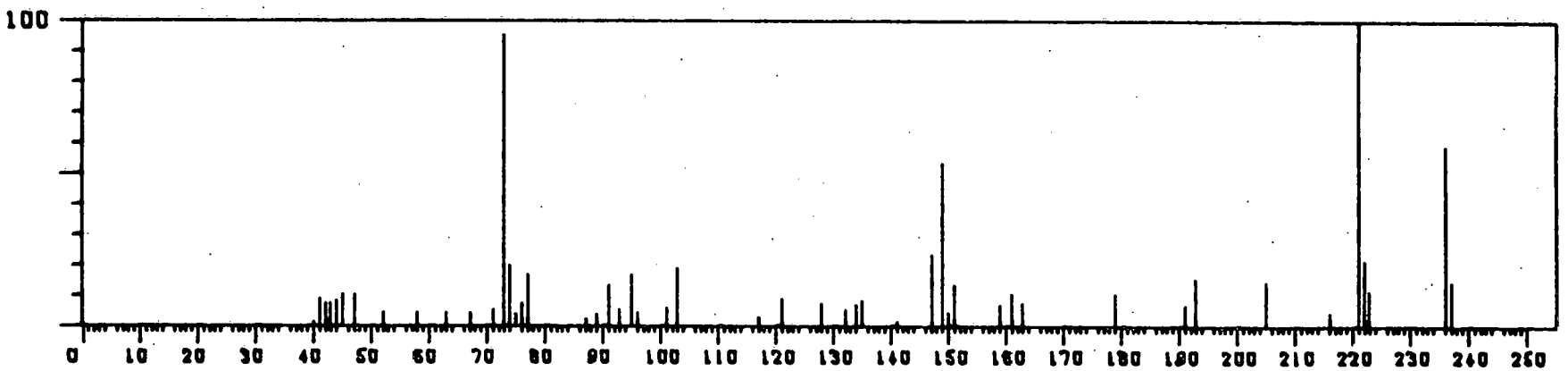
Hydroxybenzothiophene, TMS ether

Retention Time 72.2



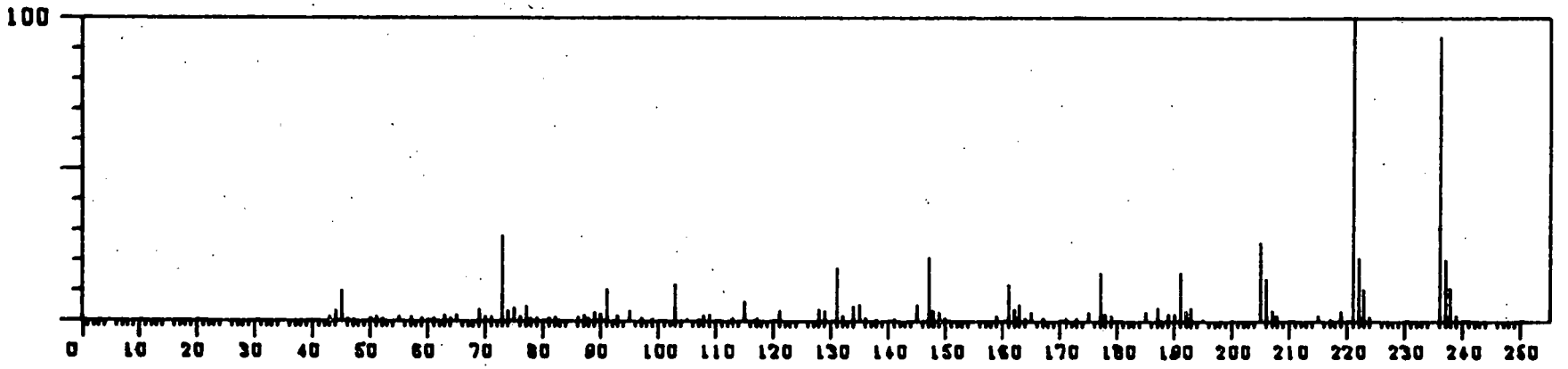
Hydroxybenzothiophene, TMS ether

Retention Time 74.0



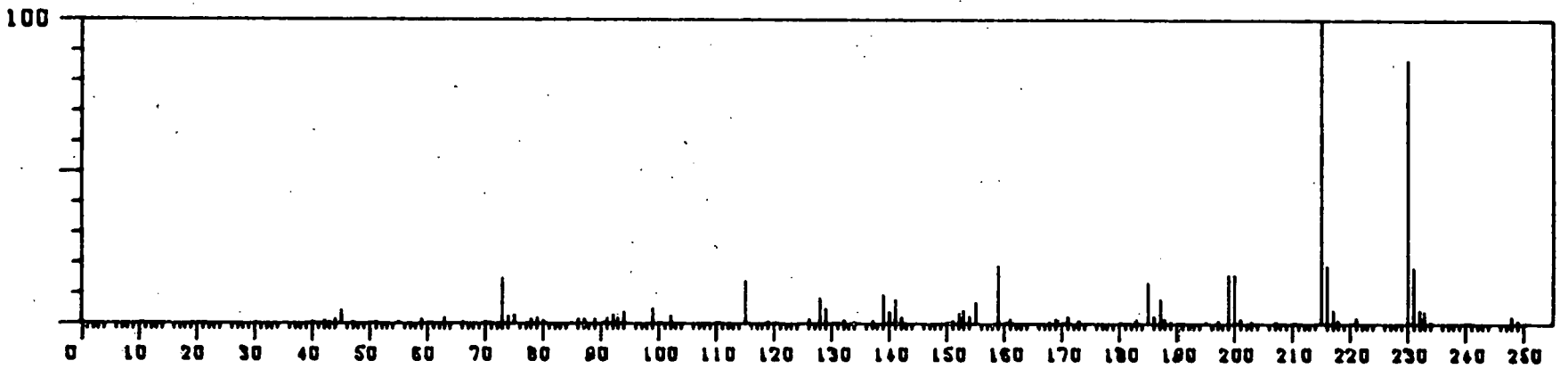
Methyl hydroxybenzothiophene, TMS ether

Retention Time 76.2



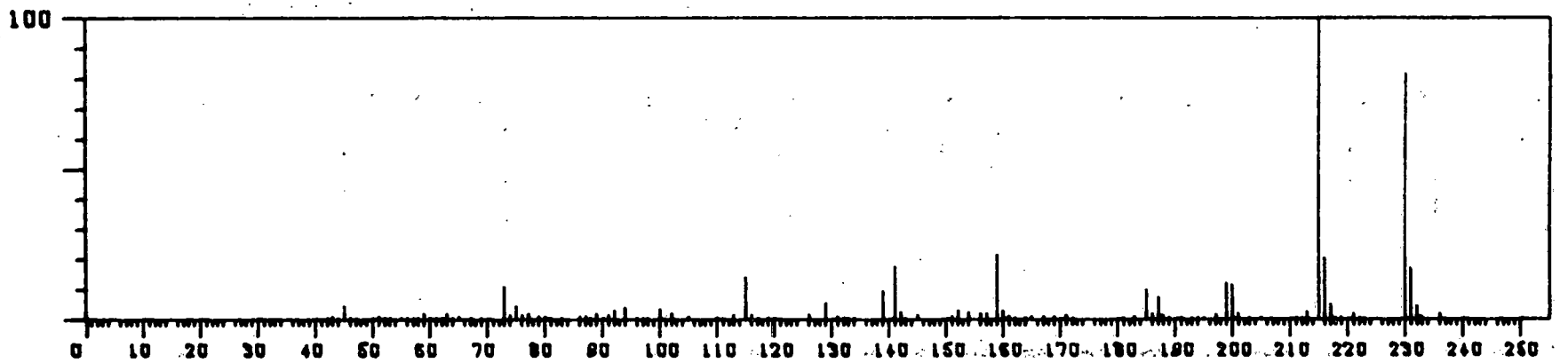
Methyl hydroxybenzothiophene, TMS ether

Retention Time 77.2



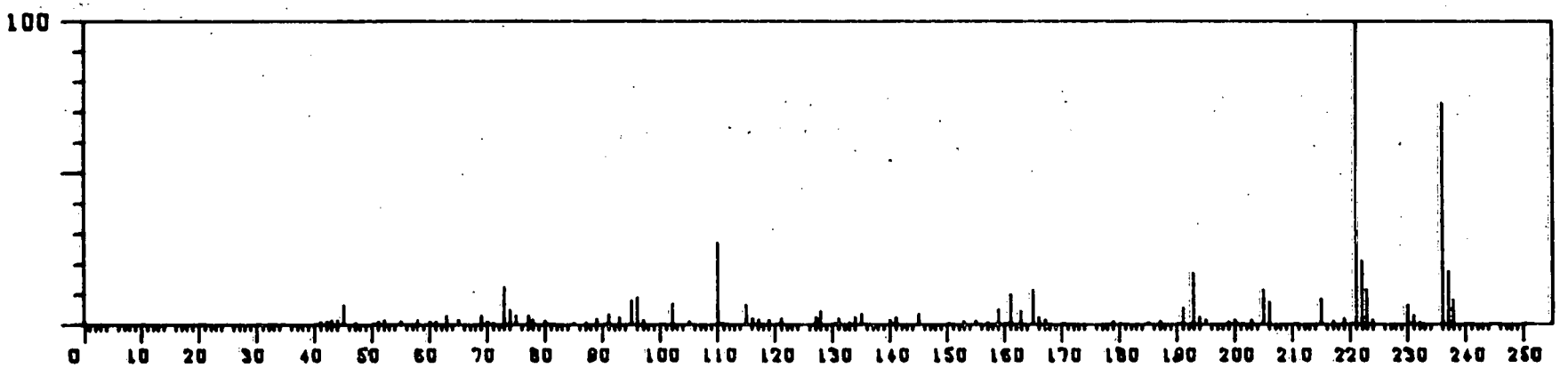
Methyl naphthol, TMS ether

Retention Time 79.3



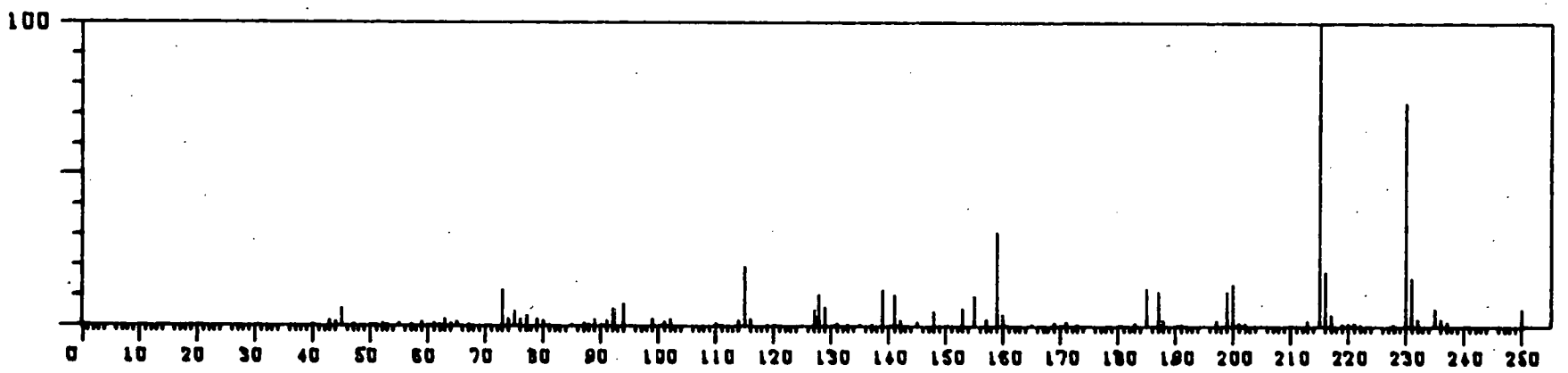
Methyl naphthol, TMS ether

Retention Time 80.0



Methyl hydroxybenzothiophene, TMS ether

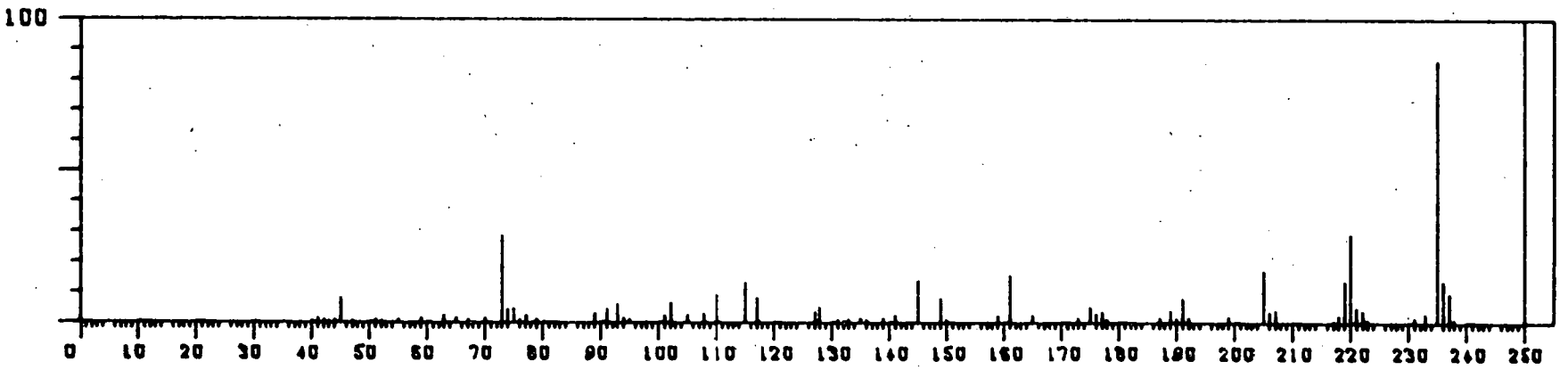
