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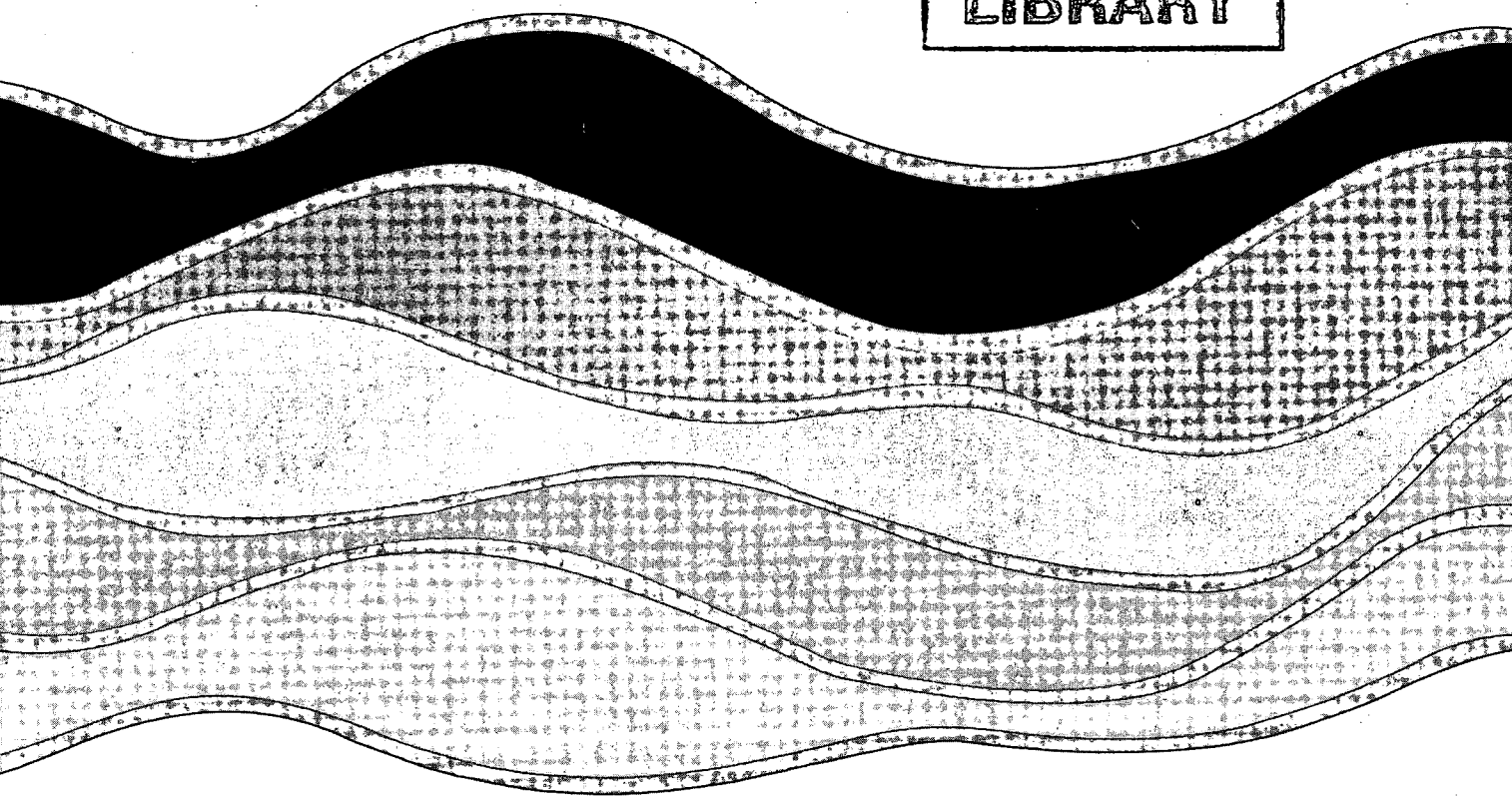

ANALYSIS OF PETROLEUM EFFLUENTS: INITIAL RESULTS

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NWRI Contribution No. 93-79

ANALYSIS OF PETROLEUM EFFLUENTS: INITIAL RESULTS

by

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MANAGEMENT PERSPECTIVE

This study was undertaken as part of the federal Greenplan initiative related to refinery effluents. Emphasis was placed on the organic extractables, using solvents of various polarities on the extraction of refinery effluents as well as from produced water. This investigation supported concurrent biological studies and examined specific questions related to the "grease and oil" measurement. The chemical studies were carried out using the latest analytical chemical techniques, namely gas chromatography/mass spectral detector and GC/atomic emission detection. It was determined that dichloromethane is the best replacement solvent for the freon currently recommended. There is a substantial amount of organosulphur compounds in the effluent whose structure and ecological effects are unknown. In addition, it was shown that the effluent undergoes subtle changes when stored and this could influence toxicity tests.

SOMMAIRE À L'INTENTION DE LA DIRECTION

Cette étude s'inscrit dans le cadre du Plan vert fédéral et porte sur les effluents des raffineries. On a mis l'accent sur les fractions organiques extractibles et on a eu recours à des solvants de différentes polarités pour pratiquer des extractions sur les effluents de raffinerie ainsi que sur l'eau produite. Cette étude venait appuyer des études biologiques simultanées et portait sur des aspects précis de la mesure des «graisses et huiles». Les études chimiques ont été faites au moyen des techniques d'analyse chimique les plus récentes, notamment la chromatographie en phase gazeuse et détection par spectrographie de masse et par chromatographie en phase gazeuse et détection d'émission atomique. Il a été déterminé que le dichlorométhane constitue le meilleur solvant de remplacement du fréon, qui est recommandé à l'heure actuelle. Il y a une quantité substantielle de composés organosoufrés dans l'effluent, dont la structure et les effets sur le milieu sont inconnus. En outre, il a été montré que l'effluent subit des changements subtils lorsqu'il est entreposé, et cela pourrait avoir des effets sur les tests de toxicité.

ABSTRACT

A number of refinery effluent and "produced water" samples were subjected to extraction by a variety of organic solvents of different polarities. These were then analyzed by GC/MS and GC/AED. The studies showed that acidification of the samples enhanced the extraction and reduced the difficulties caused by emulsions. Dichloromethane was the solvent of choice as it provided the most fine structure in the resulting chromatograms as well as providing optimum extraction capabilities as shown by the individual PAH and n-alkane concentrations. The complexity and response observed in the S-chromatograms of the effluent extracts indicate a large number of S-containing compounds present. Changes were noted in the S-chromatograms of the effluent during storage. The lack of reproducibility of the results of the extracts collected during the same sampling period suggests the heterogeneity of the effluent. The C chromatogram profiles were compared to the S and H chromatogram profiles and the O and P chromatograms were obtained.

RÉSUMÉ

Un certain nombre d'échantillons d'effluents de raffinerie et «d'eau produite» ont été soumis à une extraction par divers solvants organiques de polarité différente. Les fractions ont ensuite été analysées par CG/MS et par CG/DEA. Les résultats montrent que l'acidification des échantillons améliore l'extraction et atténue les problèmes attribuables aux émulsions. Le dichlorométhane a été le solvant de choix car c'est celui qui permet d'obtenir les chromatogrammes aux structures les plus détaillées et qu'il offre un pouvoir d'extraction optimal, comme on l'observe par les concentrations en HAP et n-alcanes individuels. La réponse obtenue et la complexité des chromatogrammes S des extraits d'effluents révèlent la présence d'un grand nombre de composés soufrés. On observe des changements dans les chromatogrammes S des effluents à mesure que se prolonge le stockage. L'impossibilité de reproduire les résultats à partir des extraits prélevés au cours d'une même période d'échantillonnage sont révélateurs de l'hétérogénéité de l'effluent. Les profils des chromatogrammes C ont été comparés à ceux des chromatogrammes S et H et les chromatogrammes O et P ont été obtenus.

INTRODUCTION

Effluents from chemical processes contain complex mixtures of organic compounds. One measure of the amount of organics present in the effluents is grease and oil. This parameter has been measured for many years and is usually determined by weight or by infra red spectroscopy after extraction of the aqueous effluent. The organic extraction solvent varies from jurisdiction to jurisdiction, and is also dependent on the analysis method. For the IR determination the usual solvent is CCl_4, as there is no C-H stretch vibrations from the solvent occurring at the wave length used for the measurement. When practising the measurement of grease and oil by the gravimetric method, the preferred solvent can be hexane, toluene, dichloromethane (DCM), or freon. As the solvent must be evaporated before the final weight is taken, some of the volatiles are evaporated with the solvent. Freon, having a high volatility and low boiling point, was often the preferred solvent. However, because of environmental concerns, freon is currently being phased out of use. The other commonly used solvents vary in their extraction efficiency.

Oil and grease is a bulk measurement which provides little information as to the composition of the extract. Also various solvents can be more efficient at extracting certain classes or types of solutes. The object of this study was to extract a number of petroleum related effluents with a number of solvents and examine the composition of the extracts. This was accomplished by GC/mass spectrometry (GC/MS) and GC/atomic emission detector (GC/AED). GC/MS is one of the major tools available to the analytical chemist for identification of unknown compounds. The tandem GC/AED instrument is a more recent innovation which provides information on the elemental composition of a compound. Of particular interest are S- and N-containing compounds which are naturally occurring in oil. Most oil related studies are focused on the hydrocarbons of which there can be several thousand in a given sample. The occurrence of sulphur compounds in crude oil is known and many have been identified usually by GC/MS (1). The occurrence of sulphur compounds in petrochemical effluents is less well documented. With fewer of

these compounds present coupled with the capability of detecting them with an element specific detector, these compounds were monitored in the effluent studies undertaken. In addition, these sulphur compounds, particularly the polycyclic aromatic sulphur heterocycles (PASHs) which share the carcinogenic and mutagenic properties of the PAHs (2), may give rise to health problems. Less is known of the nitrogen containing compounds in the effluents and these were monitored for in the samples.

Two types of effluents were used in this study. One was "produced water", the residual water remaining after crude oil is prepared for transport either by pipeline or other means. It includes excess water in the crude oil as well as water used to treat the oil to remove other impurities such as sulfur. The other type of effluent was from oil refineries. The extraction solvents used were hexane, dichloromethane and toluene. These solvents were selected as they cover a range of polarities.

METHODS

(a) Produced Water

Produced water samples were collected from a site near Edmonton Alberta in 1 L bottles and shipped on ice to Burlington where they were kept in a cold room. These were extracted within four days of receipt. The contents of a bottle were placed in a 2 L separatory funnel and shaken with three 50 mL aliquots of the solvent. The bottle was rinsed three times with the solvent and this added to the organic phase. If a persistent emulsion occurred, it was broken by acidifying the phases. The combined organic phase was then reduced to a volume of 1 mL. This was placed into an injector vial in preparation for analysis. The solvents used were reagent grade toluene, dichloromethane, and hexane. To measure the amount of insoluble material, the supernatant solvent was poured off the particulate material, and the remaining material was washed into a tared beaker which and air dried in a fume hood. After the solvent had evaporated, the beaker was weighed.

(b) Refinery effluents

The effluents from two refineries were sampled for biological and chemical analysis. The Shell refinery at Corunna (near Sarnia) Ontario was sampled twice. The other, the PetroCanada Lake Ontario Refinery, Mississauga Plant, now referred to as Lake Ontario Refinery, Lubricants Centre was sampled once.

Refinery samples were collected in 1 L glass bottles, sampled at intervals during the collection of larger effluent samples for biological tests. These were returned to the laboratory and stored at 4°C overnight. The samples were extracted within 48 hrs after arrival in the laboratory. The solvent of choice was dichloromethane, but additional samples were extracted with the other solvents. Prior to extraction, the effluent was acidified to pH 2 with HCl. The extraction procedure was the same as that for the produced water samples. A minimum of 6 effluent samples were collected, but some of these were allocated for phenol and volatile compound analyses. In addition, several of these samples were used for bacterial and nematode experiments. During the last collection, a 30 L sample was collected then extracted in a large sample extractor.

The effluent sample for phenol analysis was extracted and analyzed using standard methods (3). Volatiles were examined using a purge and trap method (4).

Mass spectra analysis was accomplished using an HP 5970 MSD connected to an HP 5890 GC equipped with an HP7376A automatic sampler. The GC temperature program started at 50°C and was increased to 140°C at a rate of 10°C/min. at which temperature the ramp was reduced to 4°C/min. until 280°C was reached. This temperature was held for 10 min. for a total analysis time of 54 min. All samples were run in the selective ion monitoring mode to collect the appropriate masses for the 16 priority pollutant PAHs listed in Table 1. The additional masses 57 and 71 were monitored to simultaneously analyze for normal alkanes in the C_{12} to C_{26} range. For quantitation, external standards were used for both PAHs and the alkanes.

Most of the samples were re-ran on the GC/MS in the scan mode, collecting all masses in the M40 to M400 range, to obtain qualitative information of the major organic components in the extracts.

For CG/AED analysis, the HP 5921A atomic emission detector was in tandem with an HP5890B GC which too was equipped with an automatic sampler. All operating conditions were controlled by the HP AED Pascal workstation. The elements C, N, S, O, Cl, H and P were analyzed by recording the emission lines at 193.5, 174.3, 181.3, 777, 438, 448 and 171 nm, respectively. As various dopant gases were used for the different elements and the photodiode array covered the range of 250 nm, 4 different injections were required for each sample with each sample using the same temperature program on the gas chromatograph. The initial temperature of 90°C was maintained for 2 min. then increase at a rate of 30°C/min. until 200°C at which time the rate was decreased to 6°C/min. until the temperature reached 255°C and this temperature was maintained for 10 min. The solvent vent time on the AE detector was changed, depending on the solvent used for the extraction of the sample. This varied from 1.2 min. to 2.4 min for acetone and toluene. The solvent vent was turned off at 3.4 min. regardless of solvent. The vials containing the solvent for the syringe cleaning were changed to hold same solvent used in the extraction.

RESULTS

(A) Produced Water

GC/MS

Table 2 lists the sample designations used in the study including the solvent and pH used for extractions, the amounts of PAH's and n-alkanes determined from the GC/MS chromatograms and the amount of insoluble material remaining after the extractions. Samples S1(A&B) and S2 (A&B) are both dichloromethane extractions, one encompassing neutral-acid extracts and the other, acid-base extracts. The total PAHs and n-alkane concentrations, (Table 2) are similar for both S1 and S2, differing only by about

10%. Greater differences are noted from comparison of the other two solvents tested. The toluene extract exhibits the highest n-alkane values but the lowest PAH concentration values with reasonable agreement between its two replicates. The DCM extract has the lowest value for insoluble material and toluene has the highest. The extract from hexane has values intermediate to the other solvents, as was the concentrations of PAHs and n-alkanes. The PAH and n-alkane concentrations in the extracts show that the PAHs were represented chiefly by the lower molecular weight compounds and that the n-alkanes were present only in trace amounts (Fig. 1). The major components qualitatively identified in the extracts were phenols, phenanthrenes and dibenzothiophenes, as illustrated in Figs. 2 to 5.

GC/AED

The AED element specific chromatograms for C, H, and O for each solvent used are shown in Figs. 6 through 11. For each solvent the hydrogen chromatogram is plotted with the carbon chromatogram for comparison purposes. To achieve this, the C chromatogram is scaled down by a factor of about 100. For toluene and hexane (Figs. 8 and 10), the responses derived from the carbon channel for the interval of 6 to 11 min are close to saturation so the top of the unresolved continuum is almost flat. However some fine structure resulting from resolved peaks is noted on the top of the continuum. For DCM the C chromatogram generally follows the profile of the H chromatogram indicative of hydrocarbons. If the hexane extract was not as concentrated, the C chromatogram would follow the trace of the element specific H chromatogram. Two extra peaks are visible in the C and H chromatograms from the hexane extract at times greater than 16 min. These do not occur in the exacts from the other two solvents. Also there is more fine structure in the H specific chromatograms from hexane and toluene than DCM.