Retention Time 80.4



Methyl naphthol, TMS ether

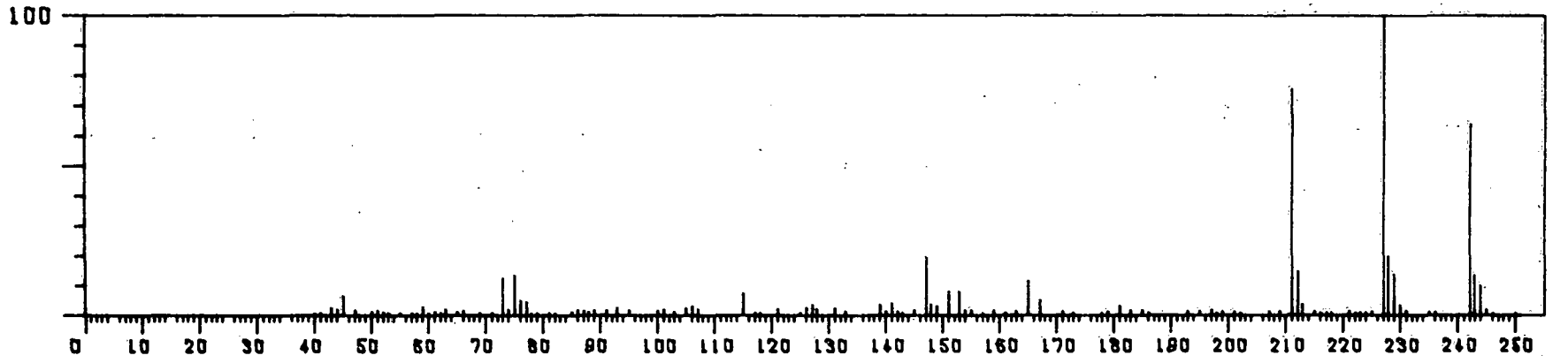
Retention Time 80.8

100



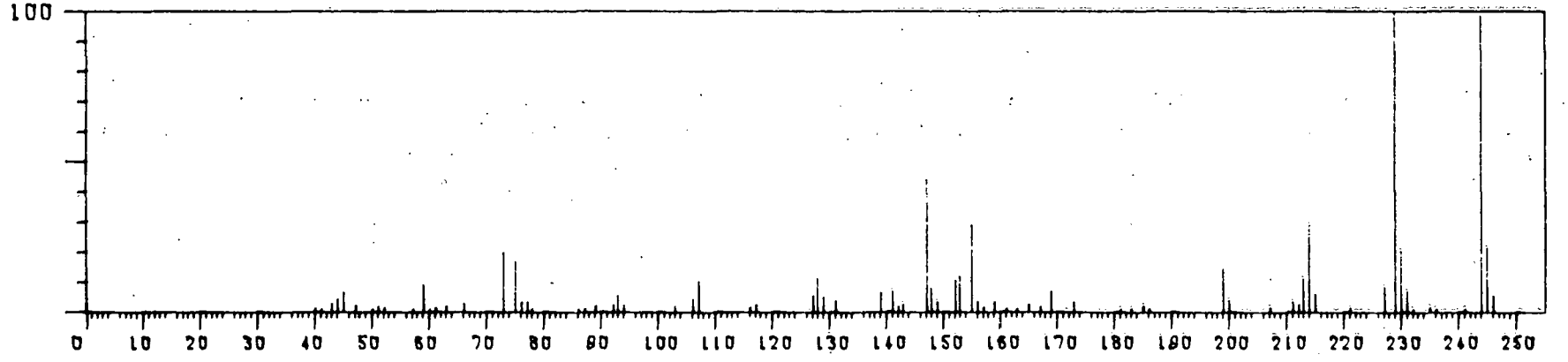
C_2-Hydroxybenzothiophene, TMS ether

Retention Time 81.8



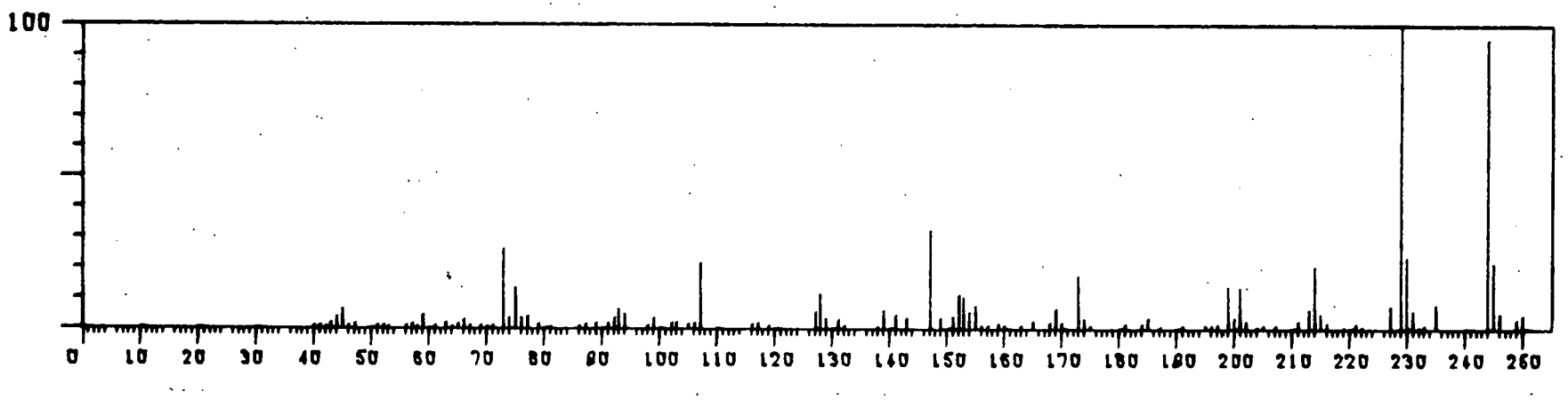
Hydroxybiphenyl, TMS ether

Retention Time 83.0



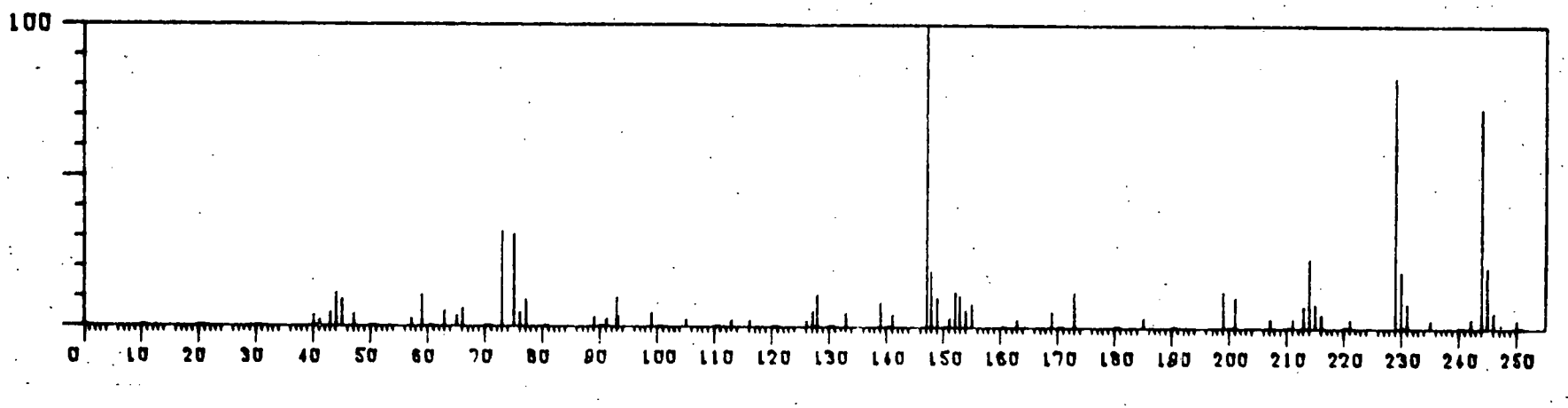
C_2-Naphthol, TMS ether

Retention Time 85.8



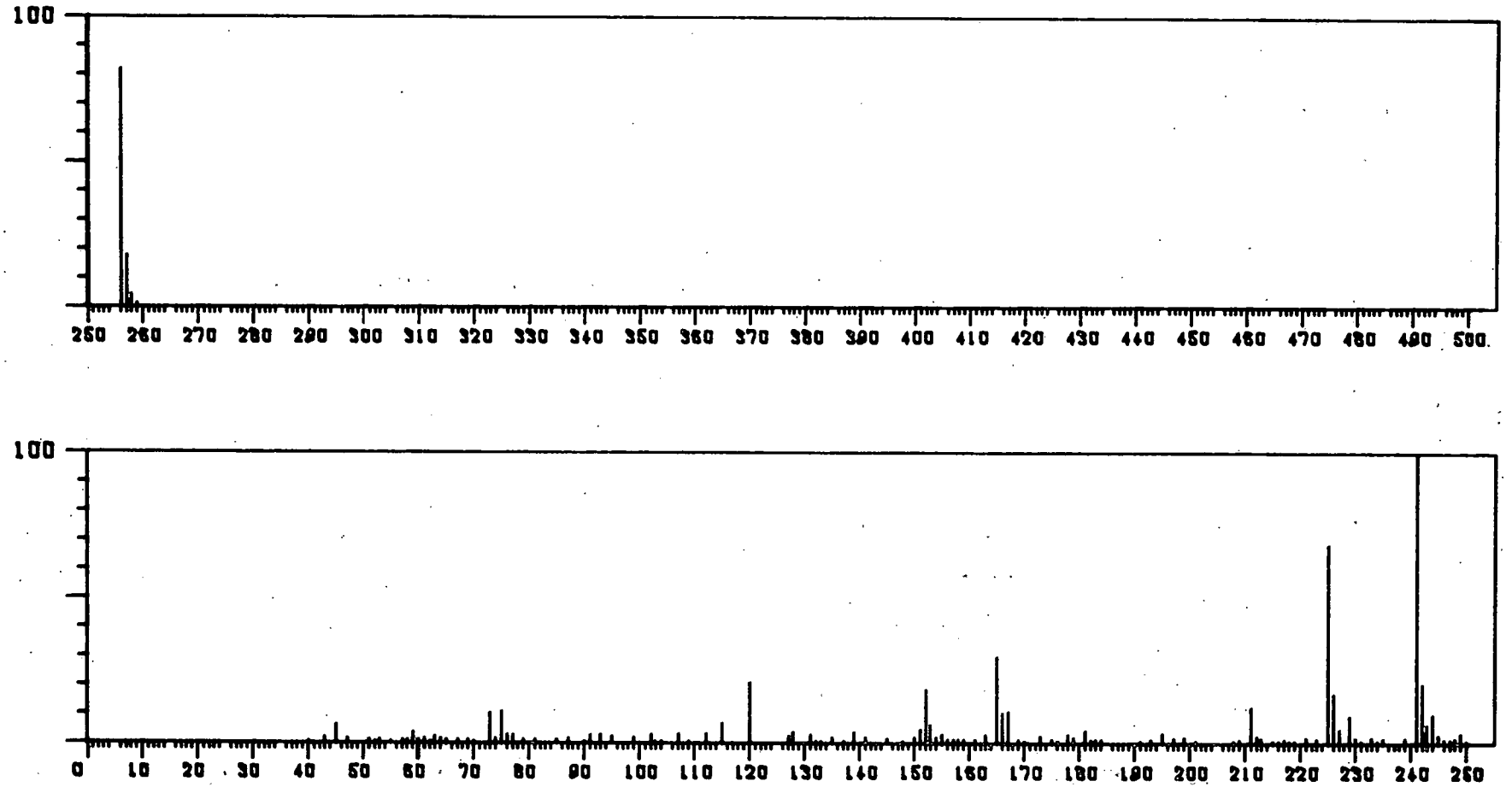
C_2-Naphthol, TMS ether

Retention Time 86.4



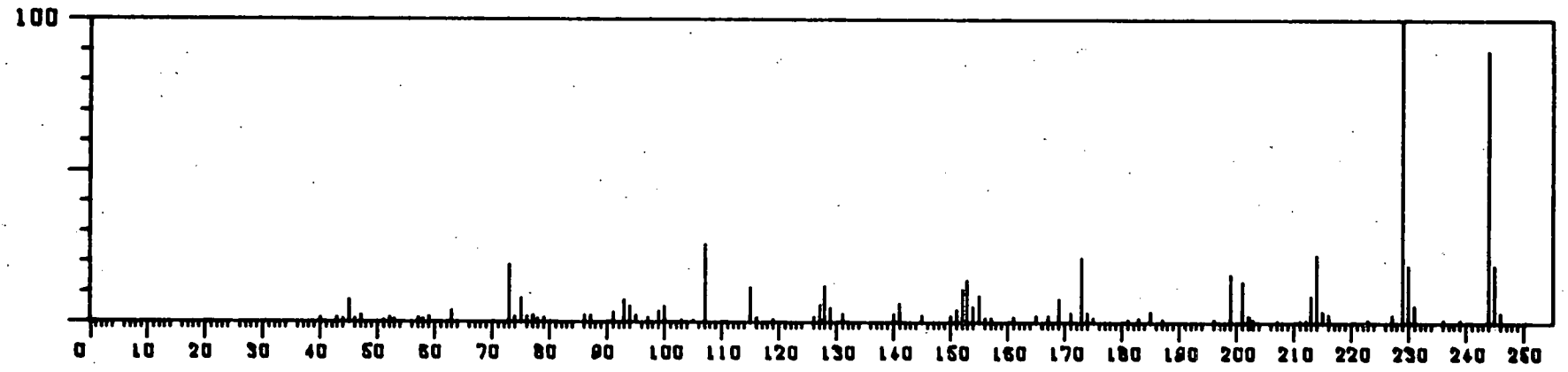
C_2-Naphthol, TMS ether

Retention Time 87.0



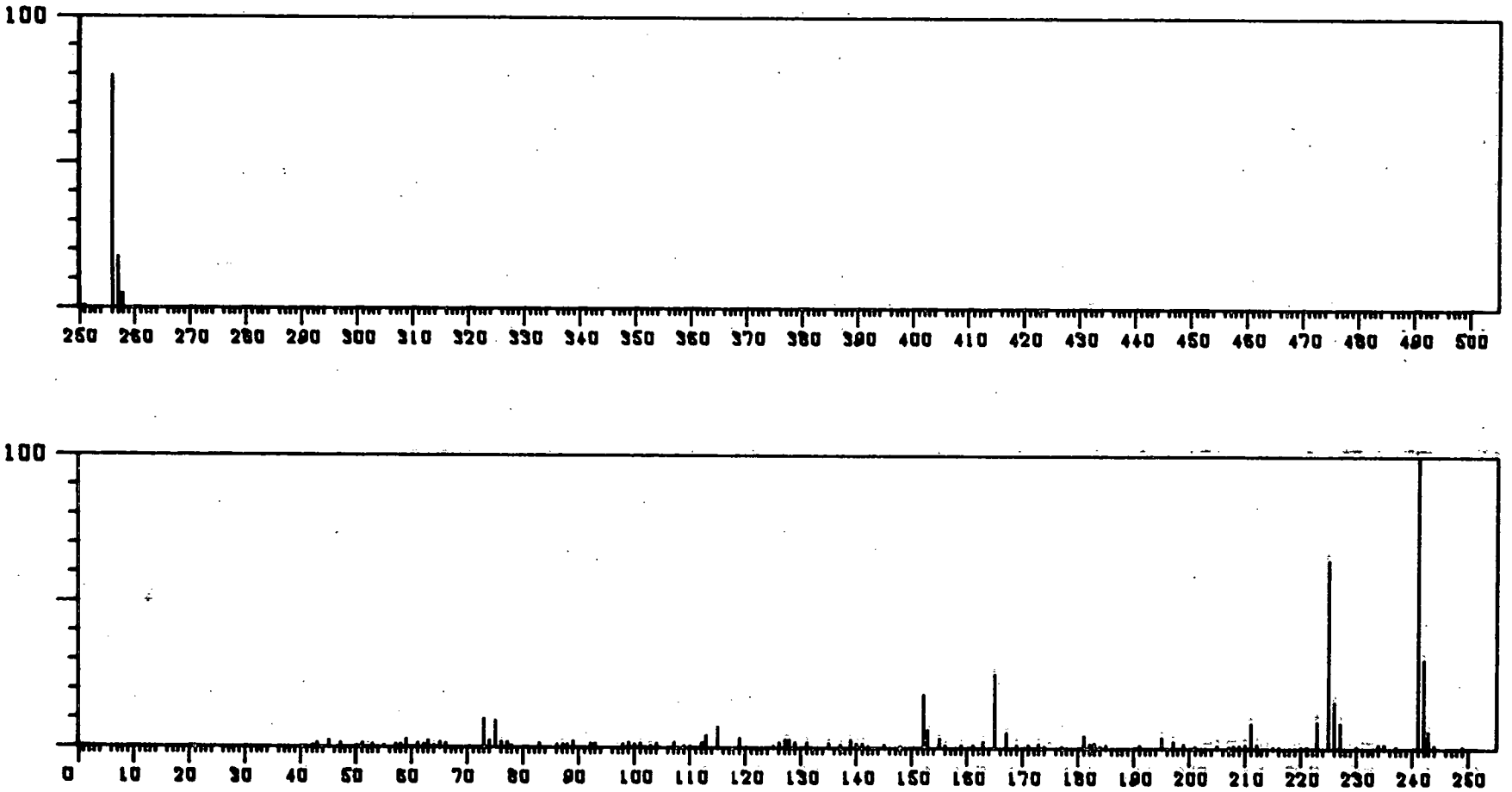
Methyl hydroxybiphenyl, TMS ether