The element specific chromatograms (ESC) show a similar pattern independent of solvent. The unresolved continuum in the sulphur chromatograms has a maximum at greater retention times that observed in either the C- or H-ESCs. As observed for the C and H ESCs, there is more fine structure in the extracts from toluene and hexane than

DCM. No adjustment of the attenuation of the S signals were made when plotting the chromatograms. The maximum response for S from the extracts from toluene and hexane were 5X greater than for DCM. This is also true for the element specific C and H chromatograms.

The element specific oxygen chromatograms of S1 and S2 are shown in Fig. 12. They show that produced water contains oxygenated compounds at measurable concentrations.

(B) Refinery Effluents

GC/MS

Table 3 lists the amounts of n-alkanes and PAHs detected in effluent samples collected from refineries. Included in this table are 3 replicates, S6 & S7, S12 & S13, and S16 & S17. The sample designated S11 is a subsample taken from a large volume toxicity sample. This was collected during the same sampling from which S6 and S7 were taken. S14 is a hexane extract of the sample taken January 26 and S15 is a toluene extract of the same sample. S18 denotes a 30 L sample which was extracted with the Goulden large sample extractor. The PAH profiles in the effluents from the two refineries are shown in Fig. 13 and the n-alkane profiles in these effluents are depicted in Fig. 14. Total ion chromatograms of the effluents with specific compounds identified in each are shown in Figs. 15 and 16. Phthalates were identified in both effluents and cholesterol-type compounds were identified in the effluent extract of refinery B.

(ii) GC/AED

The element specific chromatograms for C, H and S are shown in Figs 17 through 22 for the first refinery visited on the two separate samplings with 1 and 3 and 2 and 4 being replicates from the first sampling using DCM as the extraction solvent All samples were extracted with DCM unless specifically stated. The C-specific chromatograms are co plotted with the H-specific chromatograms. Figs. 23 and 24 are the

C, H and S chromatograms for the second refinery sampled. Replicate samples were collected at intervals between the water collected for the bioassays. Figs. 25 and 26 contain the element specific chromatograms derived from a composite bioassay water sample analyzed 96 hrs. after preparing the composite. Two significant observations are obtained from these chromatograms. The first is that the H specific chromatogram follows the trace of the element specific carbon chromatogram of the same sample indicative of hydrocarbons. The second observation is that the maximum of the sulphur ESC occurs at the same time as the maximums of the C and H chromatograms obtained from the same sample. This is different than what was observed in the produced water extracts.

Figures 27 and 28 show the element specific chromatograms for C, H and S for refinery effluent extracted with toluene. Figures 29 and 30 show the element specific chromatograms for the same effluent but extracted with hexane.

The 30L effluent sample was specifically collected to analyze for dioxins. None were found.

The upper chromatogram in Fig. 31 is the element specific P chromatogram derived from the refinery A extract. The lower chromatogram in Fig. 31 is the P chromatogram for refinery B. The upper chromatogram is derived from the extract from a 1 L sample and the bottom chromatogram, from a 30 L sample extracted with a large volume extractor.

Using a separate method of analysis, no phenols were detected in any of the refinery effluent extracts. The O ESCs, which are not shown, contained no evidence of oxygenated compounds present in the samples. However at the low concentrations of individual compounds and because of the low sensitivity of the AED to O-containing compounds, they would not be detected.

DISCUSSION

Although the produced water analysis was a preliminary part of this study, several interesting observations were derived from the results and used for the other analyses. First, after the neutral extraction then acidification to pH 2, the acidic extraction resulted in a small additional amount of material from the aqueous phase (S1A and S1B). As seen from the results of sample S2B in Table 1, there were no measurable amounts of material extracted by the basic extraction after that sample had been extracted at pH 2. Acidifying to pH 2 before extraction reduces the problems related to emulsions formed at the solvent- water interface. As no measurable concentrations of components were detected in the basic extracts made after acidic extraction, all samples were acidified before extraction.

The weight of material in the flasks after extraction of the produced water samples show that DCM extracted the most material, when compared to the solvents of n-hexane and toluene. However, the chromatograms do not reflect this observation as the toluene extracts contained more measured n-alkanes as shown in Table 1. Although a particular solvent may extract more material, this may not be gas chromatographable.

The figures which illustrate the element specific chromatograms of C and H plotted together, the H chromatograms follow the same pattern as the C chromatogram. In the produced water and refinery effluent samples analyzed in this study, the original material was petroleum based. This means that there is a complex mixture of alkanes, PAHs and cyclic compounds. Alkanes generally have formulae C_nH_{2n+x}, aromatics have formulae C_nH_{n+x}, whereas other compounds would have general formulae intermediate to these. If there was a major shift from one type of compound to another, it would be expected that the element specific H chromatogram would shift, higher or lower with respect to the element specific C chromatogram. For all samples analyzed, there is a general similarity of pattern between the C and H chromatograms.

There is a dissimilarity between the maxima of the unresolved continuum of the element specific C chromatograms for extracts from the produced water when compared with the continuum of the element specific S chromatogram of the same sample. For the chromatograms derived from the refinery effluents, the maxima for the element specific C and S chromatograms coincide.

One purpose of the study was to investigate any differences in the composition of the extracts when various solvents are used as the extraction media. Knowledge of the trends will assist interpreting data pertaining to the "grease and oil" measurement when the results obtained from different solvents are being compared. The Federal guidelines specify the use of petroleum ether (5), one jurisdiction may use DCM (6), whereas others may use n-hexane. The US EPA had selected freon as their extraction solvent, but this is being replaced as freon has deleterious effects on the environment. At present, a suitable replacement has not been found. Here the GC/MS was used to determine the chromatographic profiles of the two types of samples, produced water and refinery effluents. In addition the n-alkanes and PAHs concentrations were estimated using external standards. Each individual n-alkane or PAH is found only in small quantities in the crude oil and are found in the water extracts of the sample in trace quantities, usually about the detection limit of the instrument. The total concentrations of the n-alkanes or PAHs are the sum of several individual concentrations. These compounds represent only a small proportion of the total organics in the extracts. Accordingly, although the total values calculated for replicates in Tables 1 and 2 may differ, the actual differences of the total extract may be quite small. The duplicates collected January 25, (S12 and S13), serve as an example. One of the DCM extracts was found to contain PAHs at the same level as the toluene extract. The other DCM extract had PAHs at concentrations 5X less than its duplicate. The agreement of concentration values between the duplicates, S6 & S7, S12 &S13, or S16 & S17, in absolute values is not as good as one would prefer. An examination of the sulphur chromatograms reinforces this. Comparison of the chromatograms (S vs S, or C vs C) for S6 and S7 (Figs 18 & 20 and 17 & 19) shows that there is a difference of about 20% for the heights of the major peaks, with the sample

having the higher n-alkane content having the greater response. A similar comparison of chromatograms from S16 and S17, illustrates the same trend in the results. These differences can occur from two main sources. One is poor extraction and the other is non-homogeneity of the effluent. Similar extractions have been carried out many times during the course of other investigations (e.g. 7) with a high degree of precision. Also the duplicate results from the toluene extracts of the produced water exhibit good precision. Therefore the major source of variation is believed to be the variation of the samples. This is addressed in the recommendation section.

Different solvents were used to extract samples S14 and S15 as well as either S12 or S13 as denoted in Table 2. DCM extracts collected on Jan 26 (S12 and S13) contained more of the identified n-alkanes than the extracts from hexane or toluene. Toluene effectively extracted more of the PAH's than the other two solvents. The ESCs for the DCM extracts exhibited more fine structure than the hexane or toluene extracts.

As observed from the results derived from the MS analysis of the refinery effluents, there were more lower molecular weight compounds (PAHs and n-alkanes) in the effluent from the first refinery than the second. This suggests a more complete degradation of the organics in the latter. The presence of cholesterol-type compounds in this refinery effluent may be related to the degradation process.

The final set of chromatograms shown in the results section are the element specific phosphorus chromatograms (Figs. 29 and 30). The products of the refineries contain no measurable phosphorus, nor does the raw material, crude oil. These organo-phosphorus compounds are products of the treatment of the effluent, biological digestion. Comparison of the phosphorus chromatograms for the two refinery effluents shows that there are noticeable differences between the effluent of the two facilities.

Fig. 24 contains the element specific chromatogram of S from the composite water sample that was collected during the first site visit. Comparison of this

chromatogram with the similar chromatograms of the regular effluent samples (Fig. 18 or 20) shows several differences between the chromatograms. There is less fine structure near the maximum of the unresolved compounds and increases of the heights for several peaks. As the composite sample was allowed to sit in the dark at 4°C for 4 days before extraction, the changes are probably a result of bacterial action on the effluent.

For this study, the broad spectrum analysis approach was used in support of the biological studies. For the refineries in Ontario, two of which were sampled, data on a large number of target compounds have been accumulated by the provincial authorities of a number of years under the umbrella of the MISA program of the province of Ontario(6). This includes 65 chlorinated compounds, phenols and 14 PAHs. The target compound approach is useful as each of the chemicals has a known deleterious effect. GC/MSD was used primarily to detect the presence of these compounds. However very few of these compounds are detected in the refinery effluents. Also they represent less than 1% of those chemicals which are present. The GC/AED technique was used to complement the GC/MS method. Indeed the element specific S chromatograms show there are an abundant number of S containing organic compounds of which there is only one target compound contained in the MISA list. The impact of these compounds is generally unknown and they are not generally target compounds in any list of pollutants. This arose from the fact that they are generally difficult to detect. However, other studies have investigated the S-containing compounds in various fuels (8,9) and oil shale (10). This is the first study to specifically study the sulphur compounds in refinery effluents. The AED is the most sensitive C detector available. Using the capillary GC/AED in conjunction with GC/MSD provides a more detailed picture of the contents of the effluent than most other techniques.

For both types of material, Produced water and refinery effluents, DCM appears to be the solvent of choice.

RECOMMENDATIONS

1. The results from the analysis of a series of extracts taken from a large composite sample should be compared to the results of analysis for individual samples taken at the same time. This will show the degree of non uniformity of the effluent over a small time span as well as the precision of the extraction technique. It should be noted that refineries collect and analyze composite flow proportional samples rather than individual grab samples.

2. For the extraction and chromatographic analysis, samples must be taken from the composite sample used for biological testing. The samples should be taken from the composite at least before and after the biological testing. The results this year suggested changes in the effluent over time.

3. Additional water chemistry parameters should be measured on the composite samples, including, NH_3 and pH.

4. Samples which are reduced in volume such as those used for certain bacterial tests, should be analyzed for NH_3 as well as by GC/AED and GC/MS to ensure that the composition of the sample has not been altered.

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TABLE 1

PRIORITY POLLUTANT PAHs

NO.	M.W.	CODE	NAME
1	128	N	naphthalene
2	152	AY	acenaphthylene
3	154	AE	acenaphthene
4	166	F	fluorene
5	178	PH	phenanthrene
6	178	AN	anthracene
7	202	FL	fluoranthene
8	202	PY	pyrene
9	228	BaA	benzo(a)anthracene
10	228	CHR	chrysene
11	252	BbF	benzo(b)fluoranthene
12	252	BkF	benzo(k)fluoranthene
13	252	BaP	benzo(a)pyrene
14	276	IP	indeno(1,2,3-c,d)pyrene
15	278	DA	dibenzo(a,h)anthracene
16	276	BP	benzo(g,h,i)perylene

TABLE 2

PAHs and insolubles in produced water

Sample No.	Solvent	pH[a]	PAHs[b] (ug/L)	N-ALK (ug/L)	Insolubles (mg/L)
S1A	DCM	neut.	43.77	2.01	----
S1B	DCM	acid	1.45	----	----
S1(total)			45.22	2.01	NA[d]
S2A	DCM	acid	57.99	1.75	----
S2B	DCM	basic	----	----	----
S2(total)			57.99	1.75	73.8
S3	TOLUENE	acid	40.18	27.50	176.0
S4	TOLUENE	acid	40.43	36.50	189.8
S5	HEXANE	acid	51.79	8.93	109.8

a - acid: pH 2 (with HCl); basic: pH 11 (with NaOH)
b - sum of 16 priority pollutant PAHs
d - not available

TABLE 3

REFINERY EFFLUENTS
Summary of Jan. - March, 1993 data

Sample	Solvent	Sampling details	n-alkanes ug/L	PAHs ug/L
S6	DCM	Jan. 12, 1993. Refinery A,	11.75	0.145
S7	DCM	Sarnia, Ont.	7.53	0.039
S11	DCM	Same date, subsample of large toxicity sample	1.93	0.019
S12	DCM	Jan. 26, 1993	15.03	0.251
S13	DCM	Refinery A	8.45	0.054
S14	hexane	as S12 and S13	2.35	0.013
S15	toluene		4.24	0.273
S16	DCM	March 23, 1993	1.94	0.042
S17	DCM	Refinery B, Clarkson, Ont.	3.27	0.082
S18	DCM	Large sample extractor	1.87	0.34

TABLE 4

REFINERY EFFLUENTS
Summary of Jan. - March, 1993 data

Sample	Sampling details	n-alkanes ug/L	PAHs ug/L
S7	Jan. 12, 1993. Refinery A, Sarnia, Ont.	7.53	0.039
S11	Same date, subsample of large toxicity sample	1.93	0.019
S13	Jan. 26, 1993, Refinery A	8.45	0.054
S17	March 23, 1993, Refinery B, Clarkson, Ont.	3.27	0.082

CAPTIONS FOR FIGURES

Figure 1. PAH and n-alkane profiles from produced water extract (sample S2A, with DCM as solvent).

Figure 2. Total ion chromatograph of produced water extract S2A. Identified peaks :1, phenol; 2. cycloalkane; 3. methylphenol; 4. dibenzo-thiophene; 5. phenanthrene; 6. methyldibenzothiophene; 7. methyl-phenanthrenes; 8. di-methylphenanthrenes.

Figure 3. Phenoles in produced water extract (S2A).

Figure 4. Phenanthrenes in produced water extract (S2A).

Figure 5. Dibenzothiophenes in produced water (S2A).

Figure 6. Element specific chromatograms of C and H derived from produced water extract (S2A) - DCM extract.

Figure 7. Element specific S chromatogram of produced water (S2A), DCM extract.

Figure 8. Element specific C and H chromatograms of produced water - hexane extract.

Figure 9. Element specific S chromatograms of produced water - hexane extract.

Figure 10. Element specific C and H chromatograms of produced water - toluene extract.