Retention Time 87.4



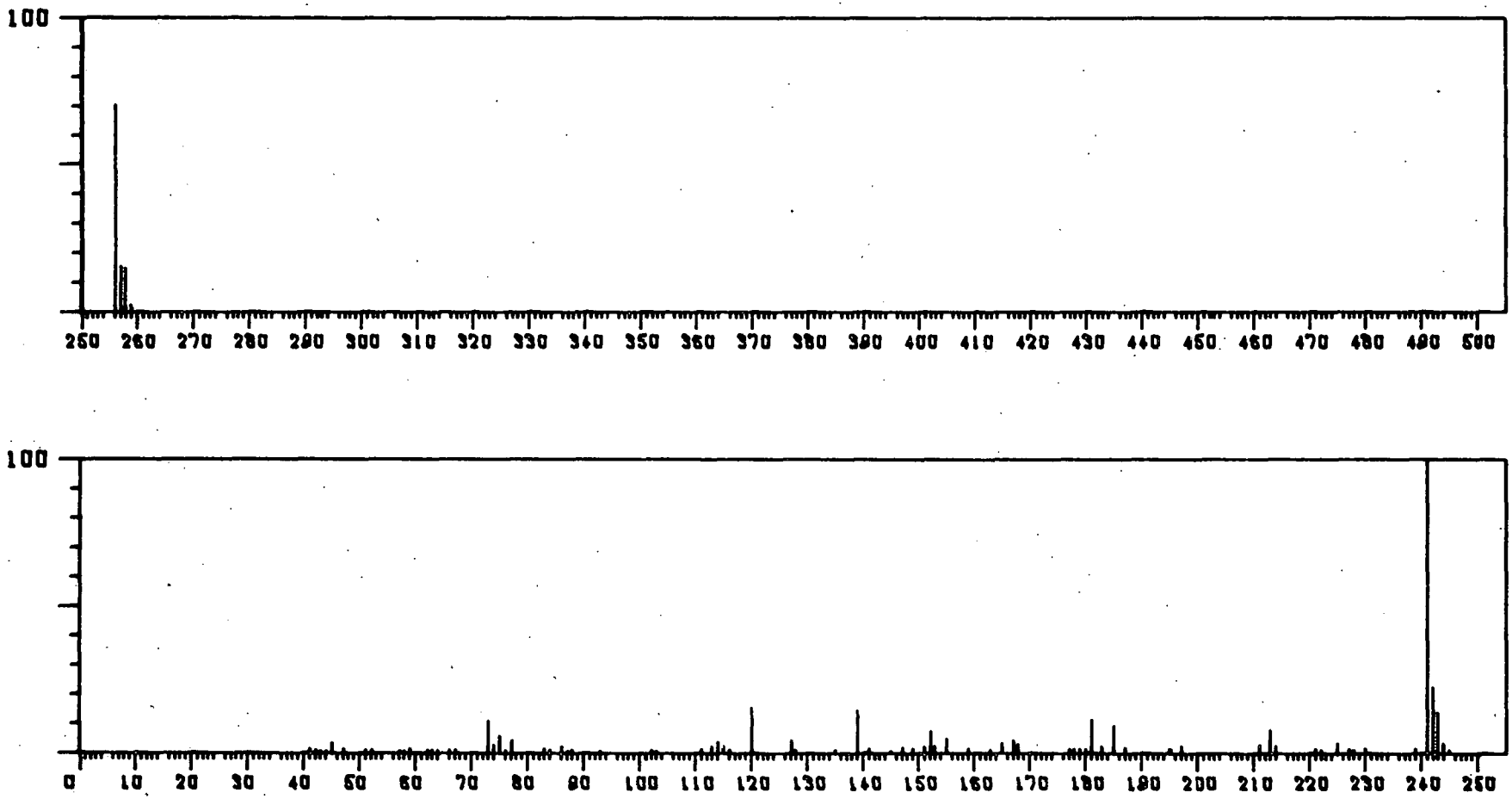
C_2-Naphthol, TMS ether

Retention Time 87.7



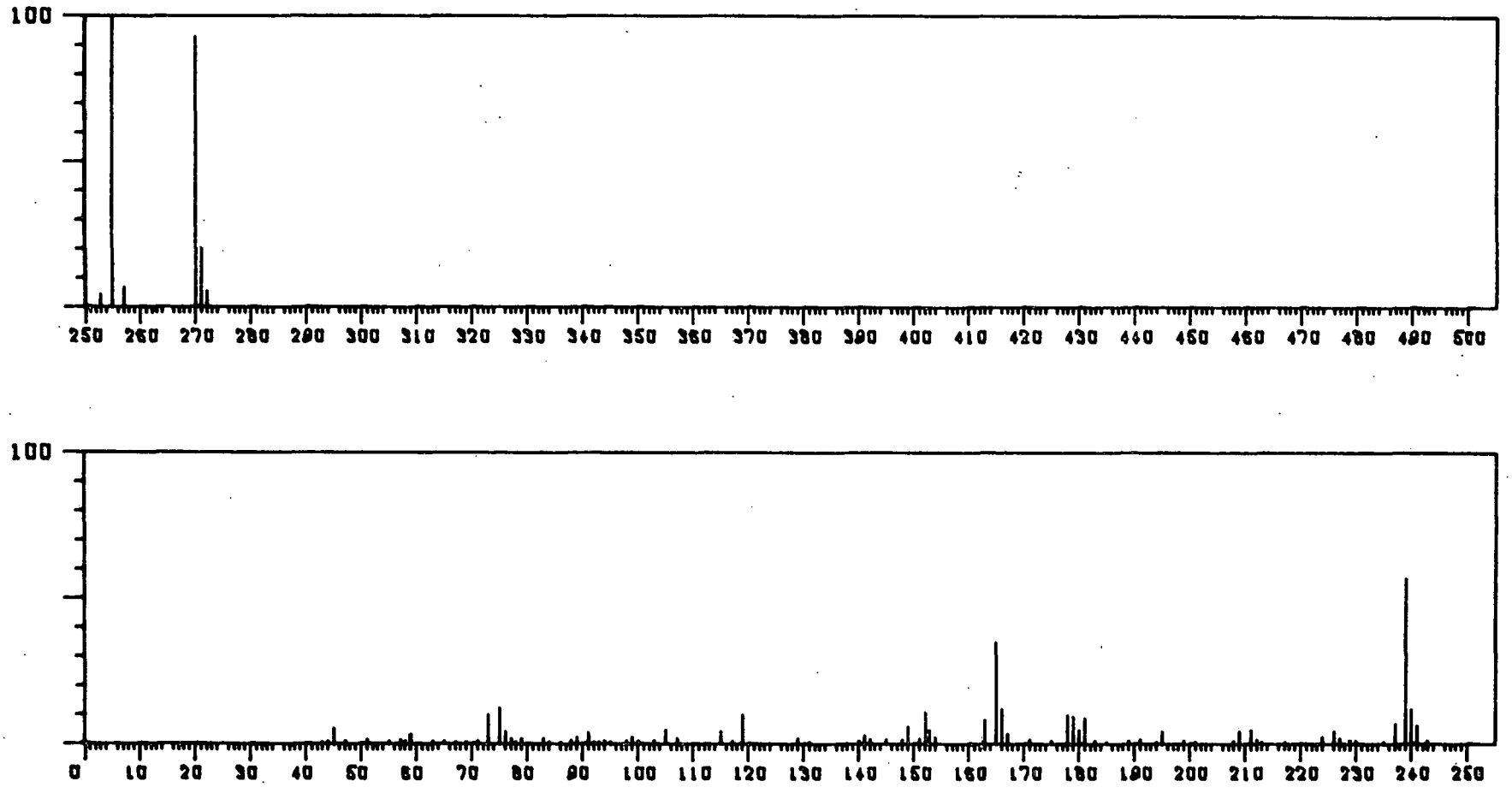
Methyl hydroxybiphenyl, TMS ether

Retention Time 88:3



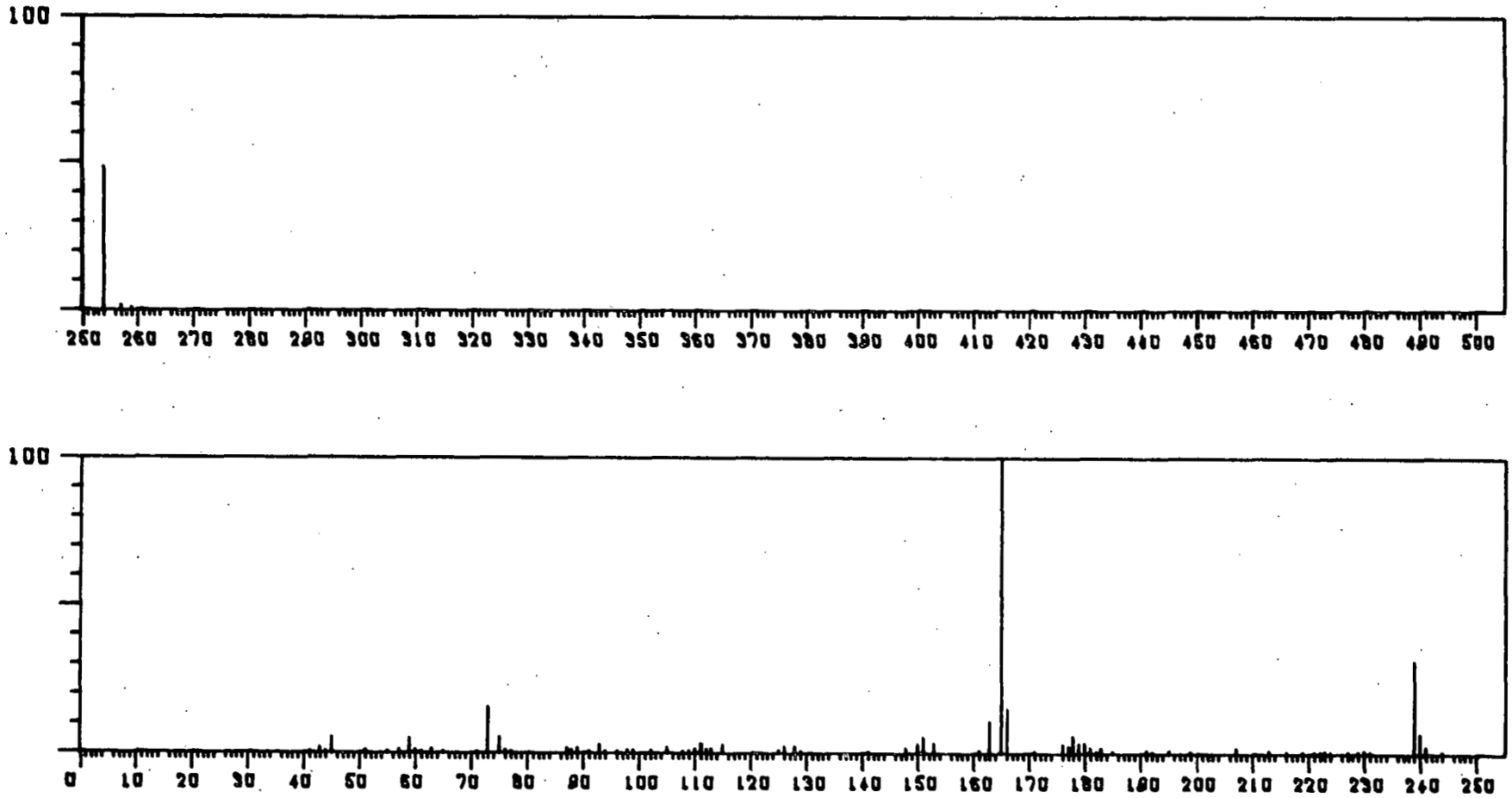
Methyl hydroxybiphenyl, TMS ether

Retention Time 91.9



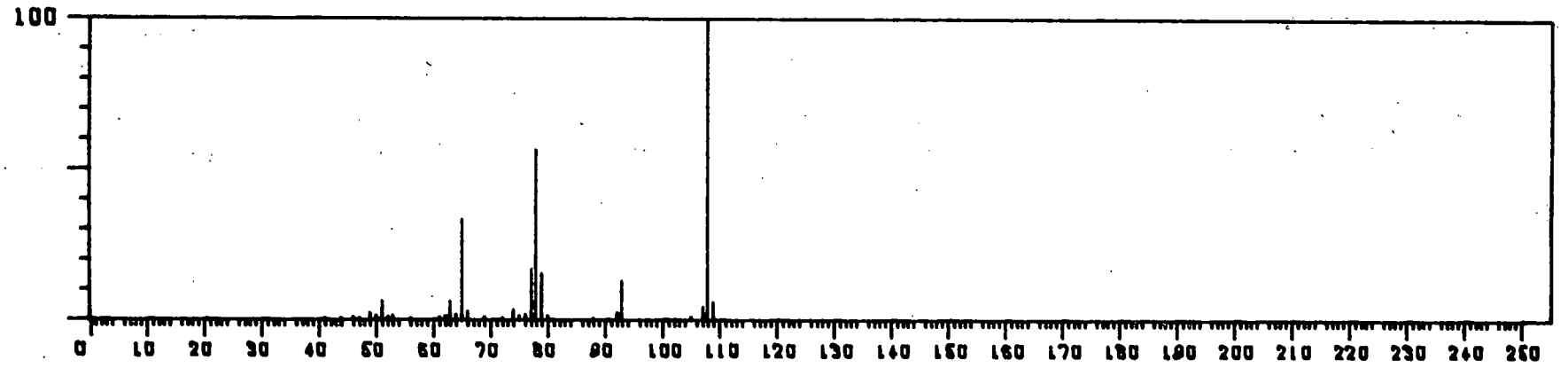
C_2-Hydroxybiphenyl, TMS ether

Retention Time 92.5



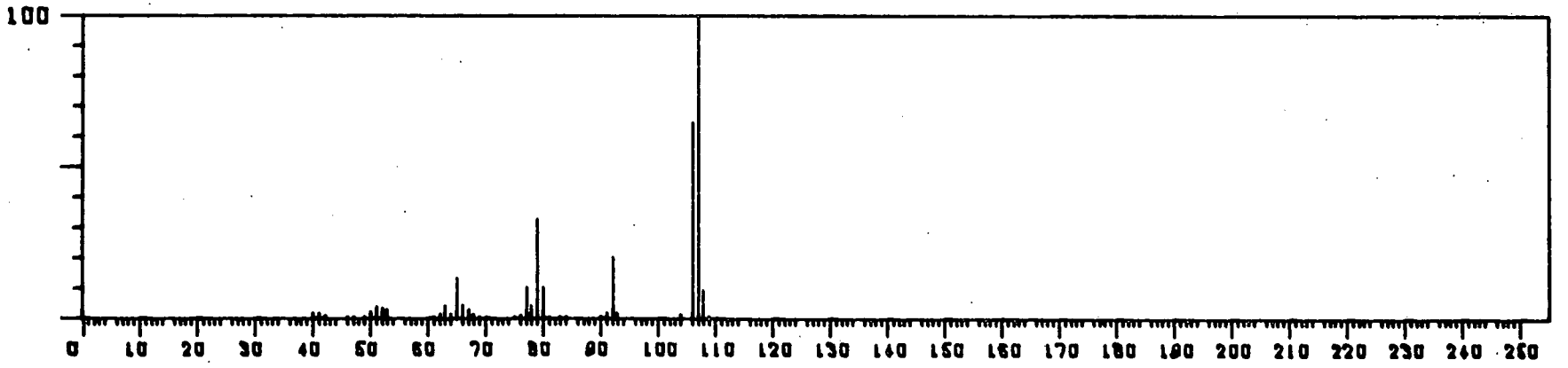
Hydroxyfluorene, TMS ether

Retention Time 93.7



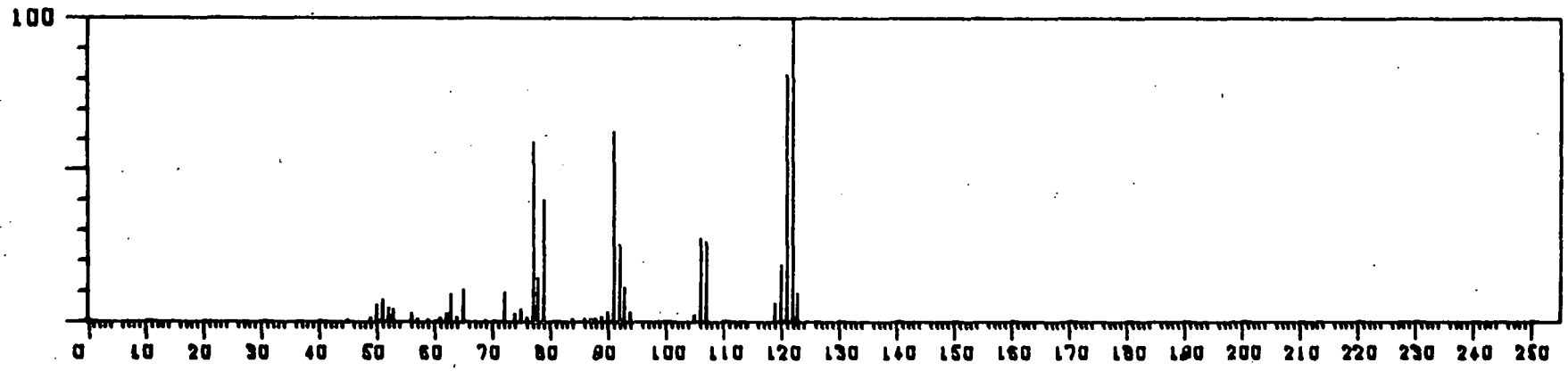
Anisole

Retention Time 28.1



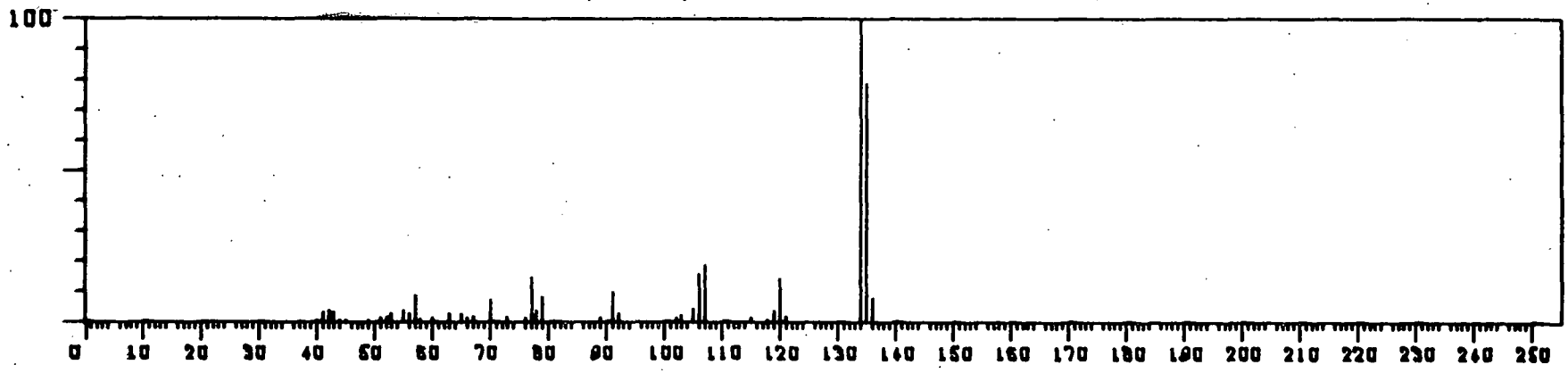
C_2-Pyridine

Retention Time 28.4



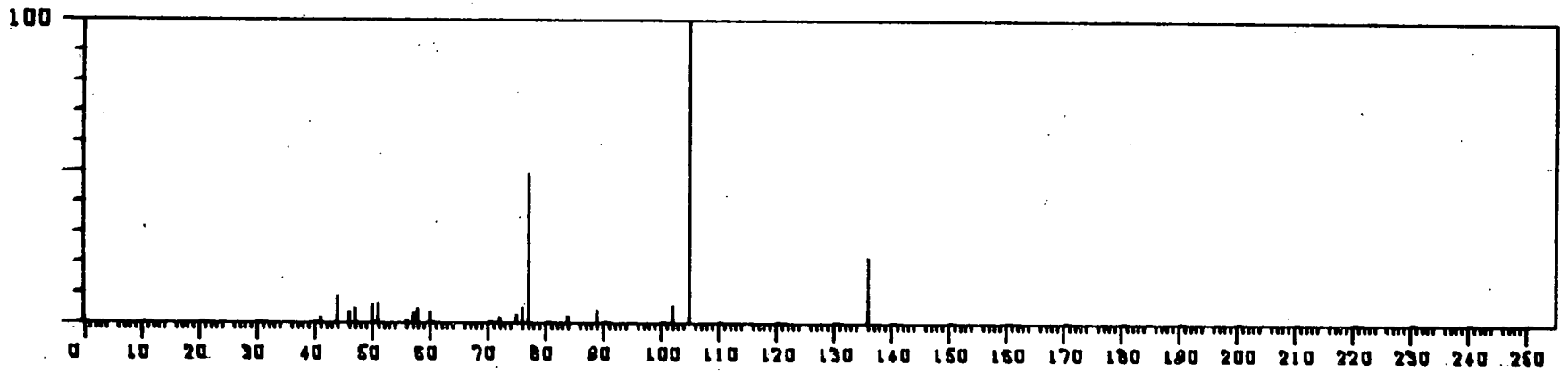
Methyl anisole

Retention Time 35.1



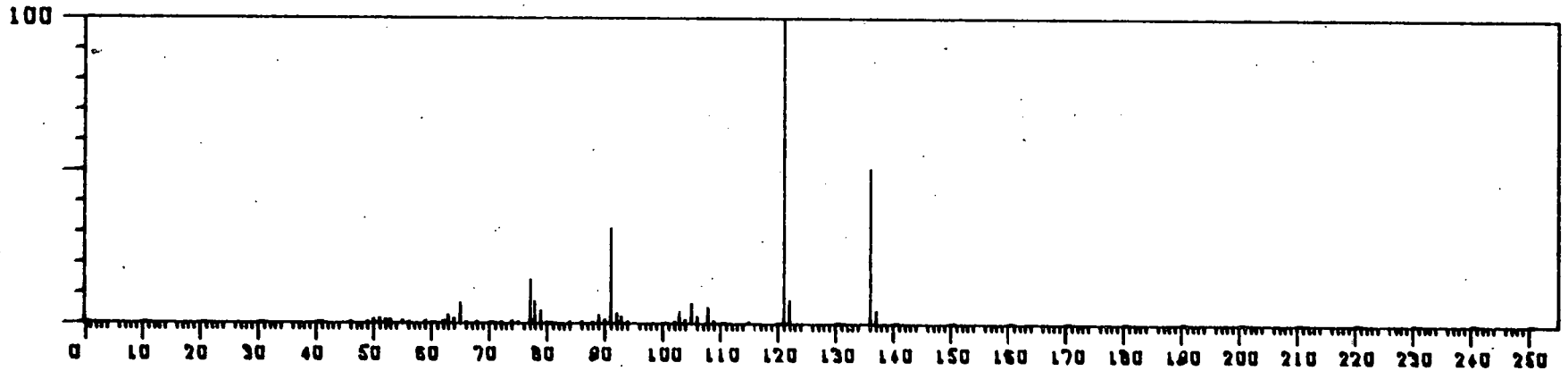
Styrene, methyl ether

Retention Time 39.4



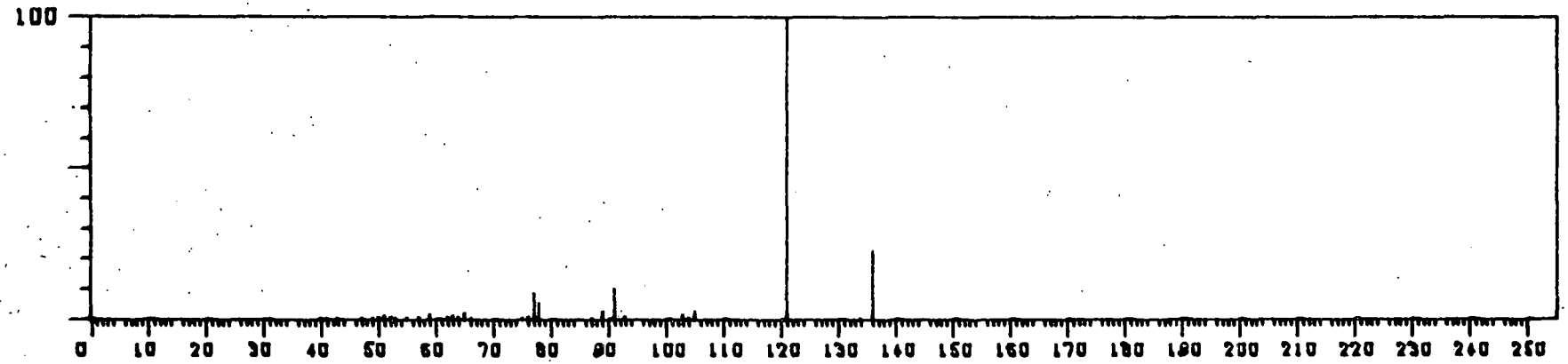
C_2-Anisole

Retention Time 40.9



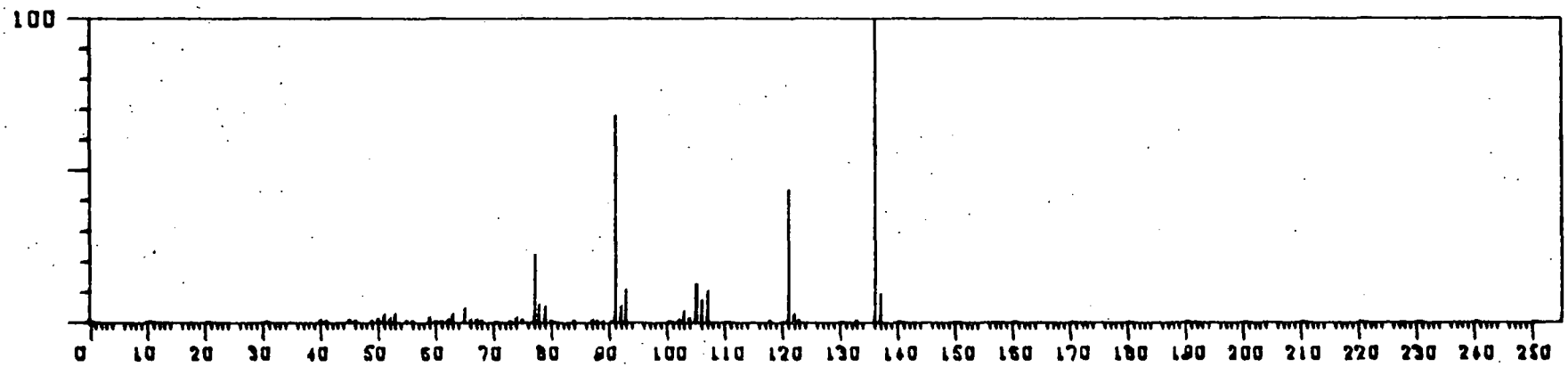
C_2-Anisole

Retention Time 41.6



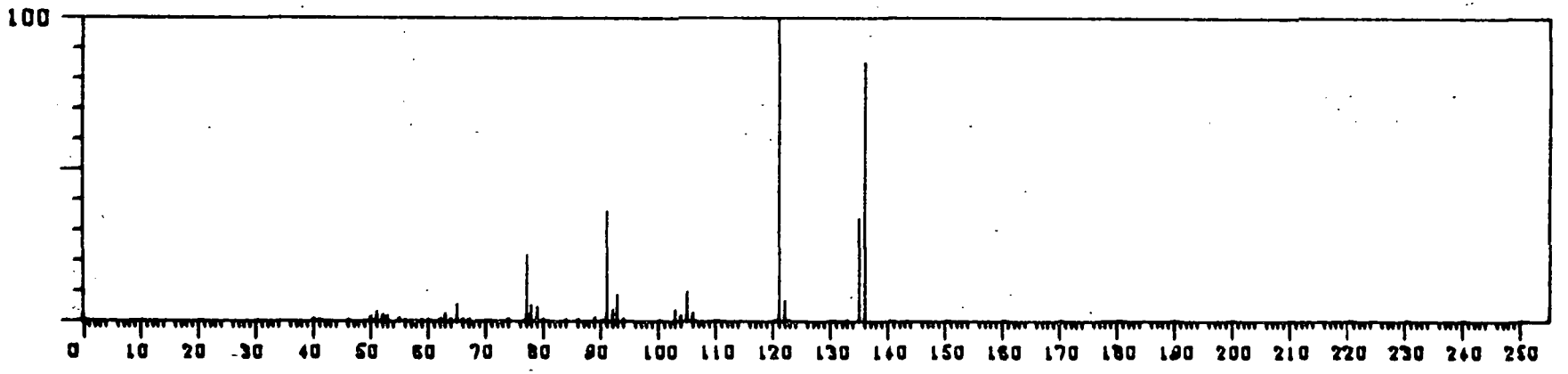
C_2-Anisole

Retention Time 41.8



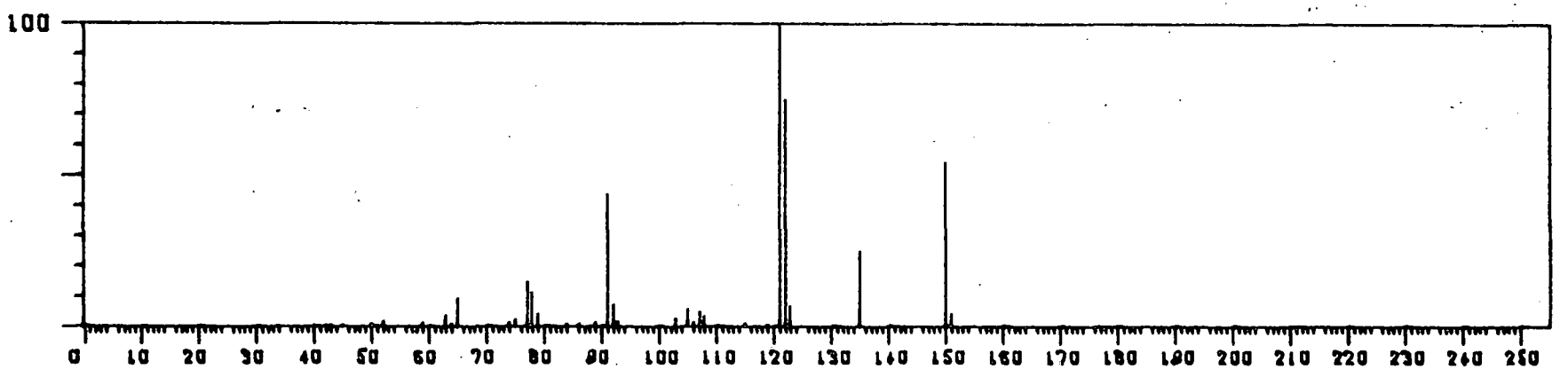
C_2-Anisole

Retention Time 42.6



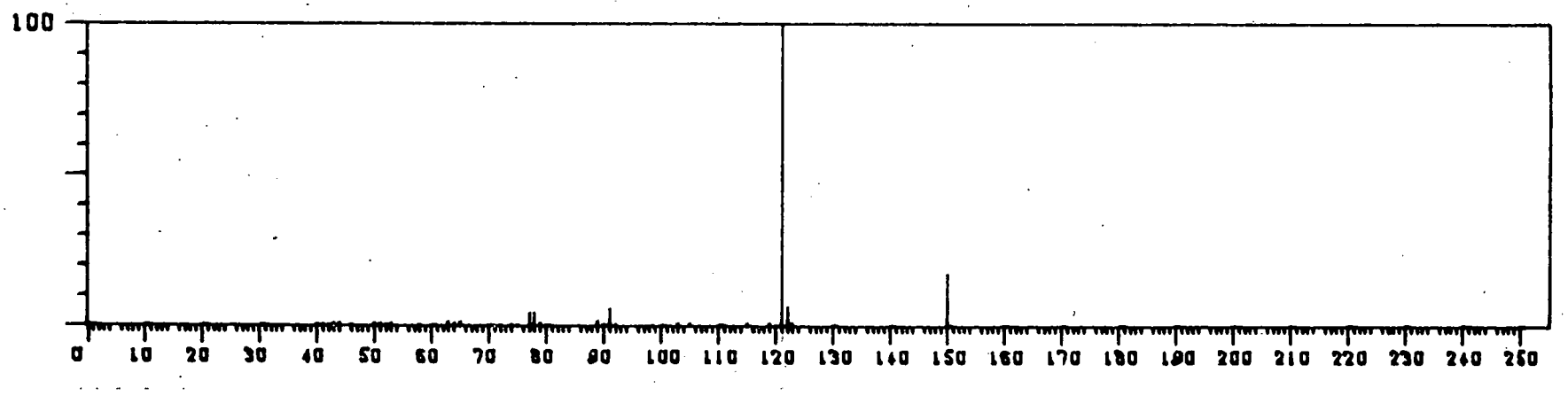
C_2-Anisole

Retention Time 44.2



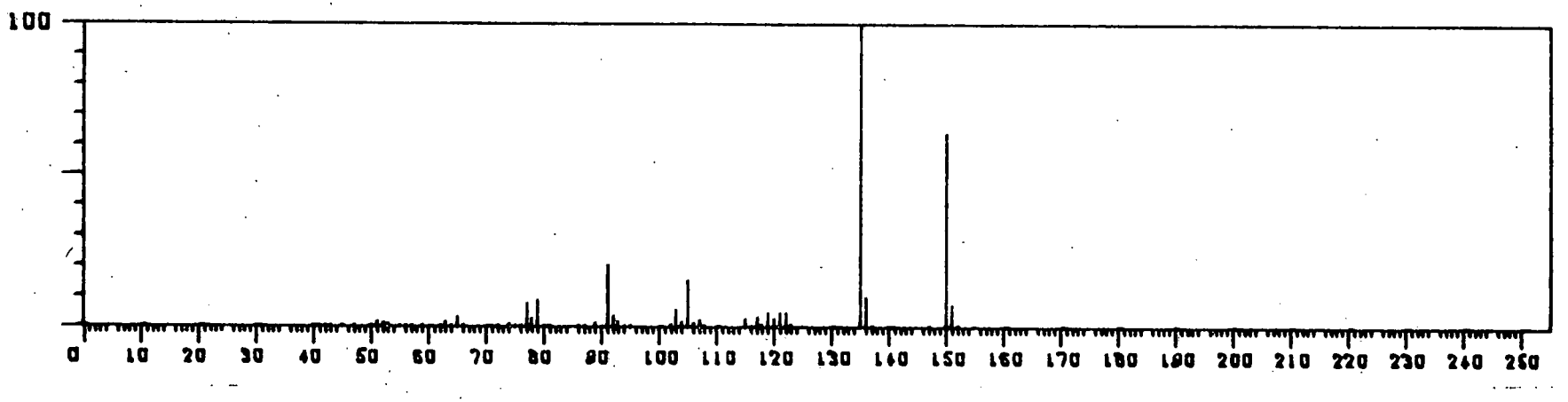
C_3-Anisole

Retention Time 48.1



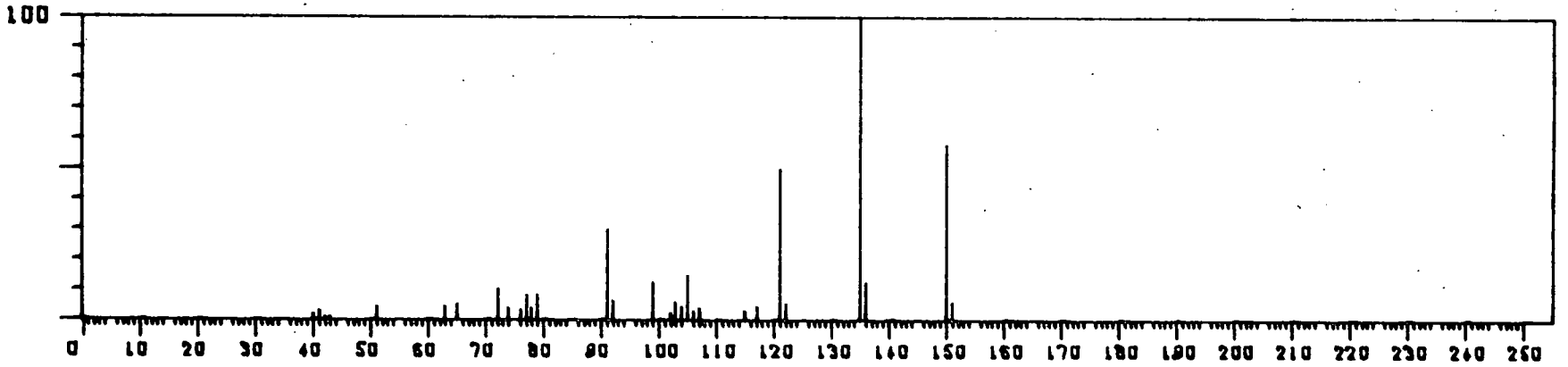
C_3-Anisole