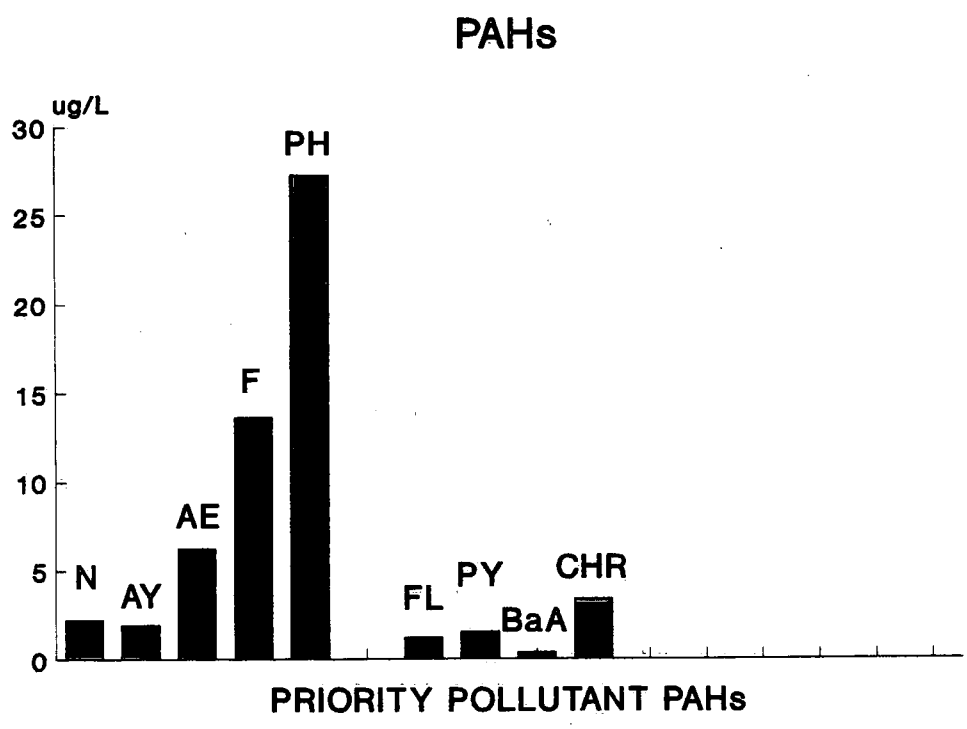
Figure 11. Element specific S chromatogram of produced water - toluene extract.

Figure 12. Element specific O chromatograms of produced water - S3 and S4.

Figure 13. PAH profiles of refinery effluent extracts (refineries A and B, samples S6 and S16).

Figure 14. N-alkane profiles in refinery effluent extracts (refineries A and B, samples S6 and S16).

Figure 15. Total ion chromatogram of refinery A effluent extract (S6). Identified peaks : 1. n-alkanes; 2. pristine; 3. phytane; 4. phthalates; 5. aliphatic acid esters.


PAHs
ug/L
30
25
20
15
10
5
0
N
AY
AE
F
PH
FL
PY
BaA
CHR
PRIORITY POLLUTANT PAHs

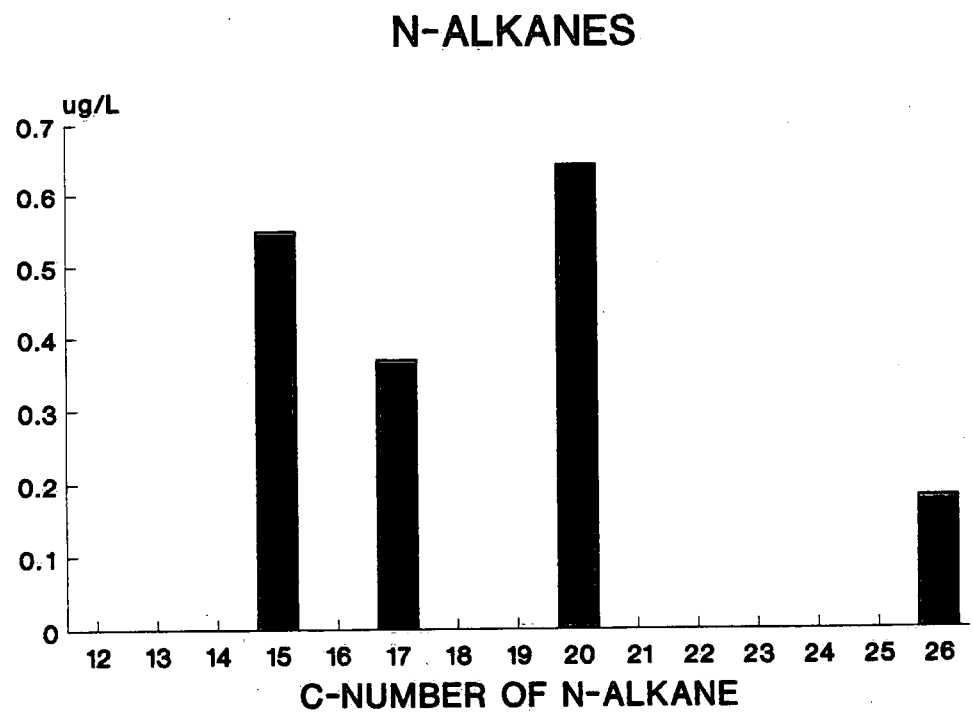

N-ALKANES
ug/L
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
C-NUMBER OF N-ALKANE

FIGURE 1.

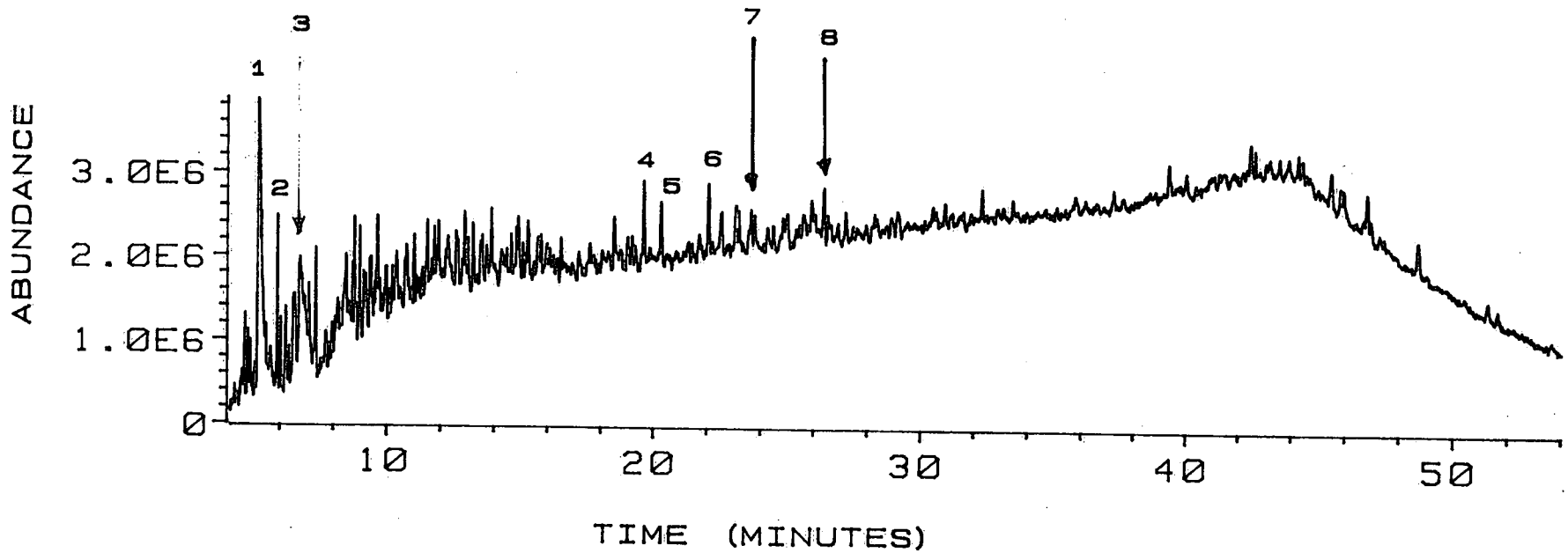

ABUNDANCE
3.0E6
2.0E6
1.0E6
0
1
2
3
4
5
6
7
8
10
20
30
40
50
TIME (MINUTES)

FIGURE 2.

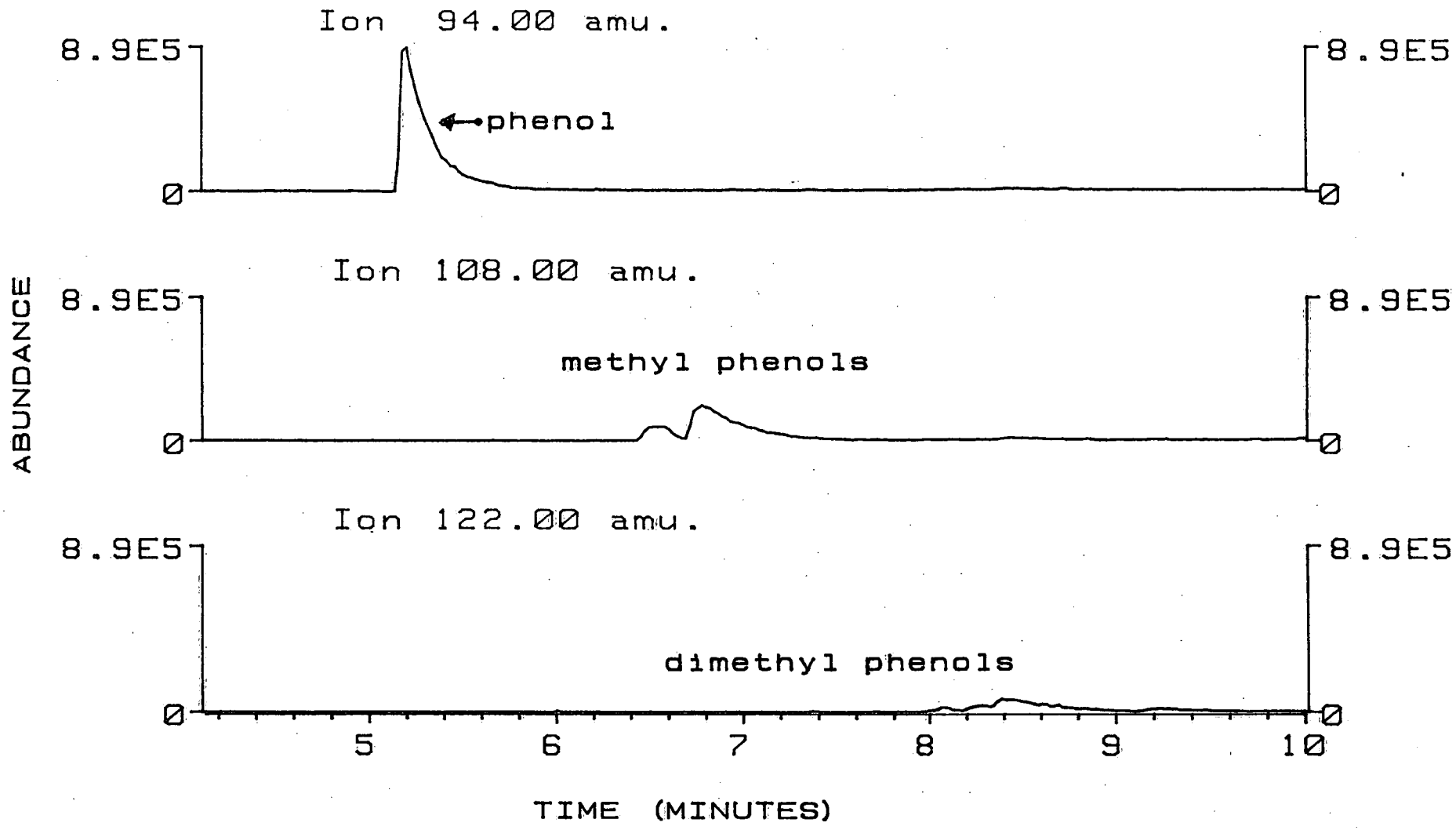

Ion 94.00 amu.
8.9E5
0
phenol
8.9E5
0
Ion 108.00 amu.
8.9E5
0
methyl phenols
8.9E5
0
Ion 122.00 amu.
8.9E5
0
dimethyl phenols
8.9E5
0
ABUNDANCE
5
6
7
8
9
10
TIME (MINUTES)

FIGURE 3.

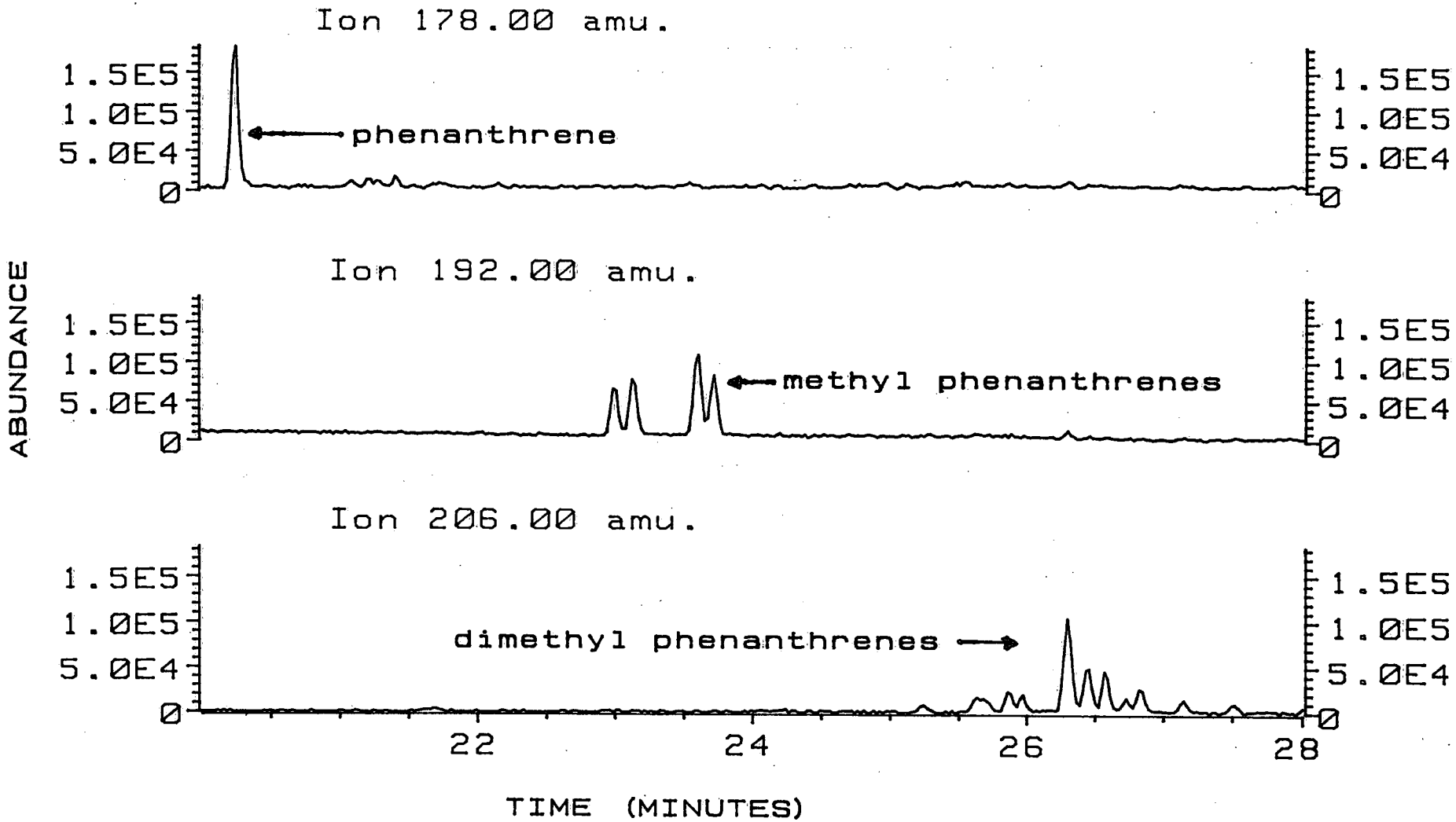

Ion 178.00 amu.
1.5E5
1.0E5
5.0E4
0
phenanthrene
Ion 192.00 amu.
methyl phenanthrenes
Ion 206.00 amu.
dimethyl phenanthrenes
ABUNDANCE
22
24
26
28
TIME (MINUTES)

FIGURE 4.