Retention Time 48.4



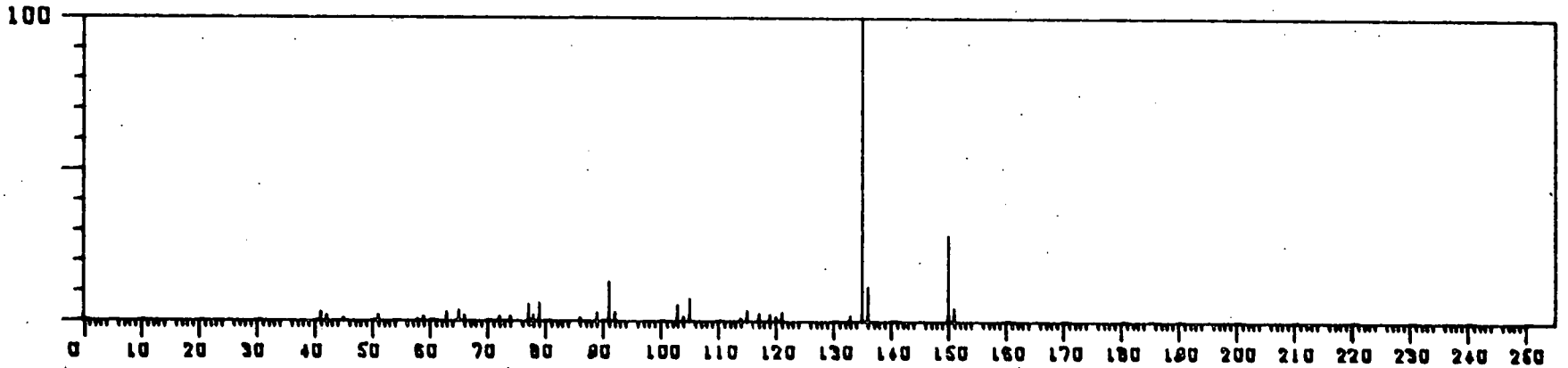
C_3-Anisole

Retention Time 48.7



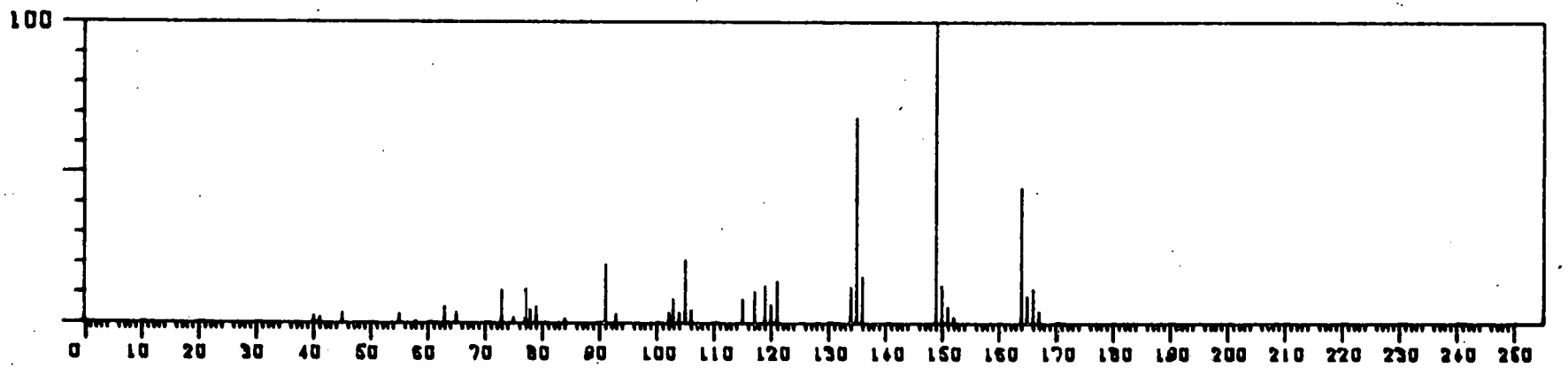
C_3-Anisole

Retention Time 50.1



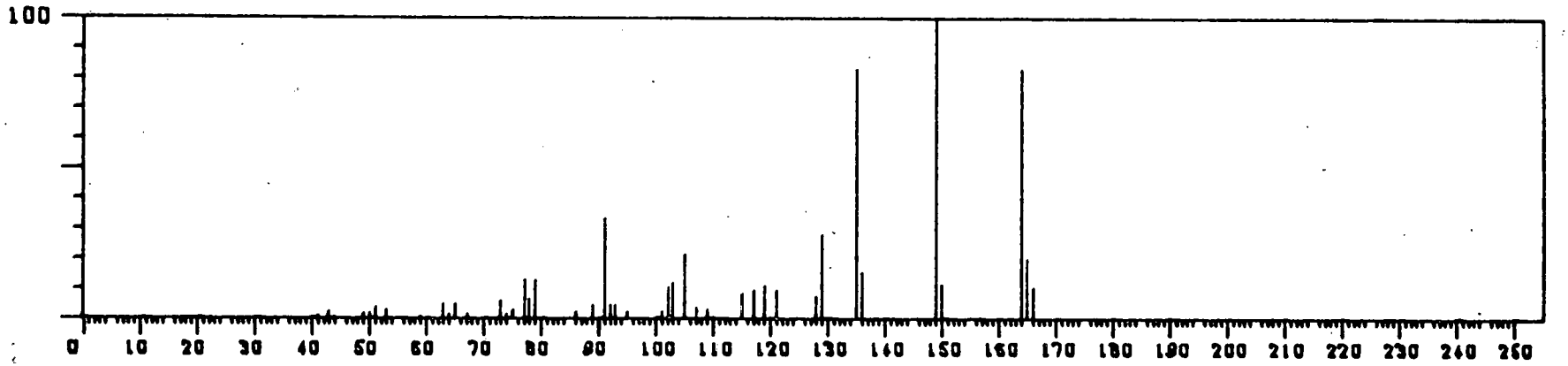
C_3-Anisole

Retention Time 50.3



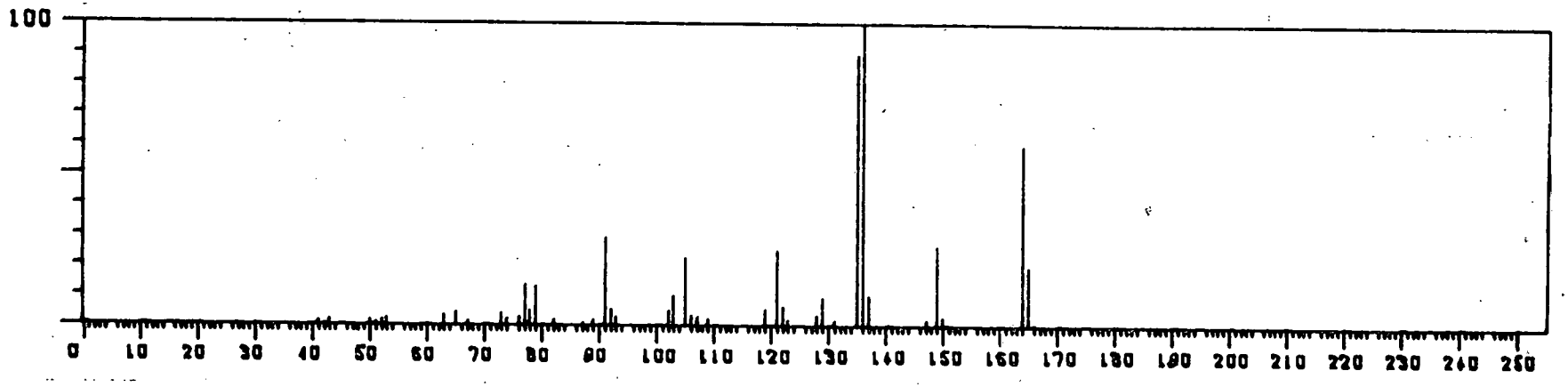
C_4-Anisole

Retention Time 52.5



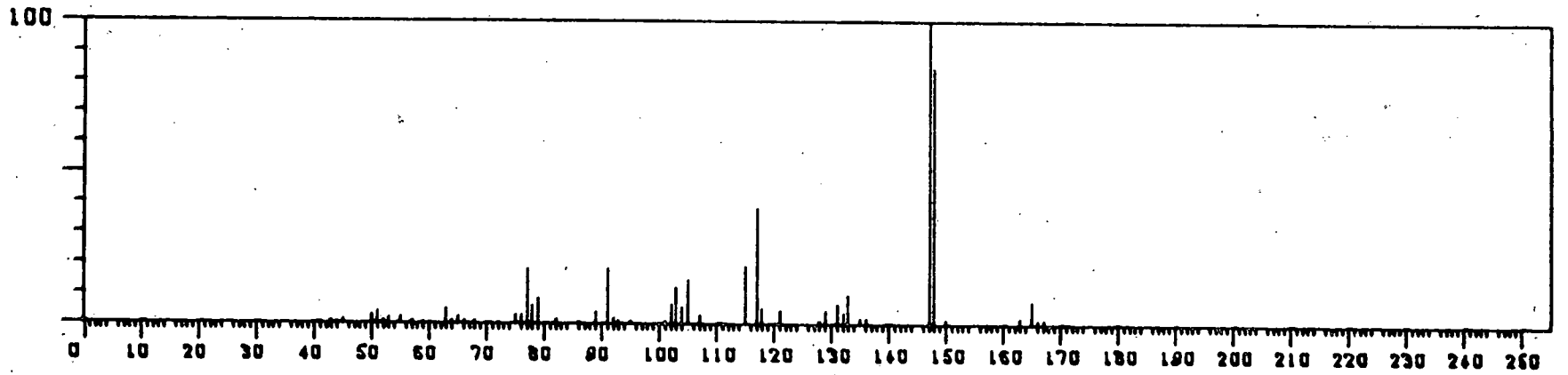
C_4-Anisole

Retention Time 54.5



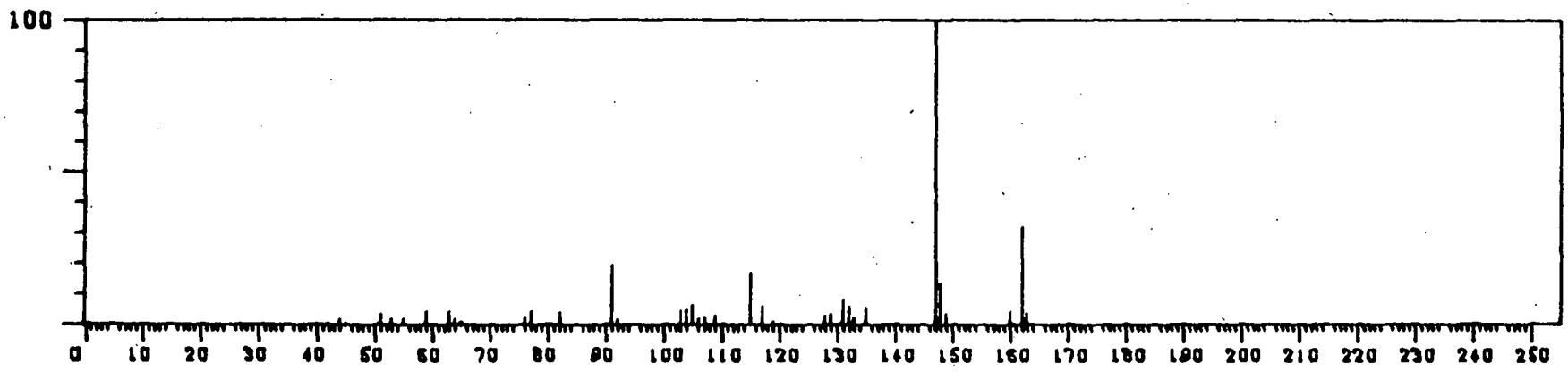
C_4-Anisole

Retention Time 54.8



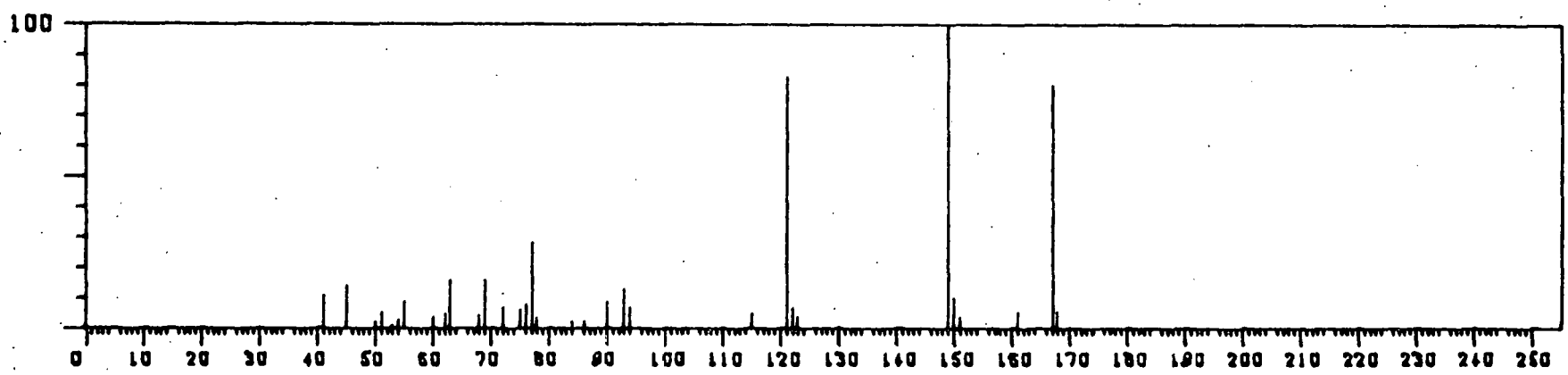
Methyl hydroxystyrene, methyl ether

Retention Time 55.0



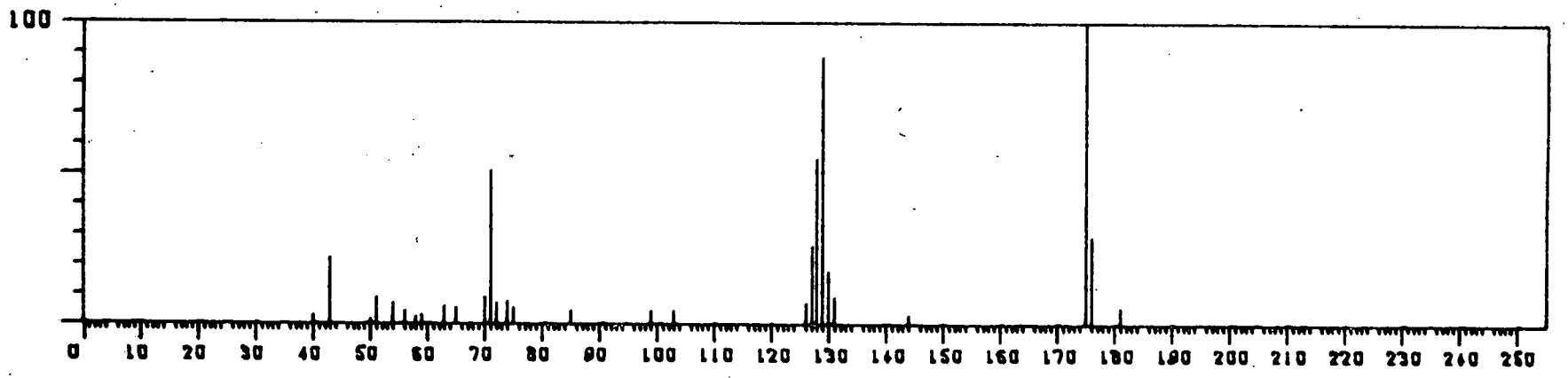
C_2-Hydroxystyrene, methyl ether

Retention Time 58.1



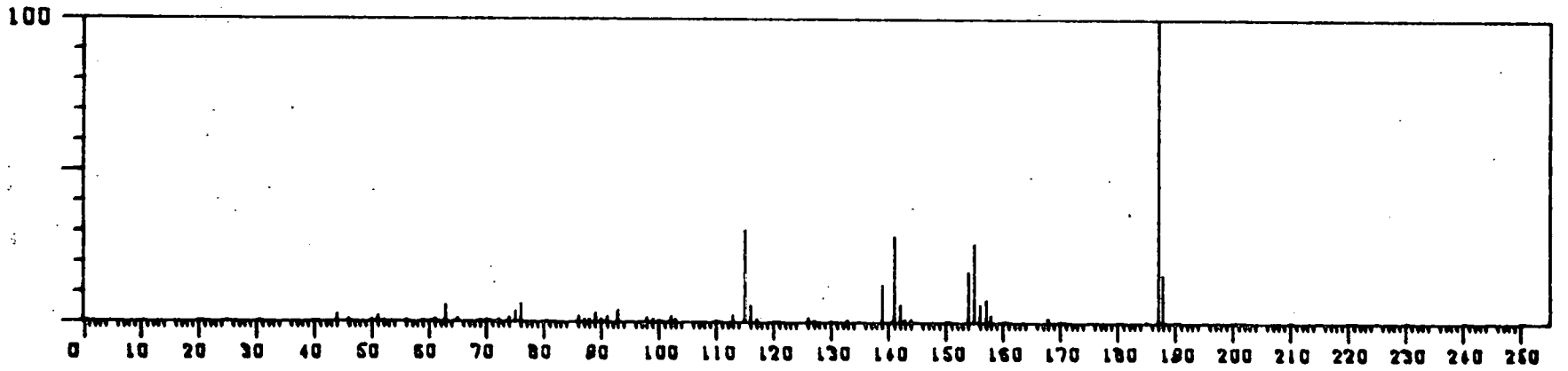
Hydroxybenzothiophene, methyl-d_3 ether

Retention Time 68.7



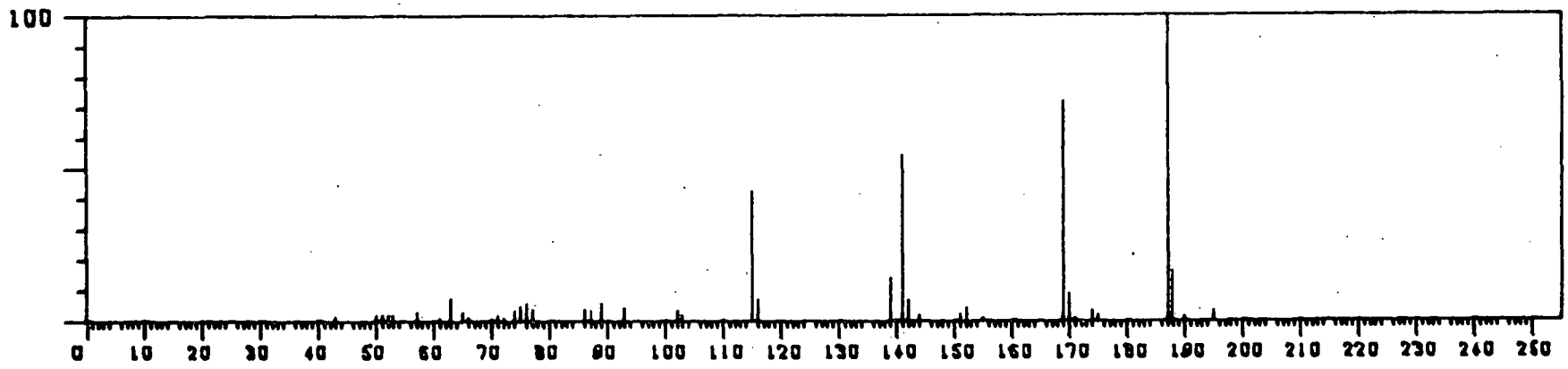
Methyl naphthol, methyl-d_3 ether

Retention Time 75.1



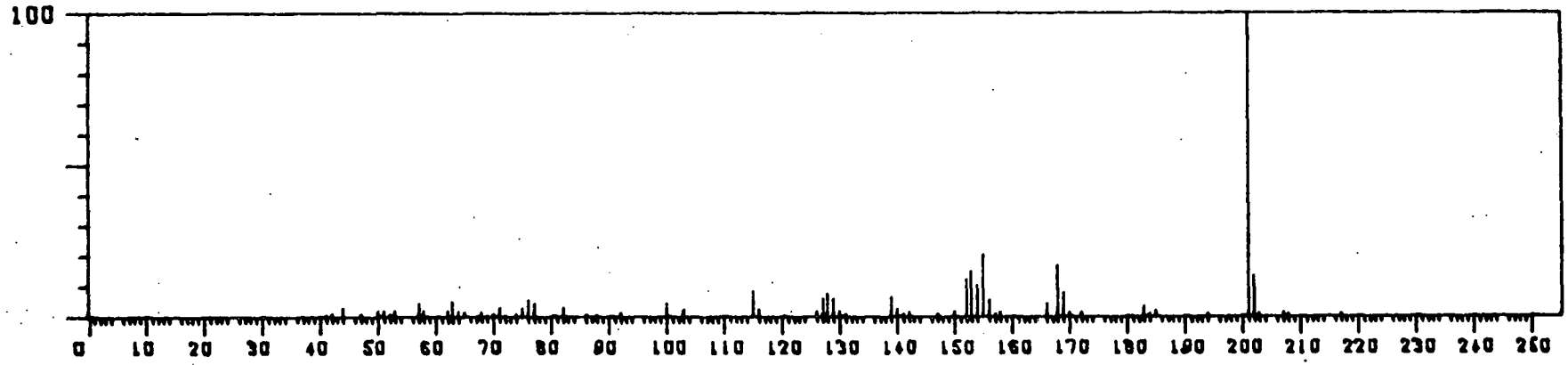
Hydroxybiphenyl, methyl-d_3 ether

Retention Time 78.2



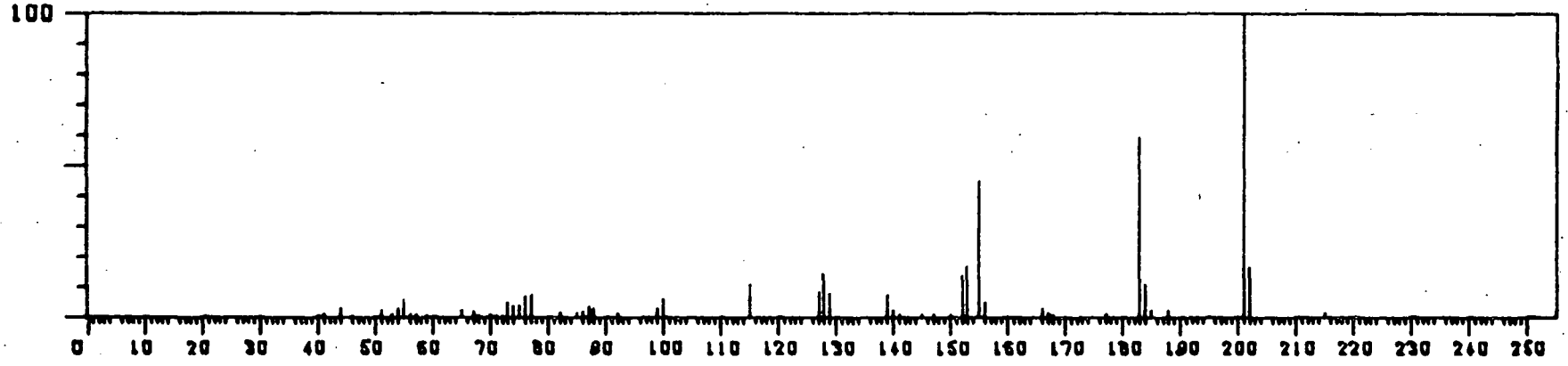
Hydroxybiphenyl, methyl-d_3 ether

Retention Time 79.3



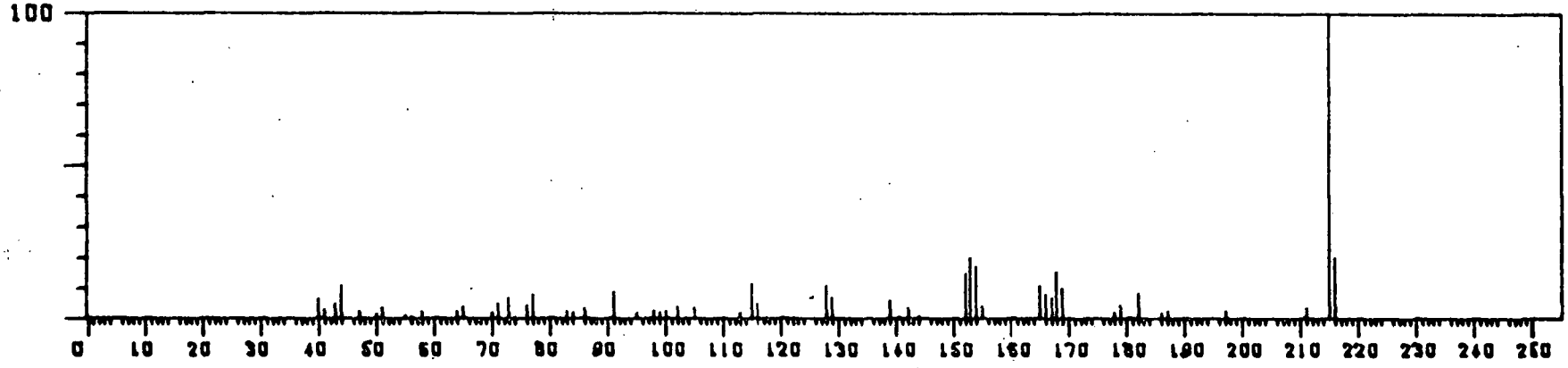
C_1-Hydroxybiphenyl, methyl-d_3 ether

Retention Time 83.8



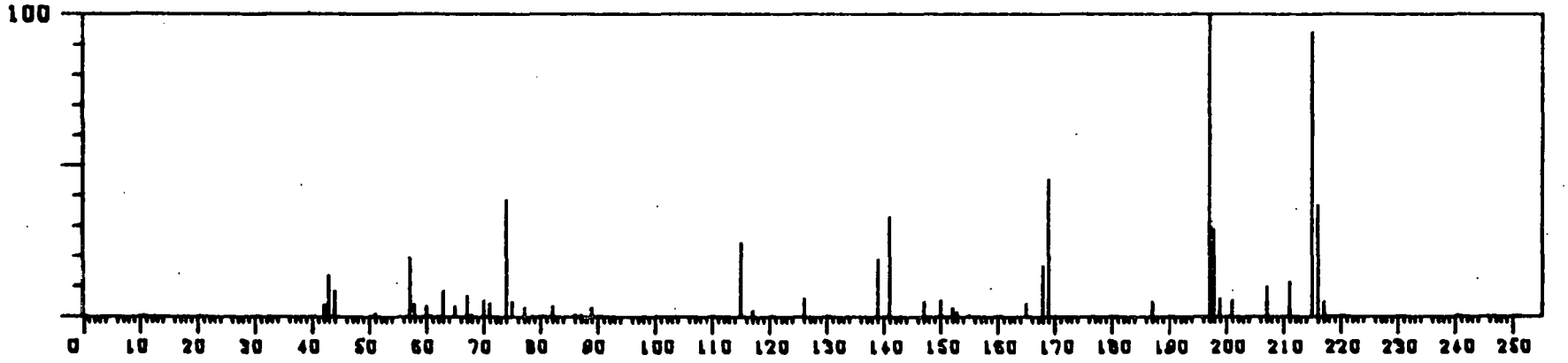
C_1-Hydroxybiphenyl, methyl-d_3 ether

Retention Time 85.1



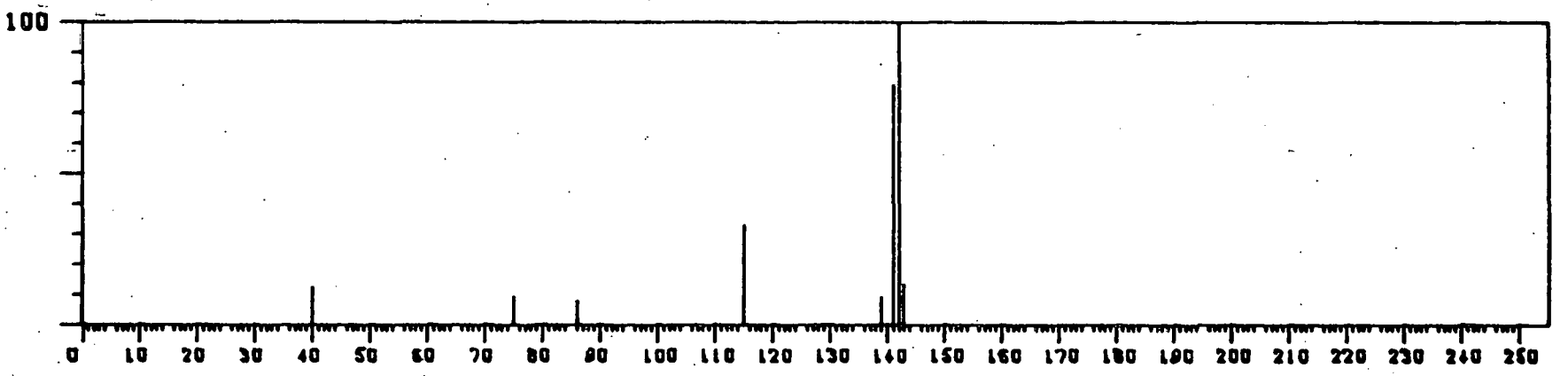