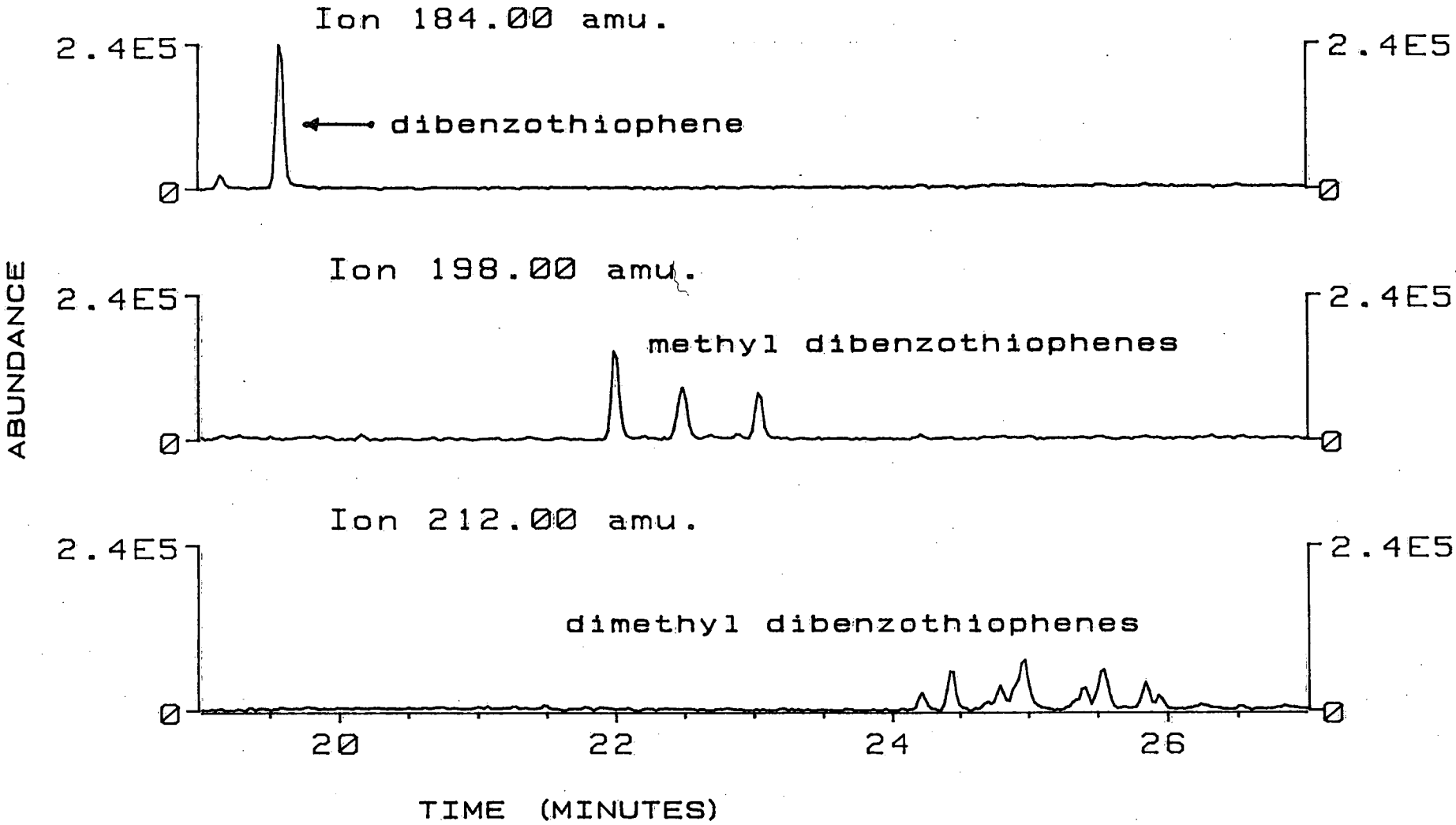

Ion 184.00 amu.
2.4E5
2.4E5
dibenzothiophene
0
0
Ion 198.00 amu.
2.4E5
2.4E5
methyl dibenzothiophenes
0
0
Ion 212.00 amu.
2.4E5
2.4E5
dimethyl dibenzothiophenes
0
0
20
22
24
26
TIME (MINUTES)
ABUNDANCE

FIGURE 5.

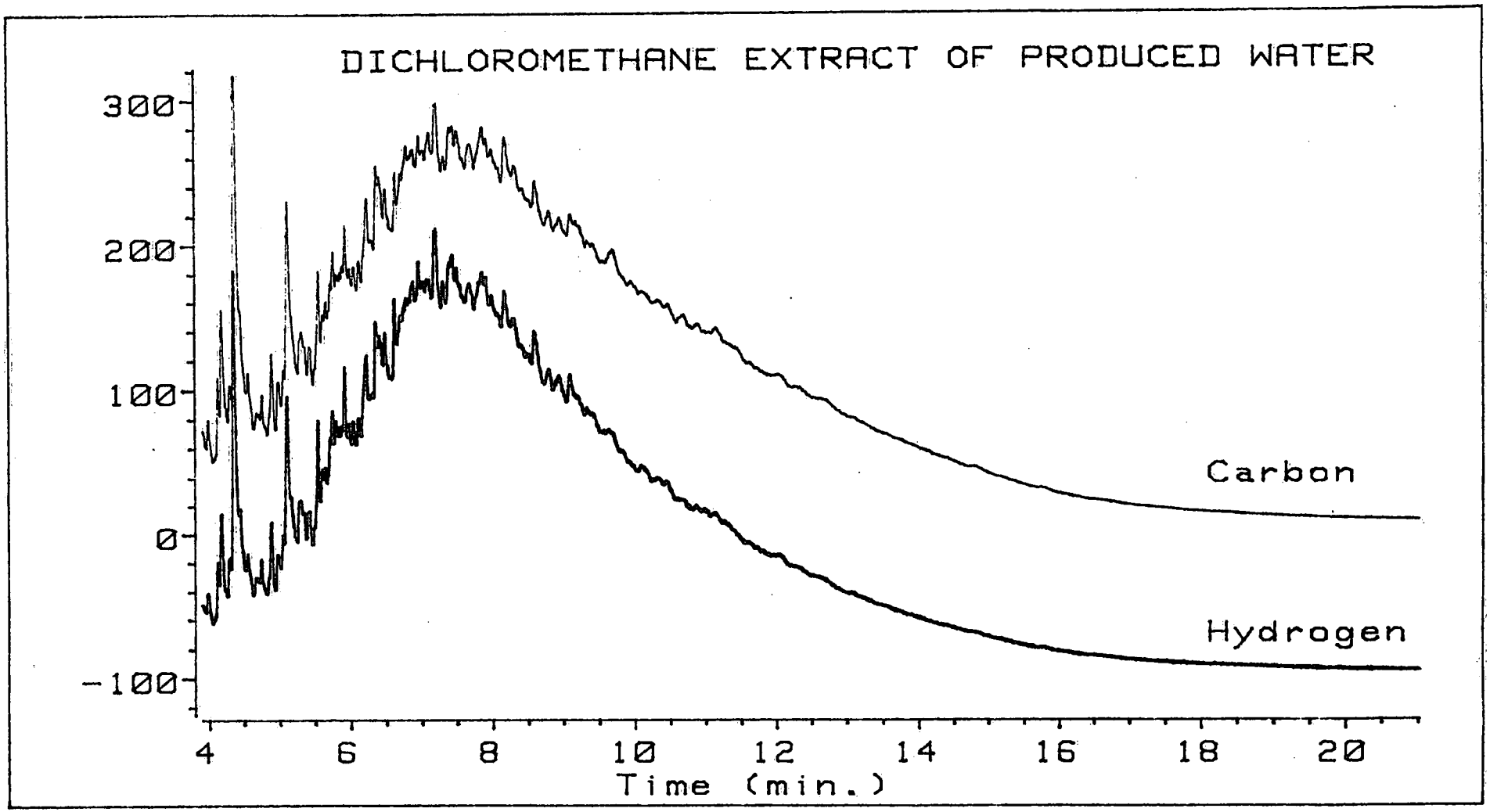

DICHLOROMETHANE EXTRACT OF PRODUCED WATER
300
200
100
0
-100
4
6
8
10
12
14
16
18
20
Time (min.)
Carbon
Hydrogen

FIGURE 6.

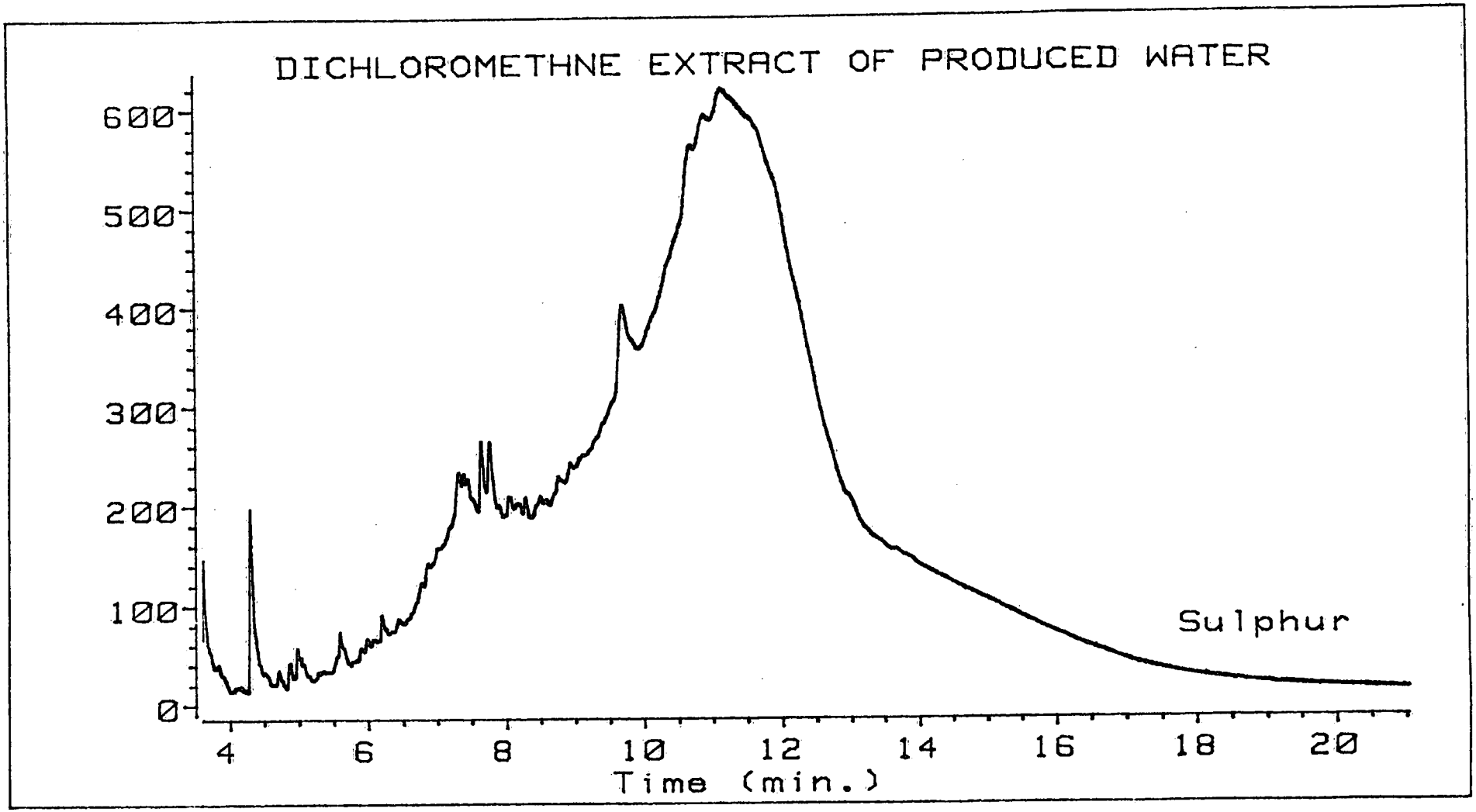

DICHLOROMETHNE EXTRACT OF PRODUCED WATER
600
500
400
300
200
100
0
4
6
8
10
12
14
16
18
20
Time (min.)
Sulphur

FIGURE 7.

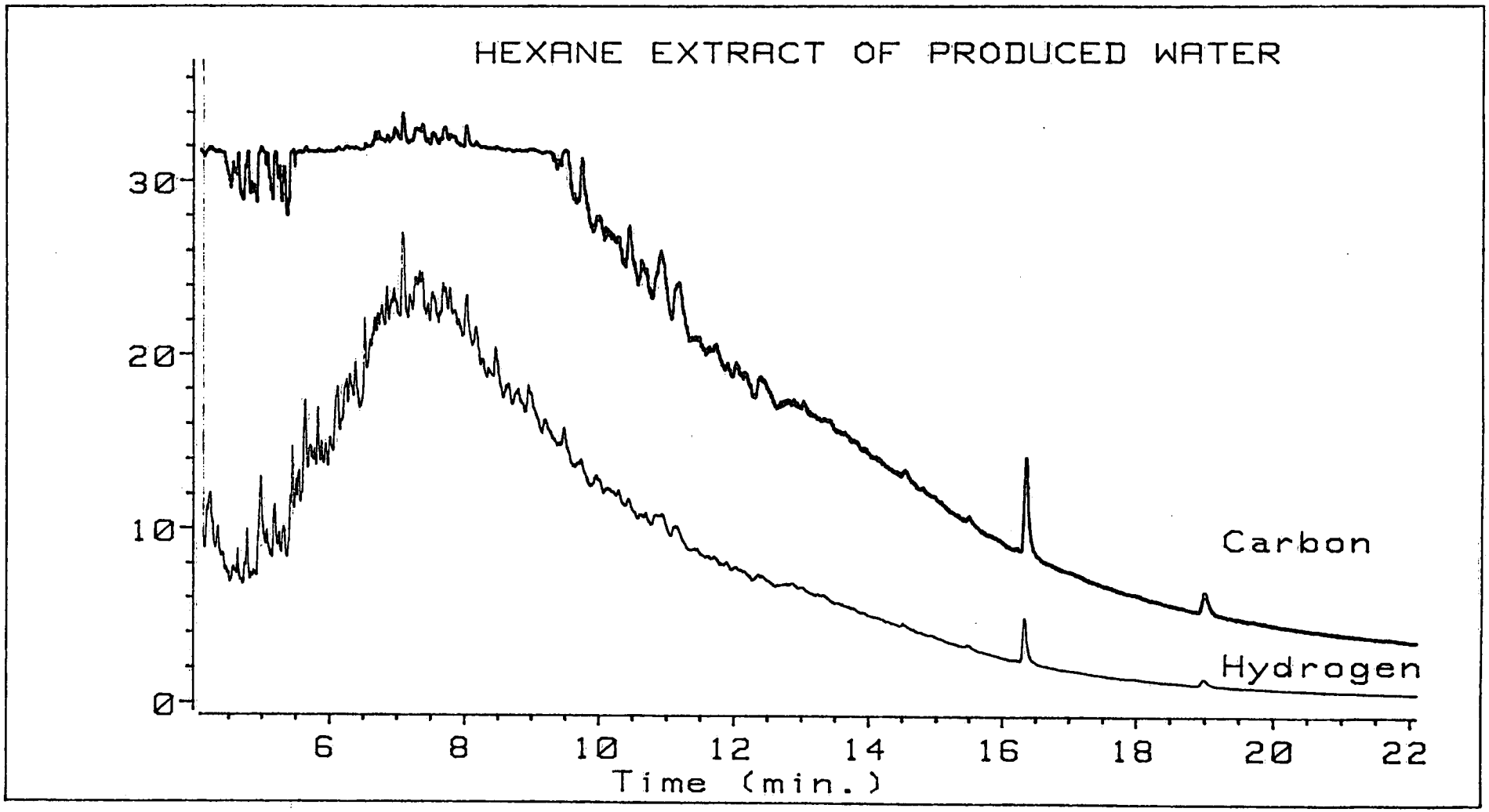

HEXANE EXTRACT OF PRODUCED WATER
30
20
10
0
6
8
10
12
14
16
18
20
22
Time (min.)
Carbon
Hydrogen

FIGURE 8.

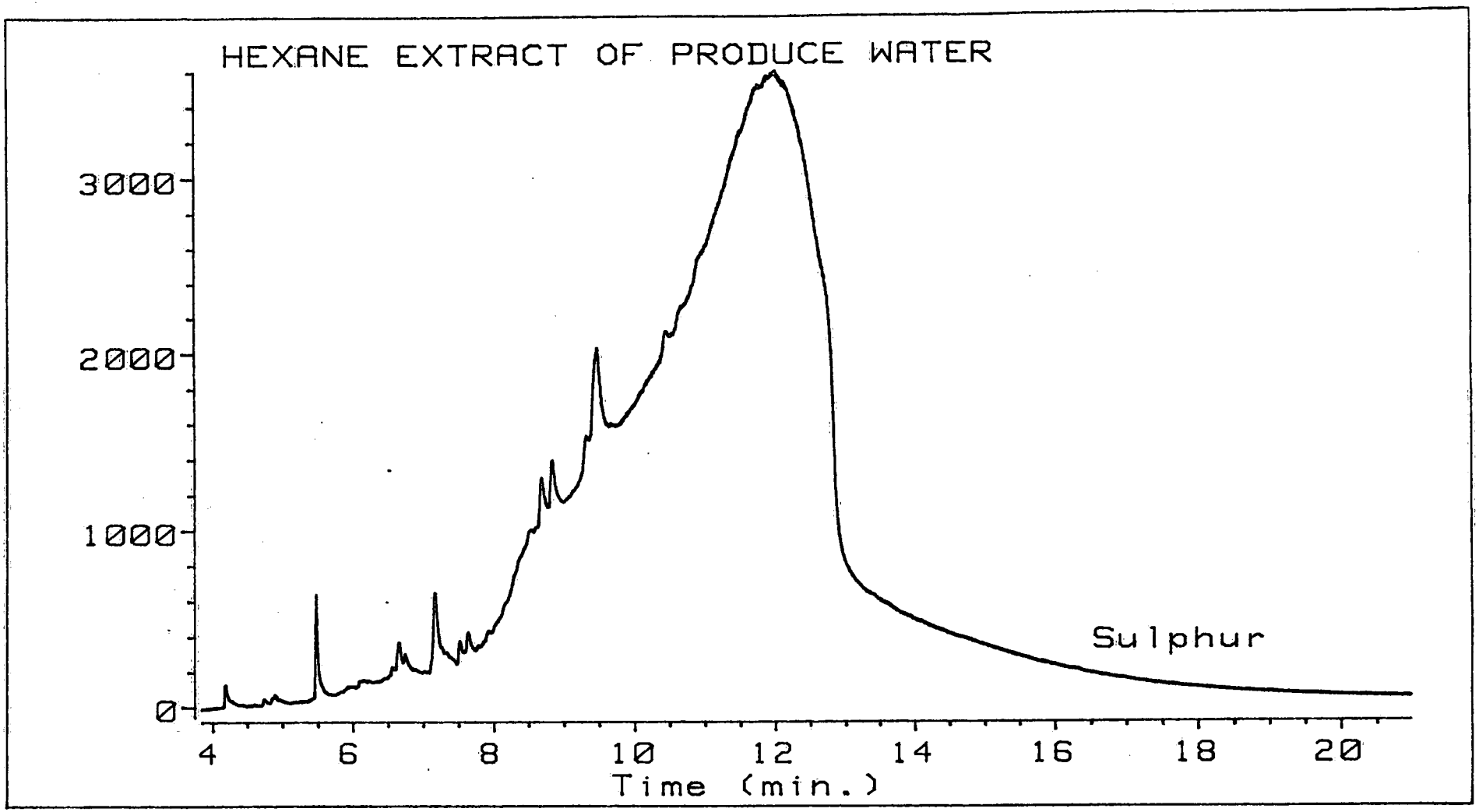

HEXANE EXTRACT OF PRODUCE WATER
3000
2000
1000
0
4
6
8
10
12
14
16
18
20
Time (min.)
Sulphur

FIGURE 9.

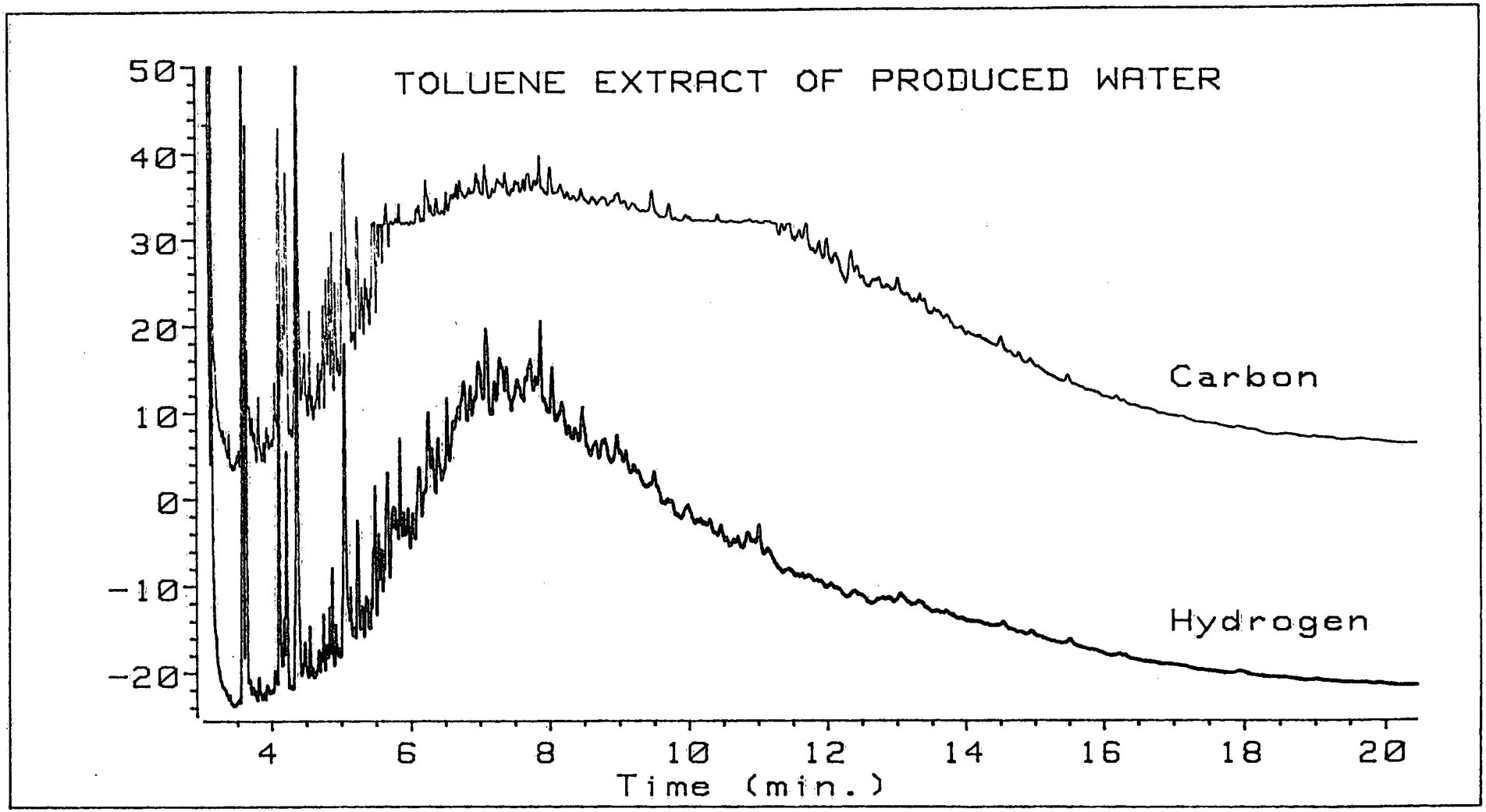

TOLUENE EXTRACT OF PRODUCED WATER
50
40
30
20
10
0
-10
-20
4
6
8
10
12
14
16
18
20
Time (min.)
Carbon
Hydrogen

FIGURE 10.

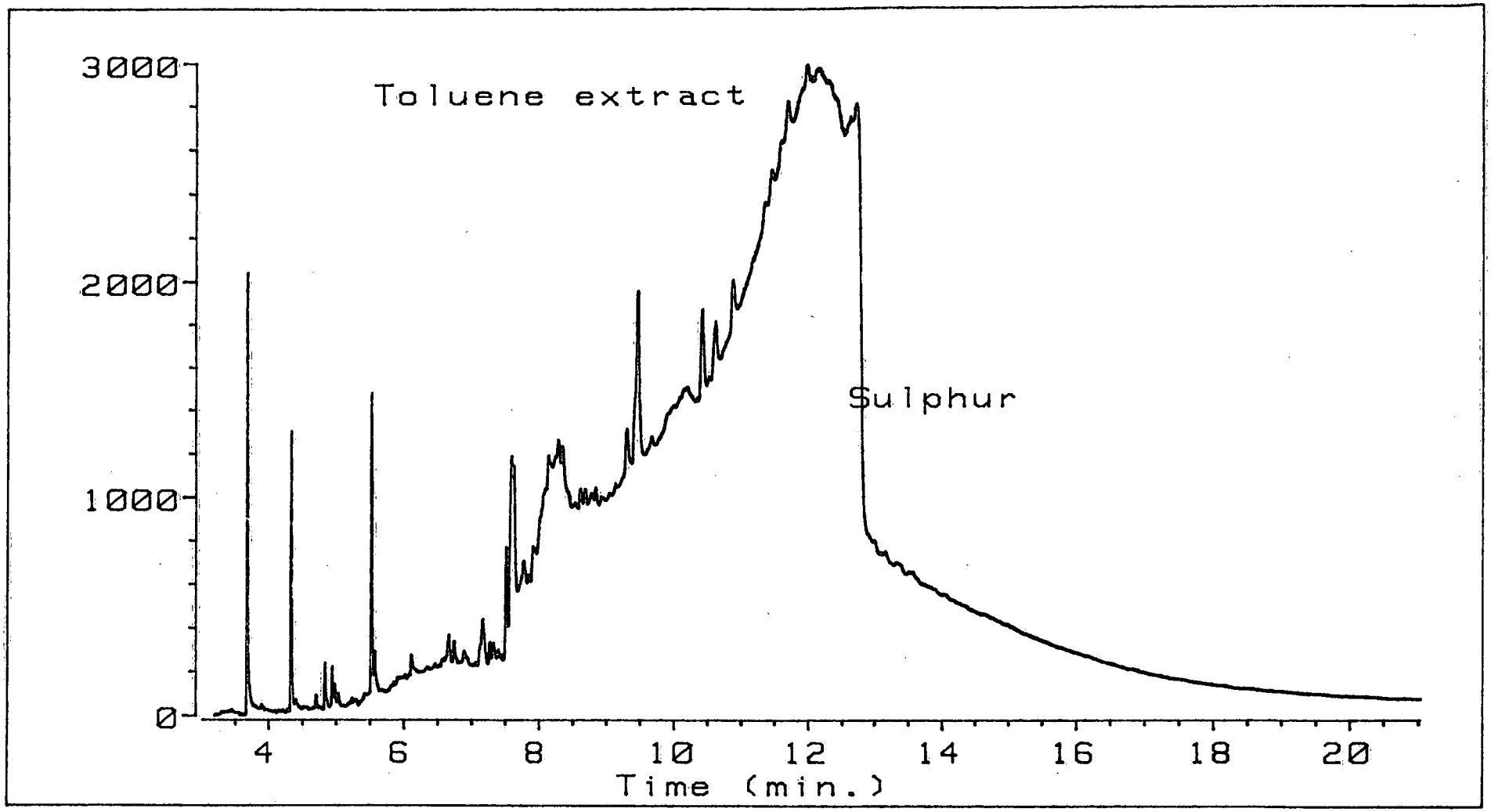

Toluene extract
Sulphur
3000
2000
1000
0
4
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 11.

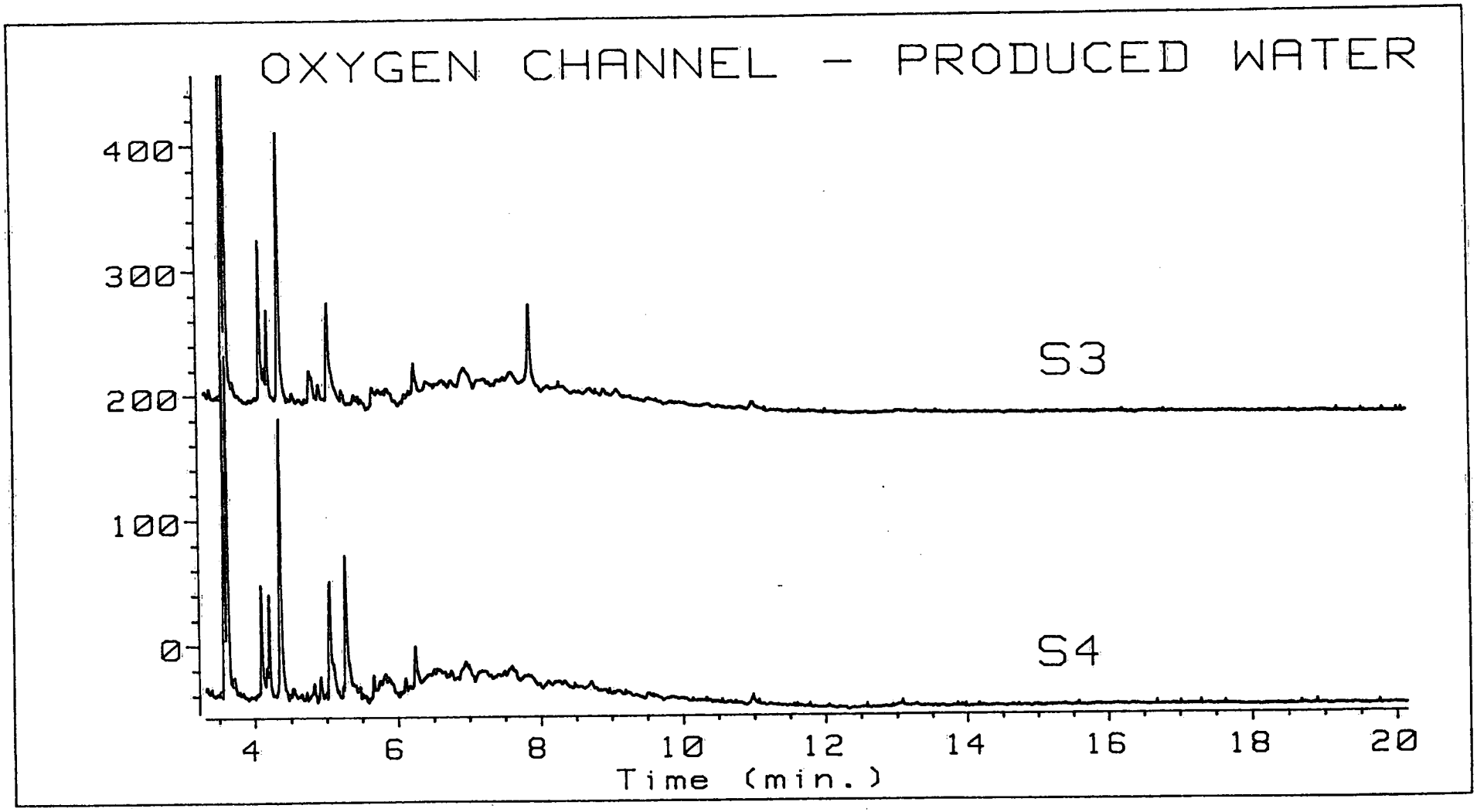
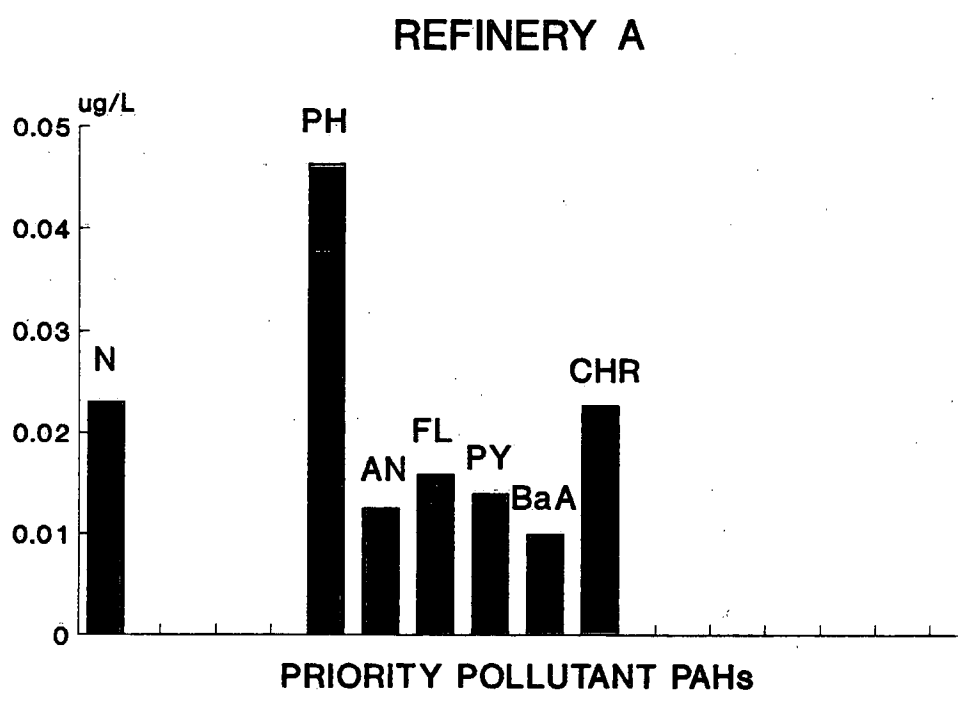