C_2-Hydroxybiphenyl, methyl-d_3 ether

Retention Time 89.0



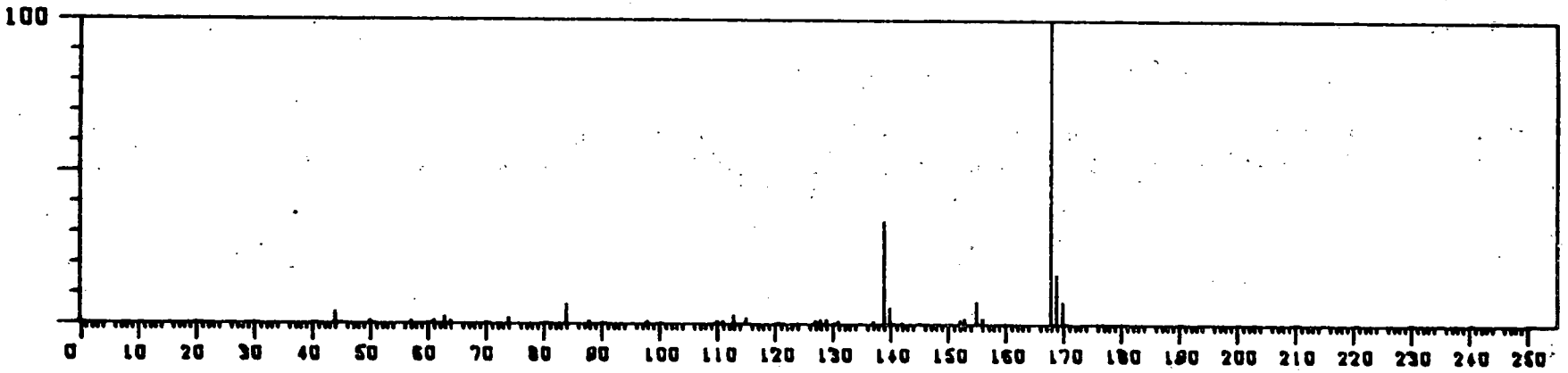
C_2-Hydroxybiphenyl, methyl-d_3 ether

Retention Time 91.8



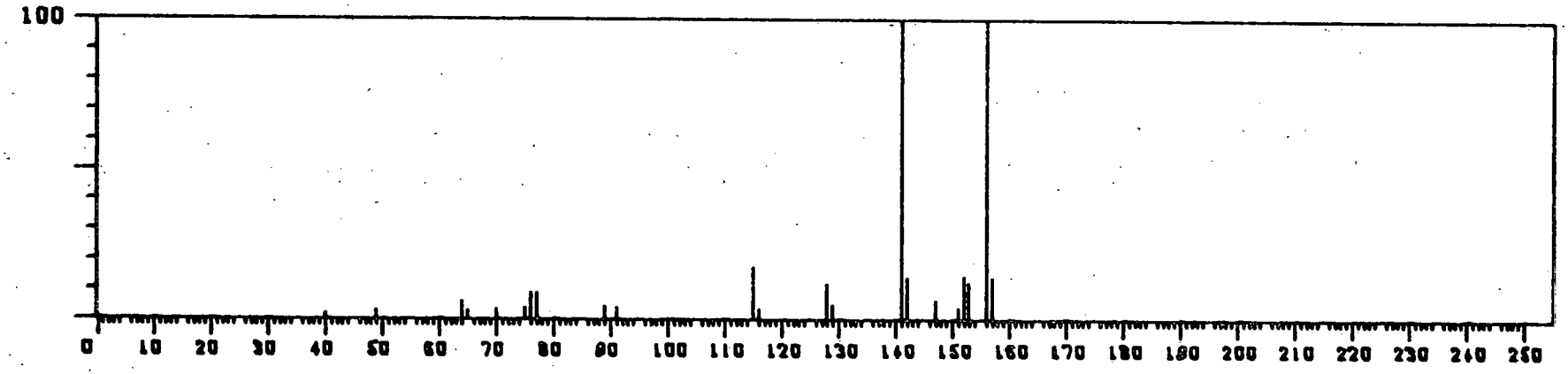
Methyl naphthalene

Retention Time 55.2



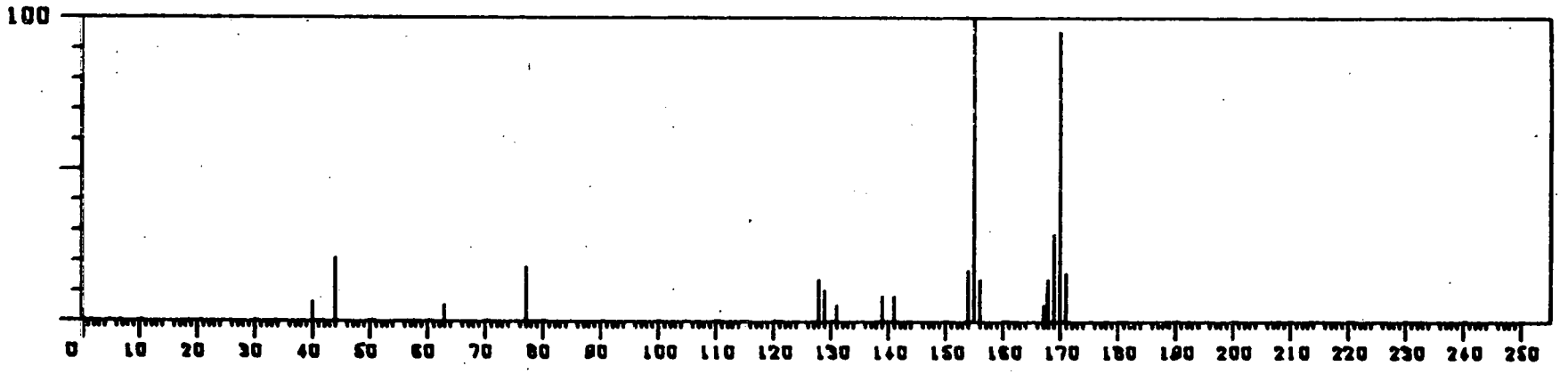
C_2-Naphthalene

Retention Time 63.5



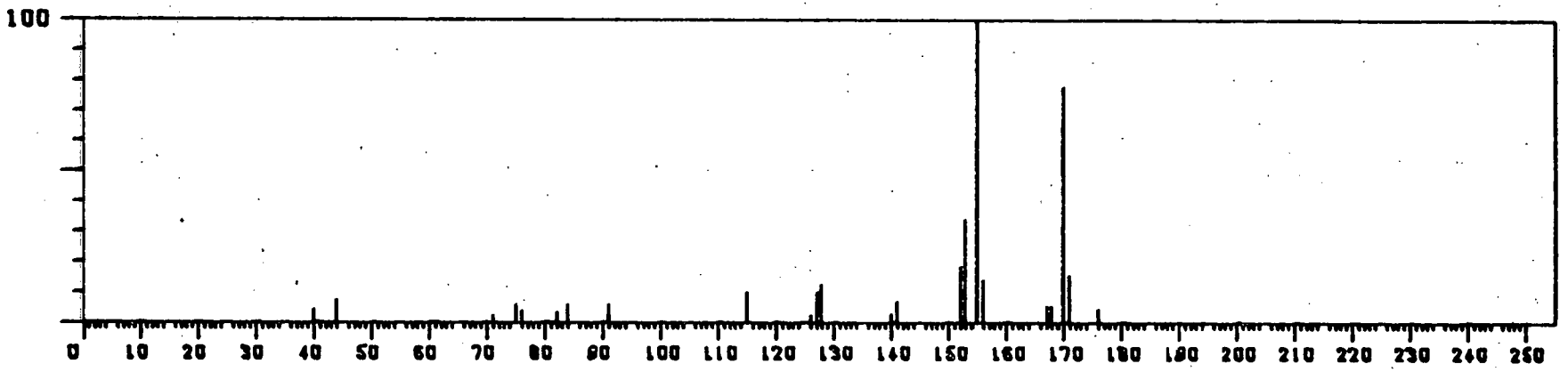
Methyl biphenyl

Retention Time 70.4



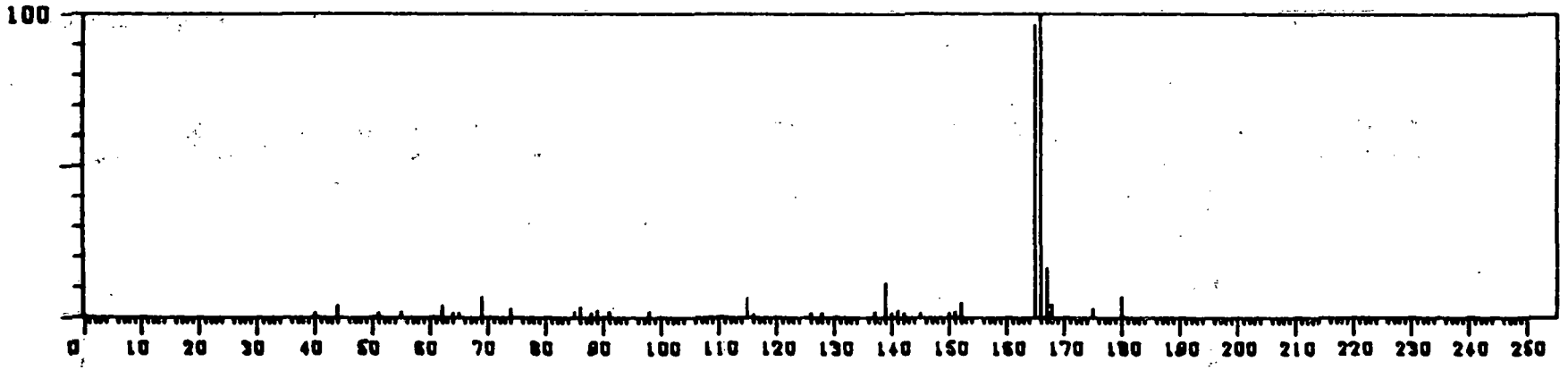
C_3-Naphthalene

Retention Time 70.9



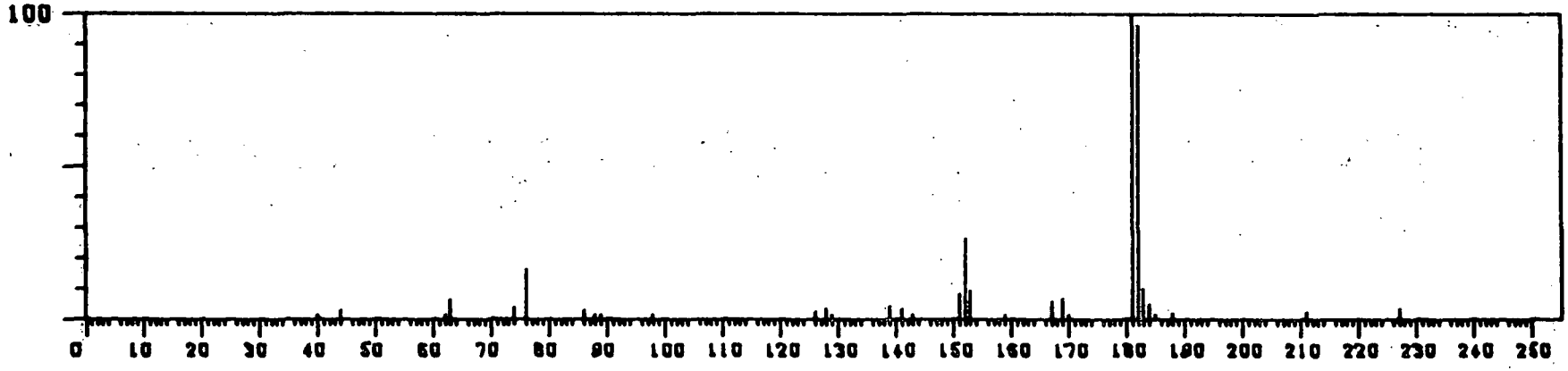
C_3-Naphthalene

Retention Time 72.7



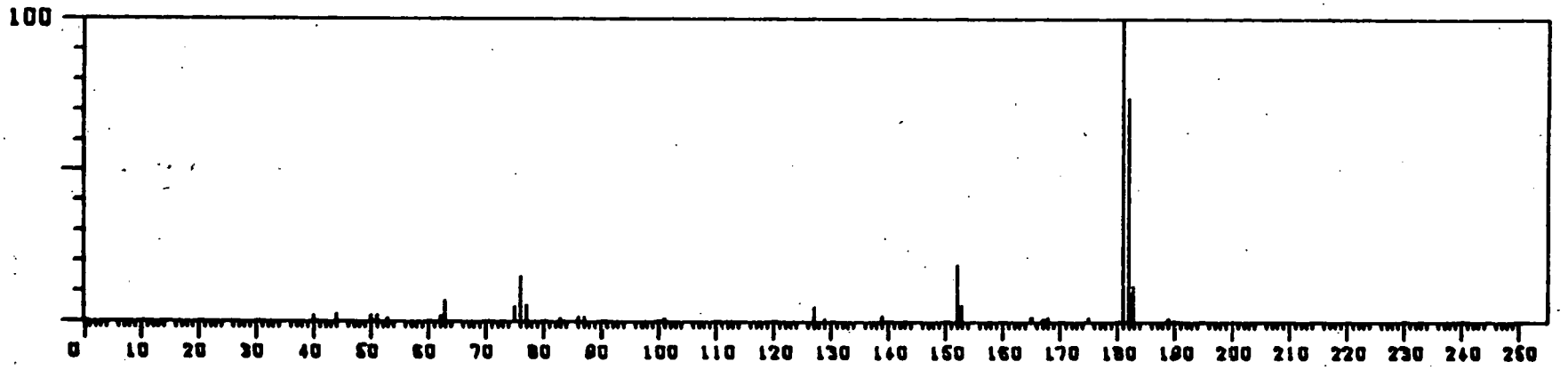
Fluorene

Retention Time 74.5



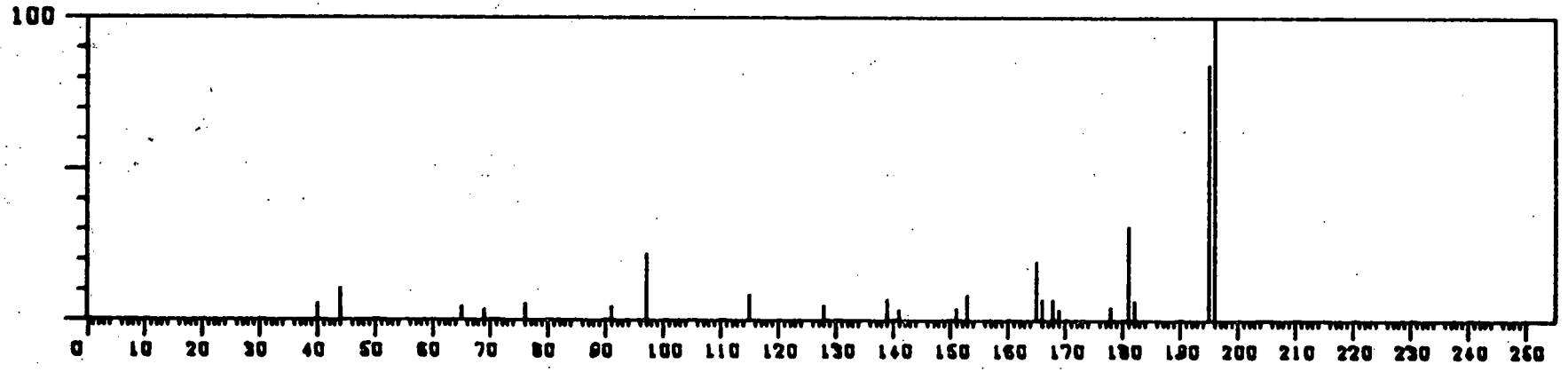