OXYGEN CHANNEL - PRODUCED WATER
400
300
200
100
0
S3
S4
4
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 12.


REFINERY A
ug/L
0.05
0.04
0.03
0.02
0.01
0
N
PH
AN
FL
PY
BaA
CHR
PRIORITY POLLUTANT PAHs

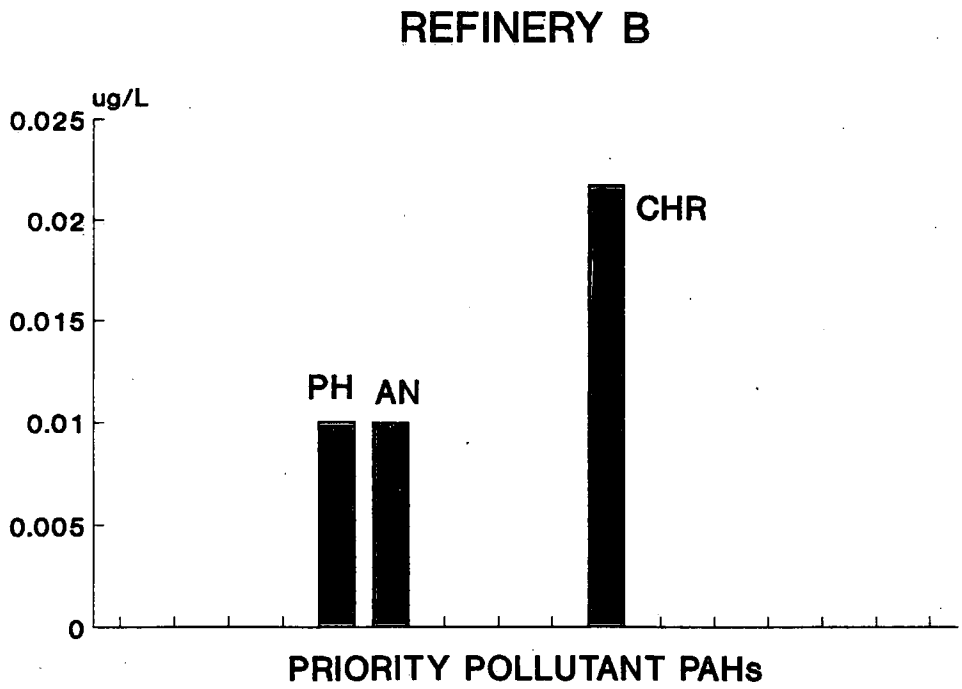
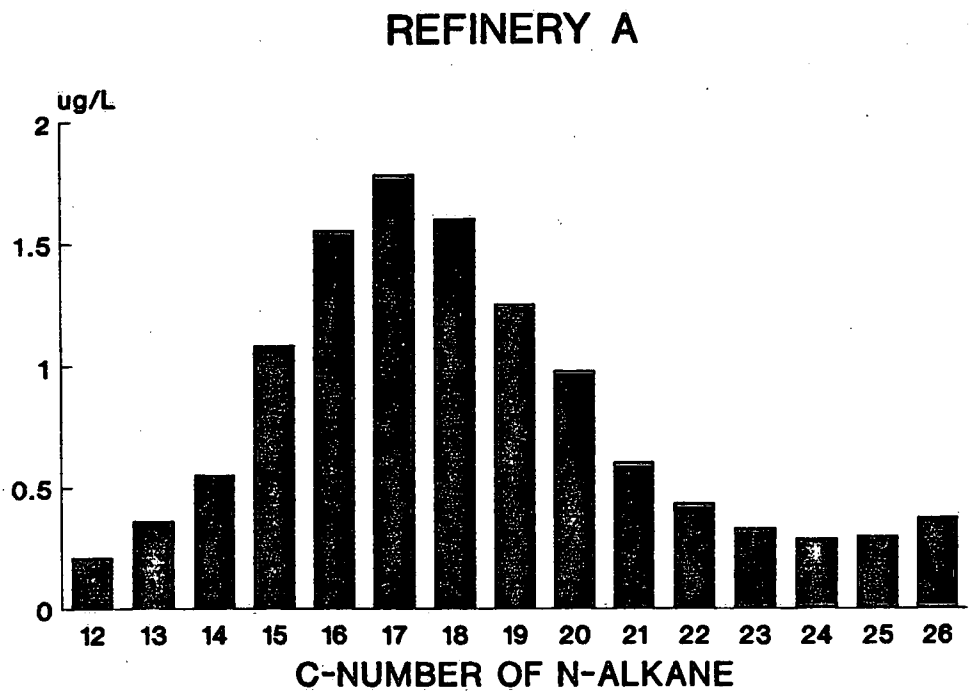

REFINERY B
ug/L
0.025
0.02
0.015
0.01
0.005
0
PH
AN
CHR
PRIORITY POLLUTANT PAHs

FIGURE 13.


REFINERY A
ug/L
2
1.5
1
0.5
0
12 13 14 15 16 17 18 19 20 21 22 23 24 25 26
C-NUMBER OF N-ALKANE

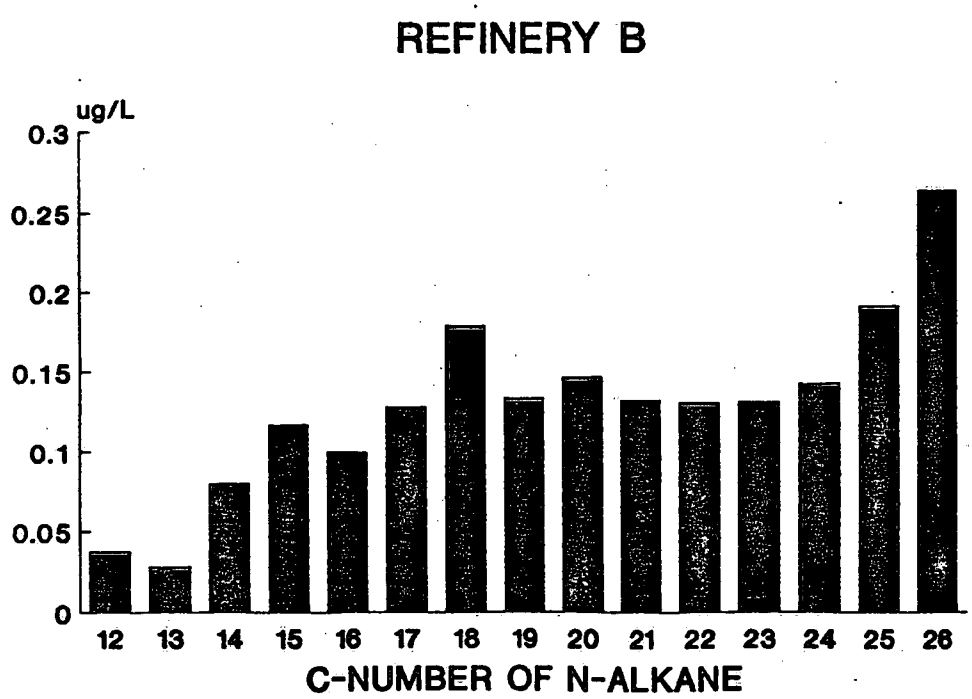

REFINERY B
ug/L
0.3
0.25
0.2
0.15
0.1
0.05
0
12 13 14 15 16 17 18 19 20 21 22 23 24 25 26
C-NUMBER OF N-ALKANE

FIGURE 14.

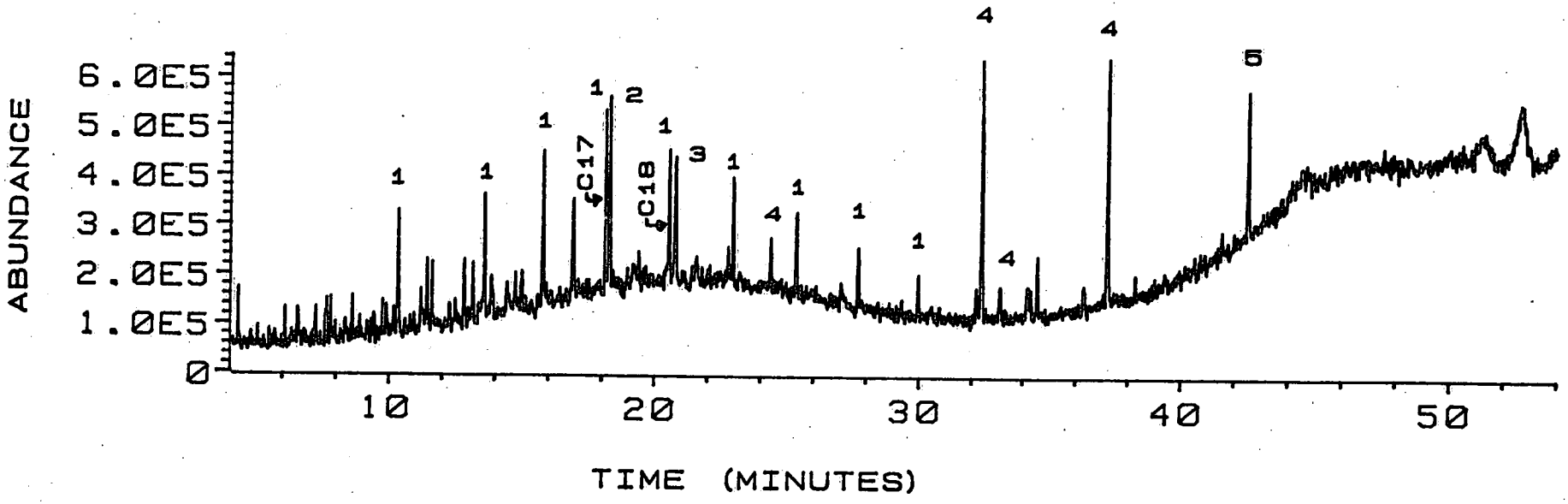

ABUNDANCE
6.0E5
5.0E5
4.0E5
3.0E5
2.0E5
1.0E5
0
C17
C18
10
20
30
40
50
TIME (MINUTES)

FIGURE 15.

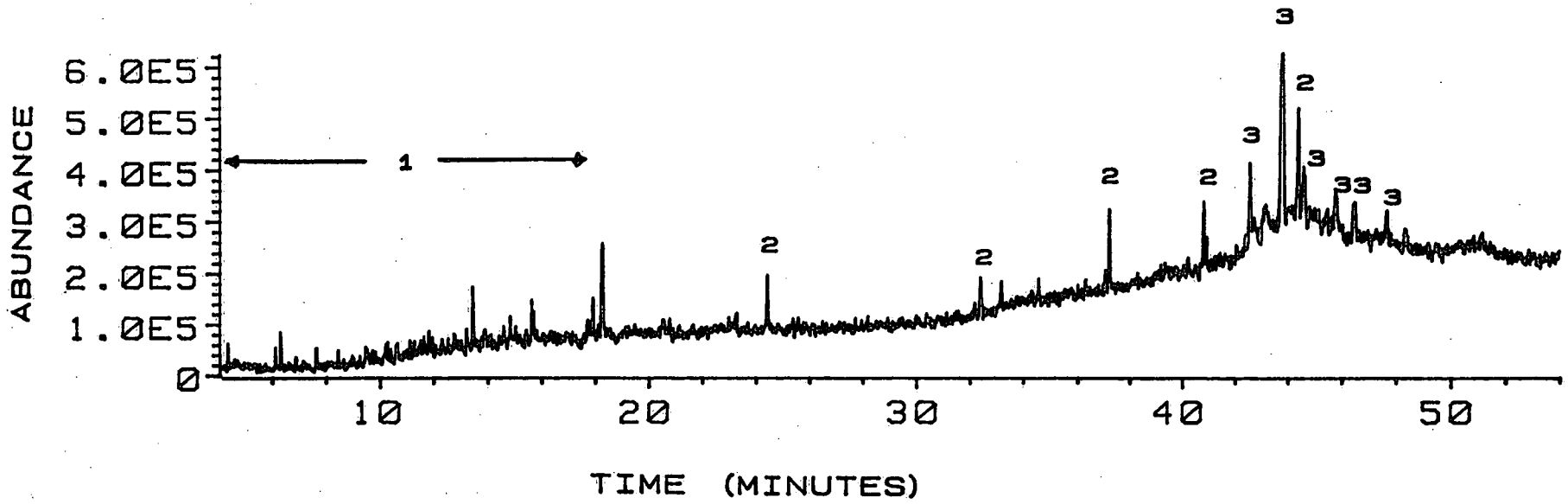

ABUNDANCE
6.0E5
5.0E5
4.0E5
3.0E5
2.0E5
1.0E5
0
1
2
2
2
2
3
3
2
3
3
3
3
10
20
30
40
50
TIME (MINUTES)

FIGURE 16.

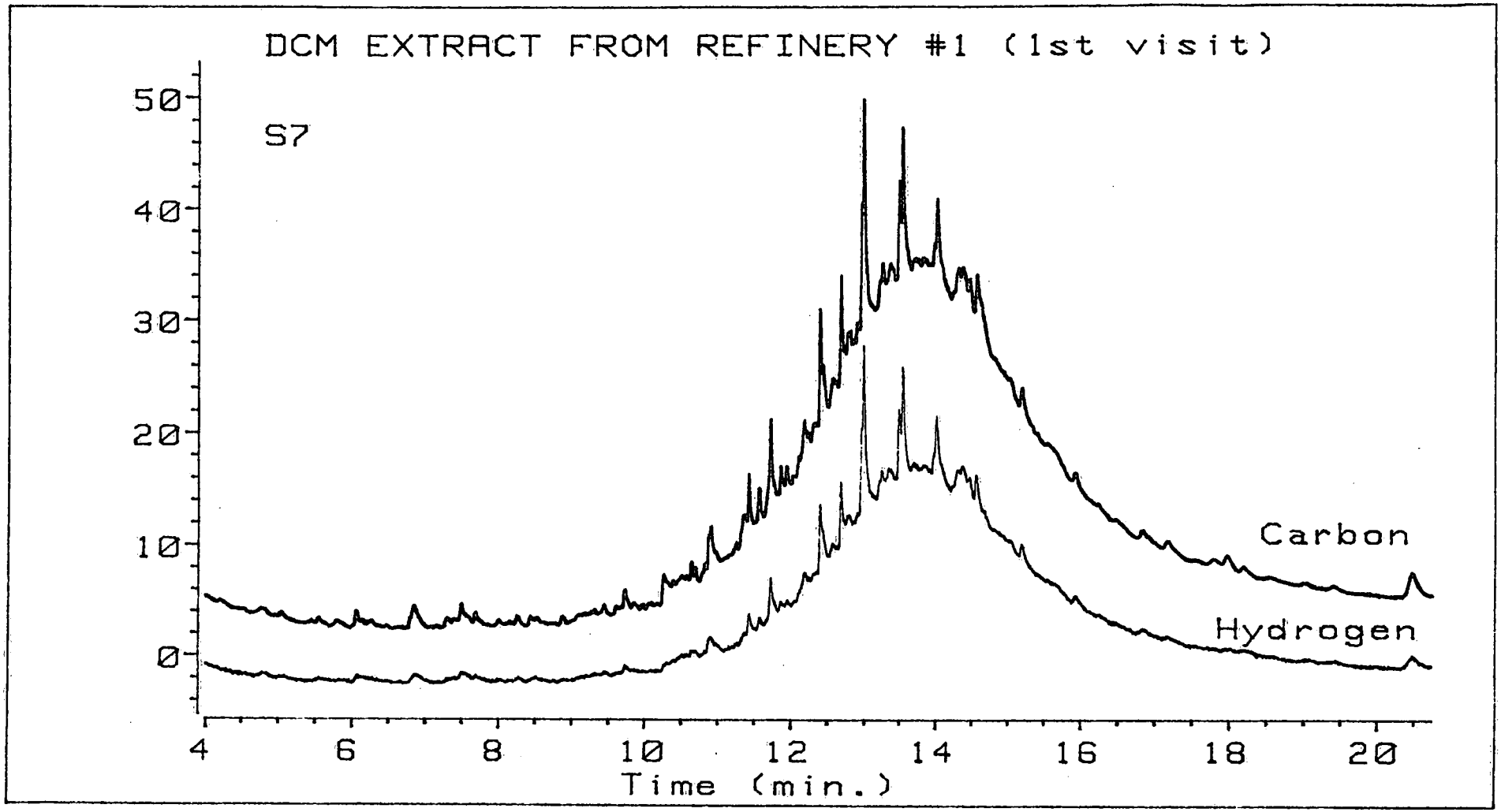

DCM EXTRACT FROM REFINERY #1 (1st visit)
S7
50
40
30
20
10
0
Carbon
Hydrogen
4
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 17.

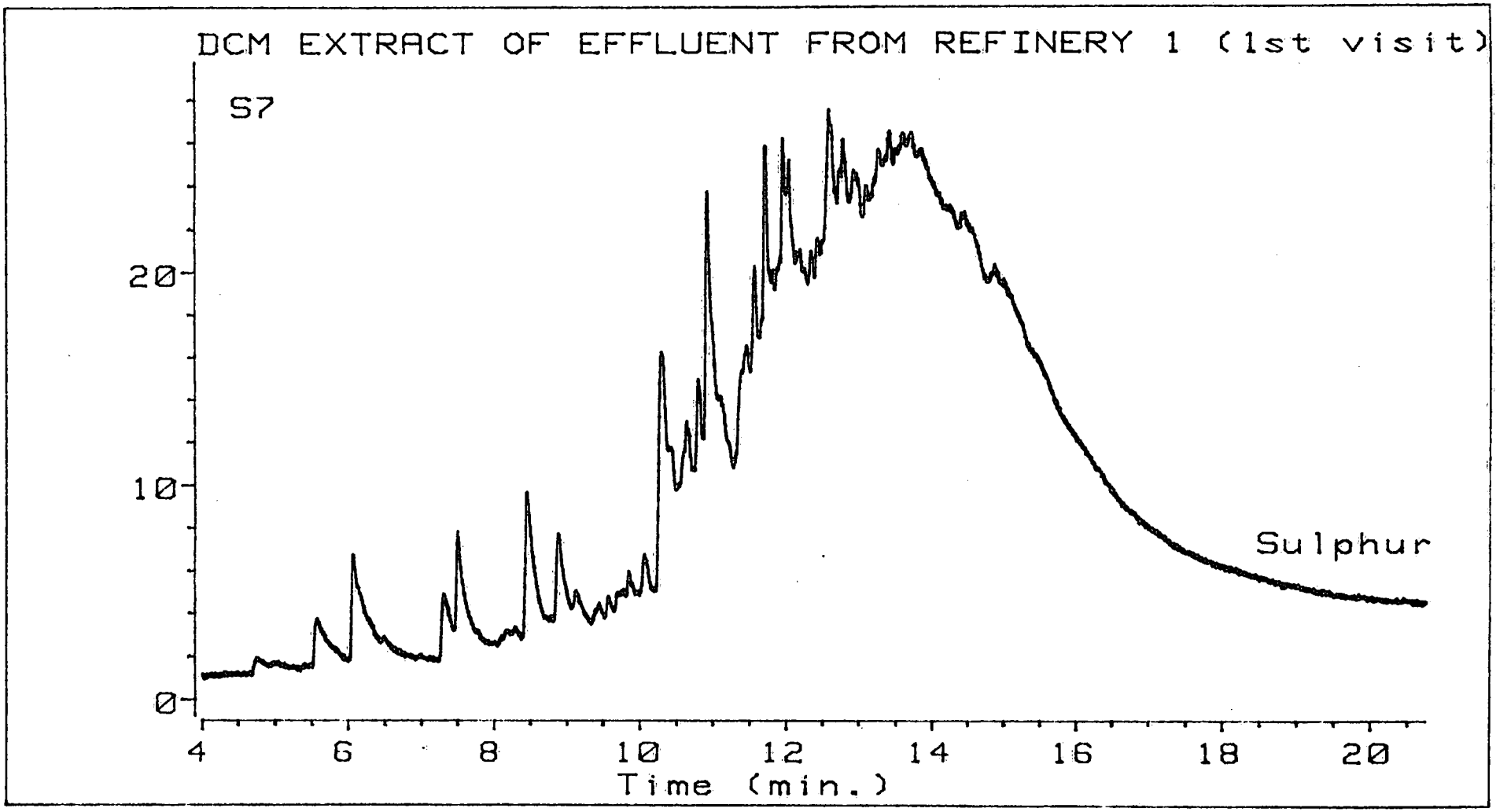

DCM EXTRACT OF EFFLUENT FROM REFINERY 1 (1st visit)
S7
20
10
0
Sulphur
4
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 18.

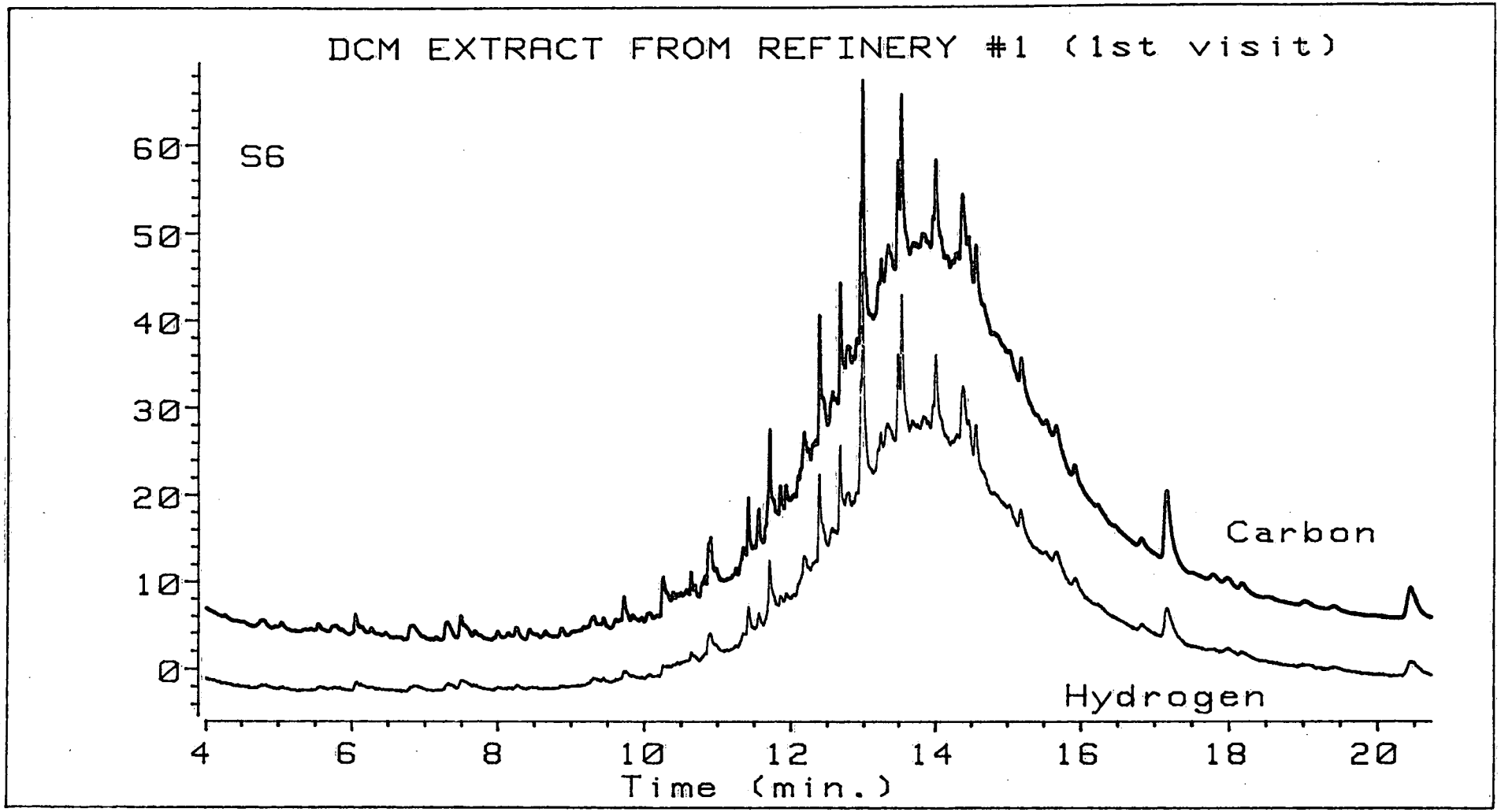

DCM EXTRACT FROM REFINERY #1 (1st visit)
S6
60
50
40
30
20
10
0
Carbon
Hydrogen
4
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 19.

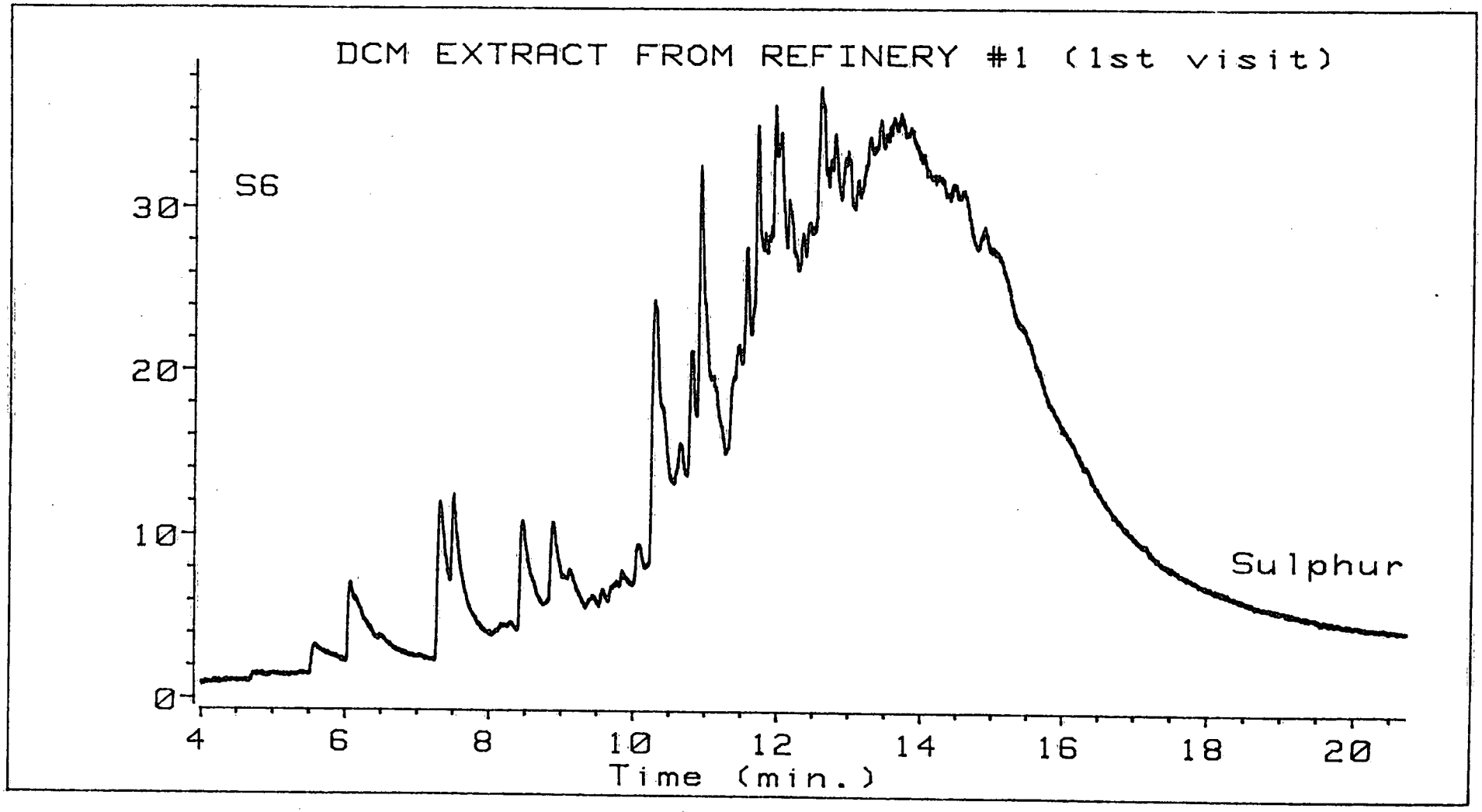

DCM EXTRACT FROM REFINERY #1 (1st visit)
S6
30
20
10
0
4
6
8
10
12
14
16
18
20
Time (min.)
Sulphur

FIGURE 20.