C_2-Acenaphthene

Retention Time 76.6



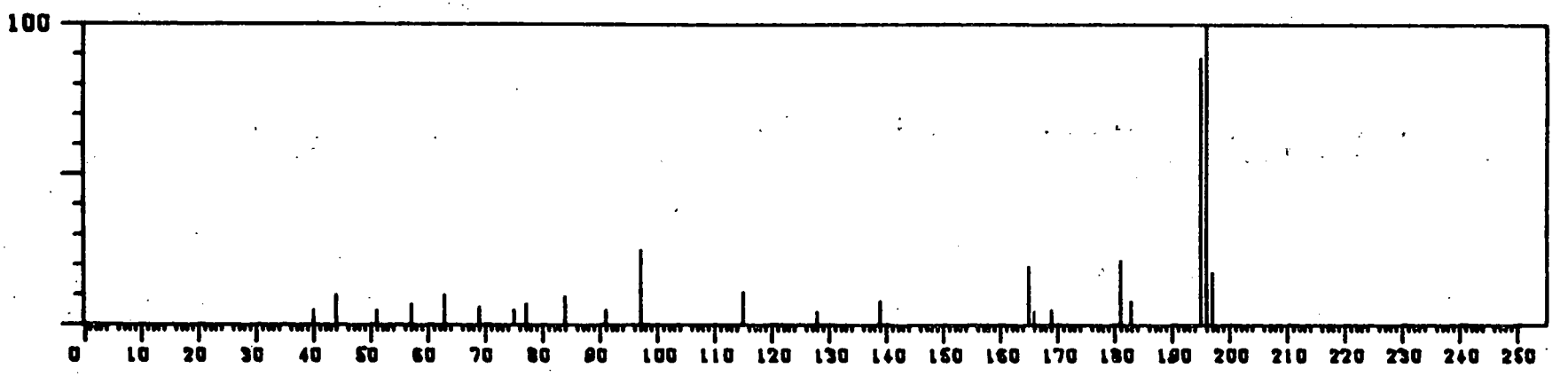
C_2-Acenaphthene

Retention Time 77.6



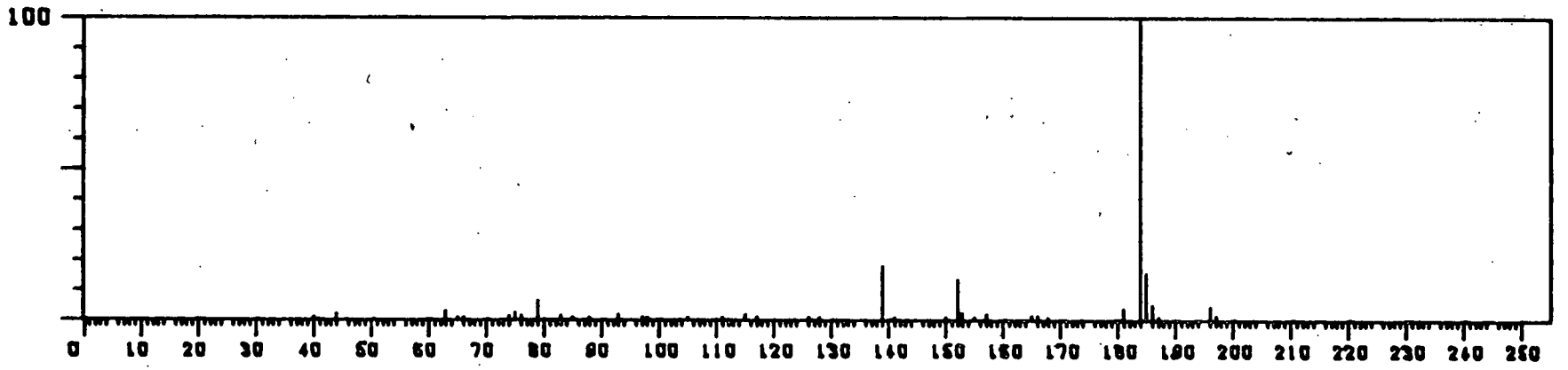
C_3-Acenaphthene

Retention Time 83.3



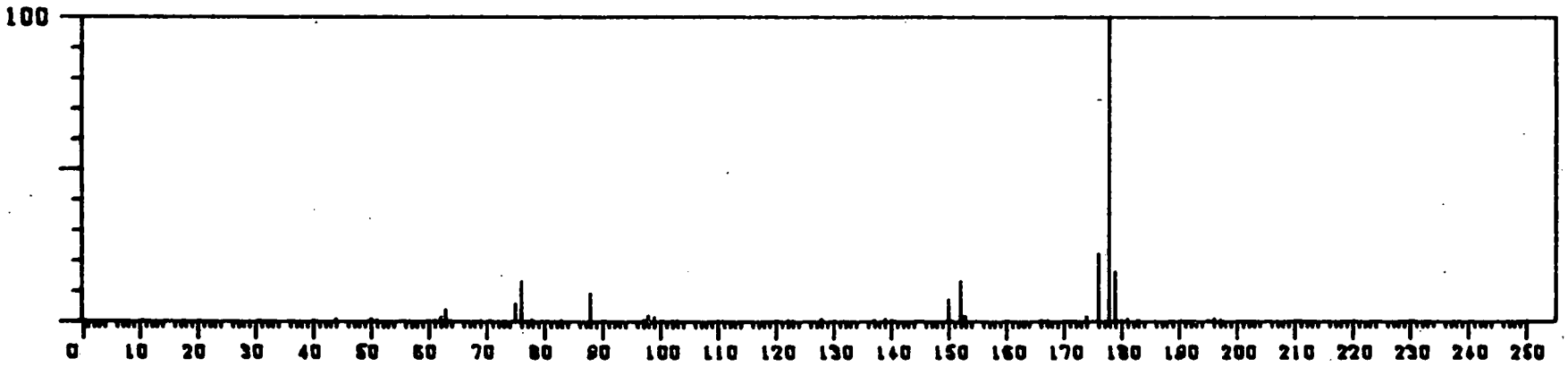
C_3-Acenaphthene

Retention Time 84.2



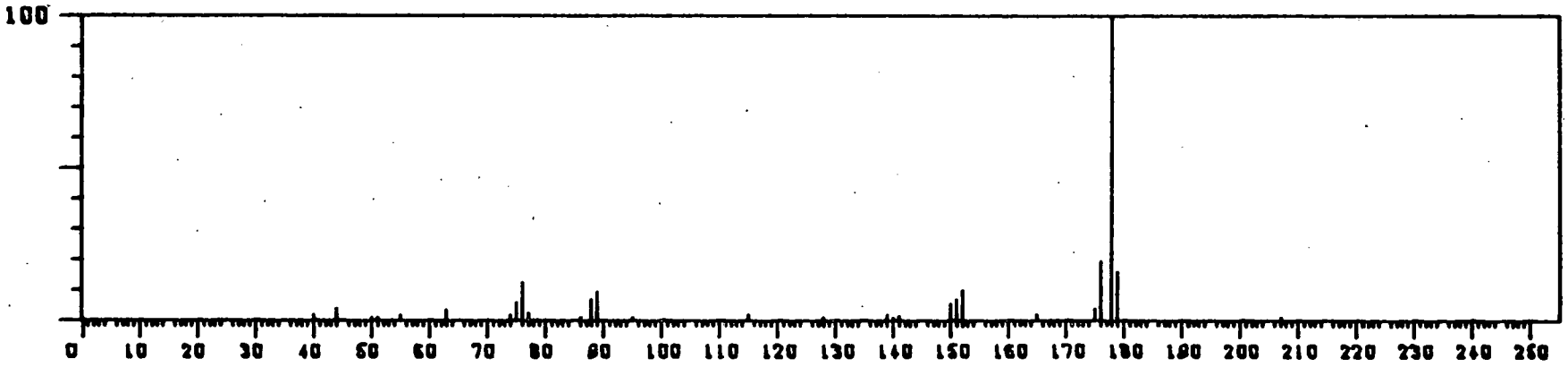
C_2-Biphenyl

Retention Time 84.7



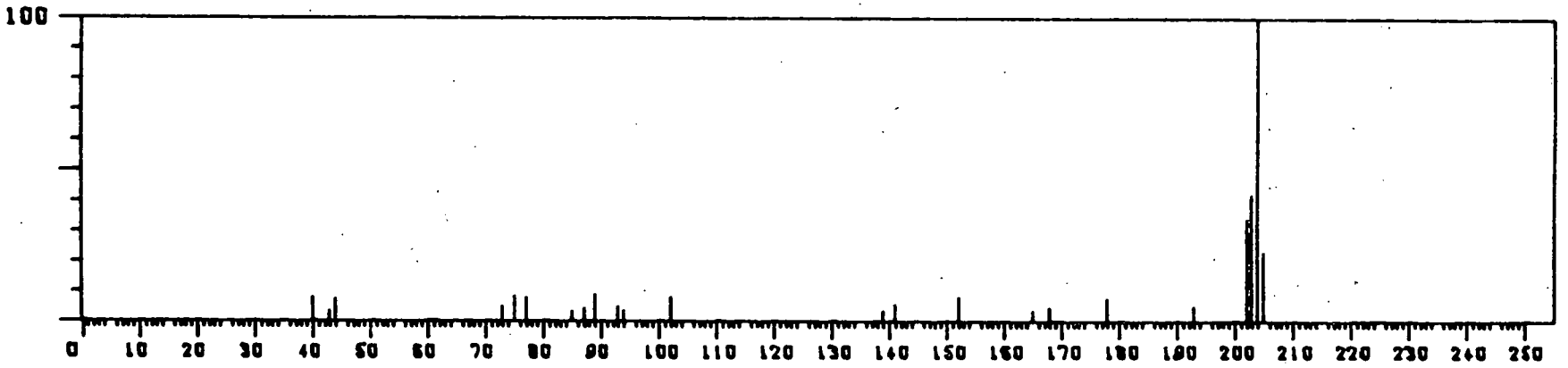
Phenanthrene

Retention Time 86.5



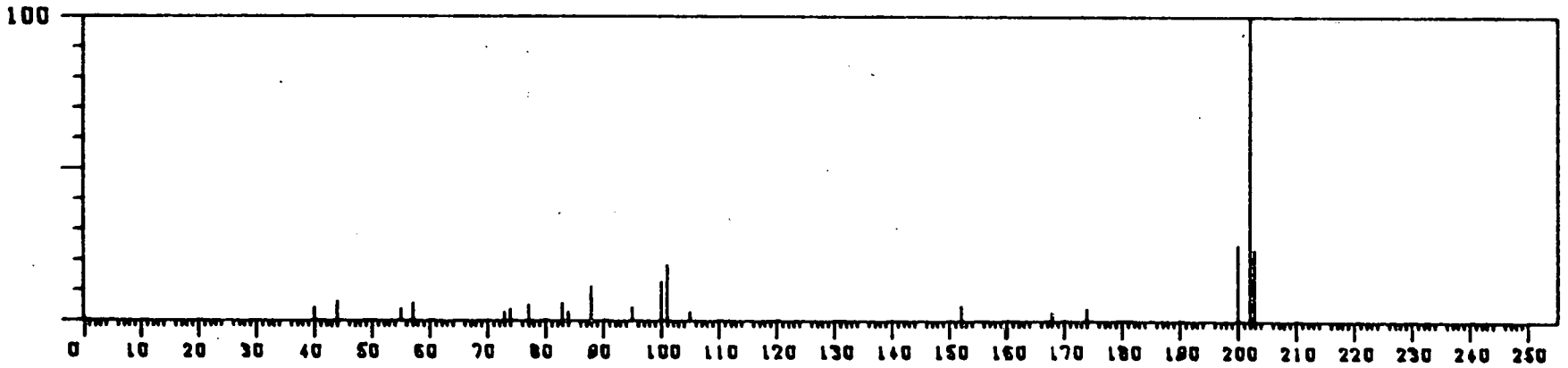
Anthracene

Retention Time 87.0



Aceanthrene/acephenanthrene

Retention Time 96.2



Pyrene

Retention Time 101.6

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