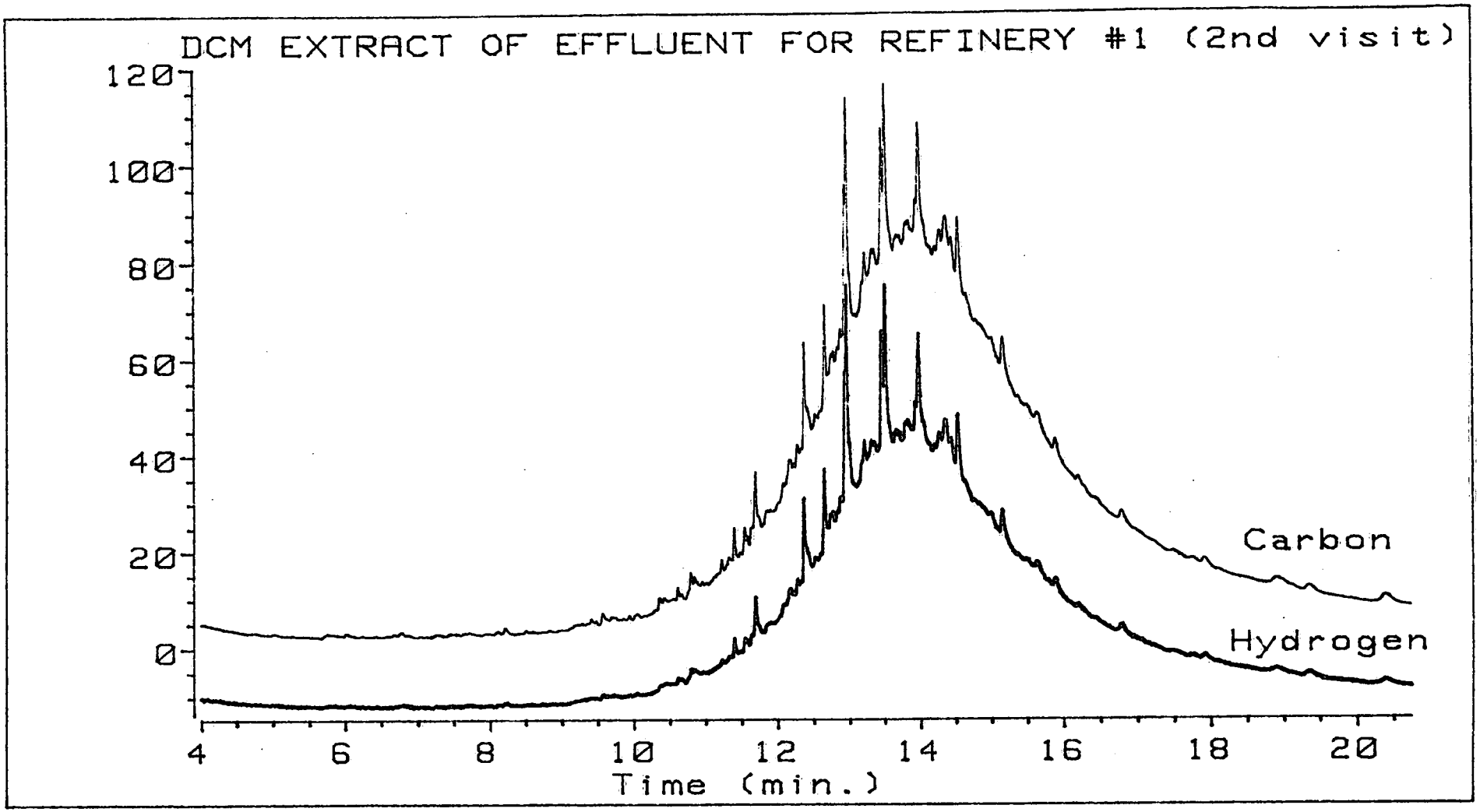

DCM EXTRACT OF EFFLUENT FOR REFINERY #1 (2nd visit)
120
100
80
60
40
20
0
4
6
8
10
12
14
16
18
20
Time (min.)
Carbon
Hydrogen

FIGURE 21.

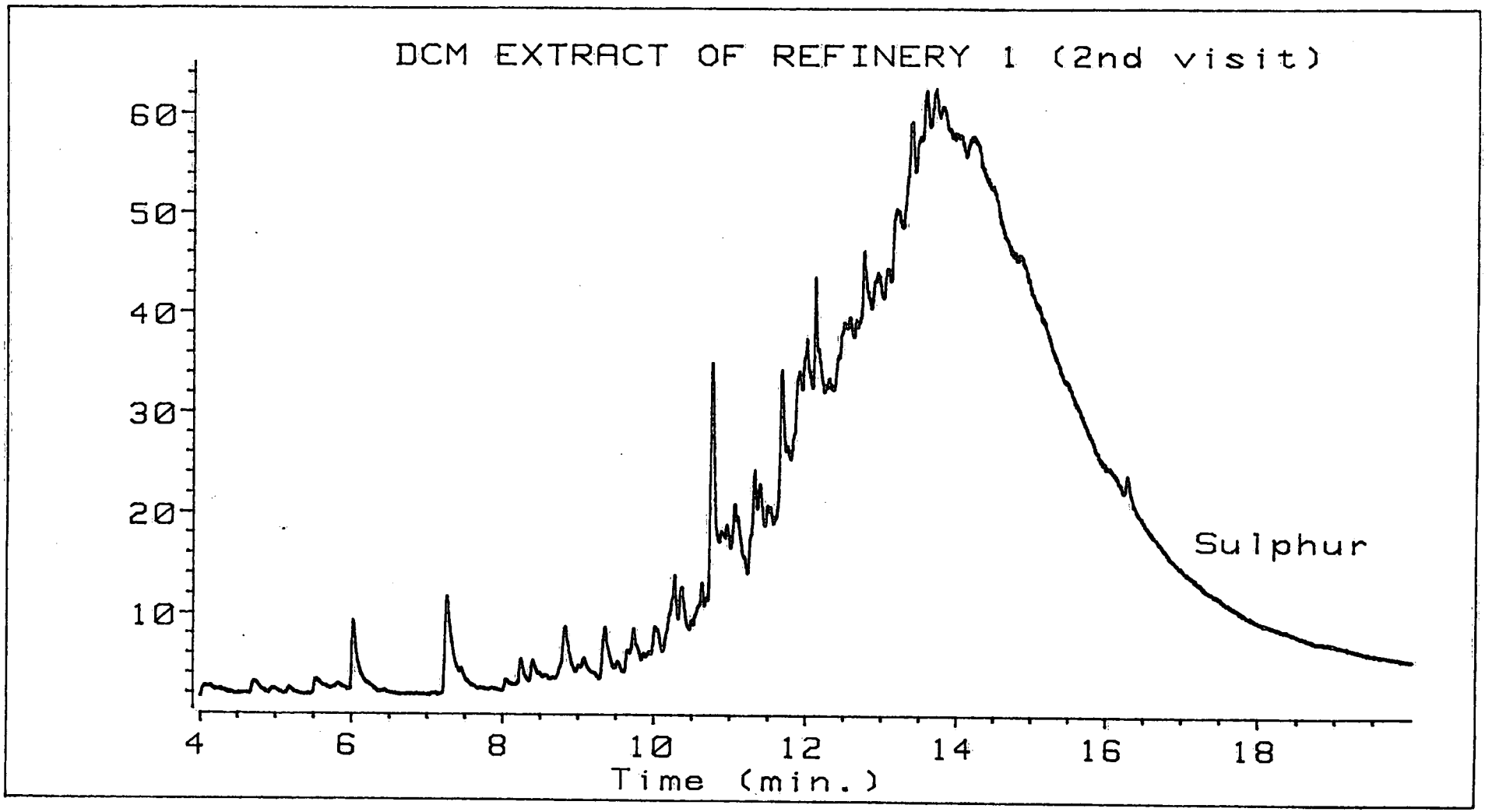

DCM EXTRACT OF REFINERY 1 (2nd visit)
60
50
40
30
20
10
4
6
8
10
12
14
16
18
Time (min.)
Sulphur

FIGURE 22.

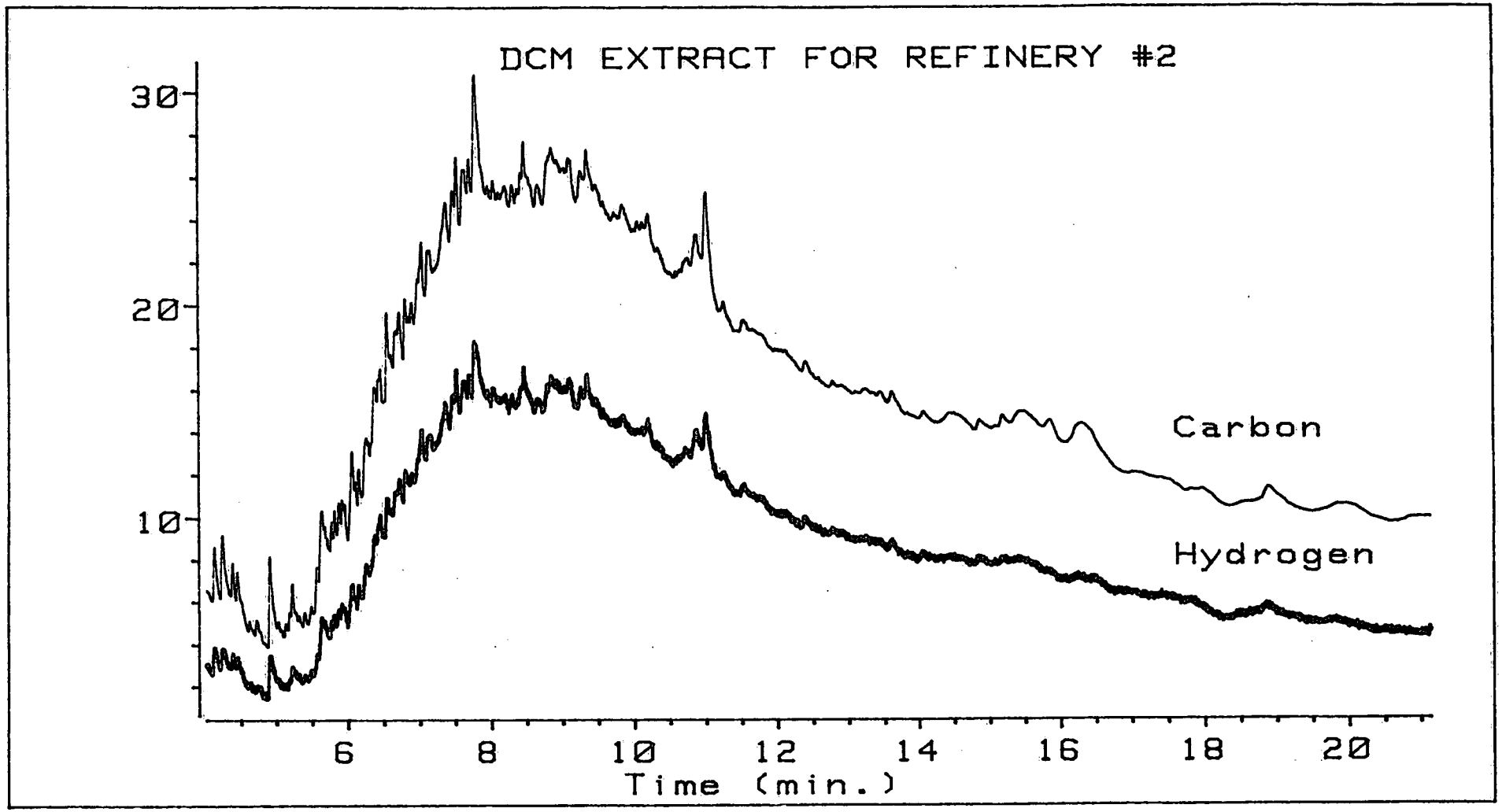

DCM EXTRACT FOR REFINERY #2
30
20
10
Carbon
Hydrogen
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 23.

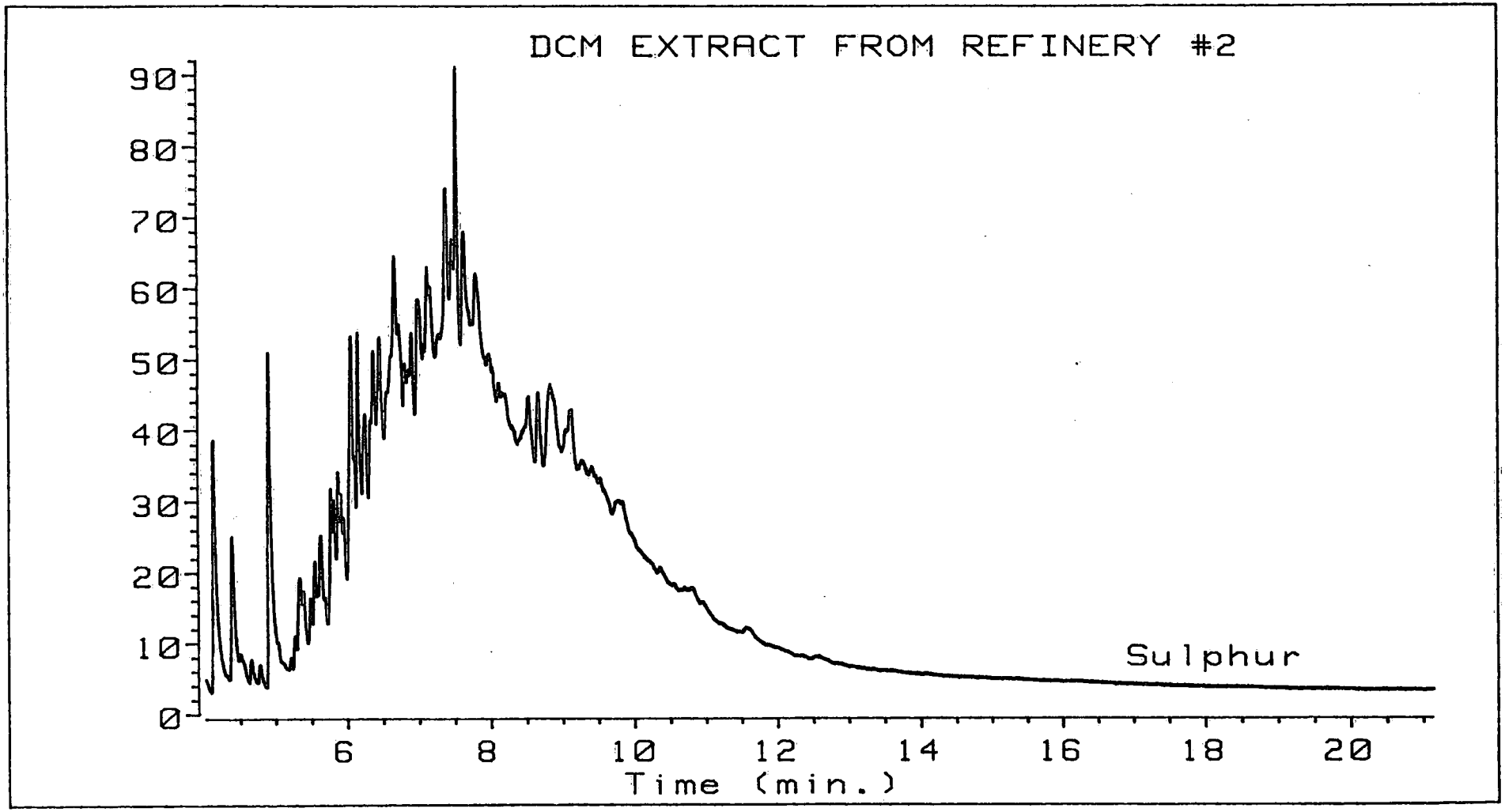

DCM EXTRACT FROM REFINERY #2
90
80
70
60
50
40
30
20
10
0
6
8
10
12
14
16
18
20
Time (min.)
Sulphur

FIGURE 24.

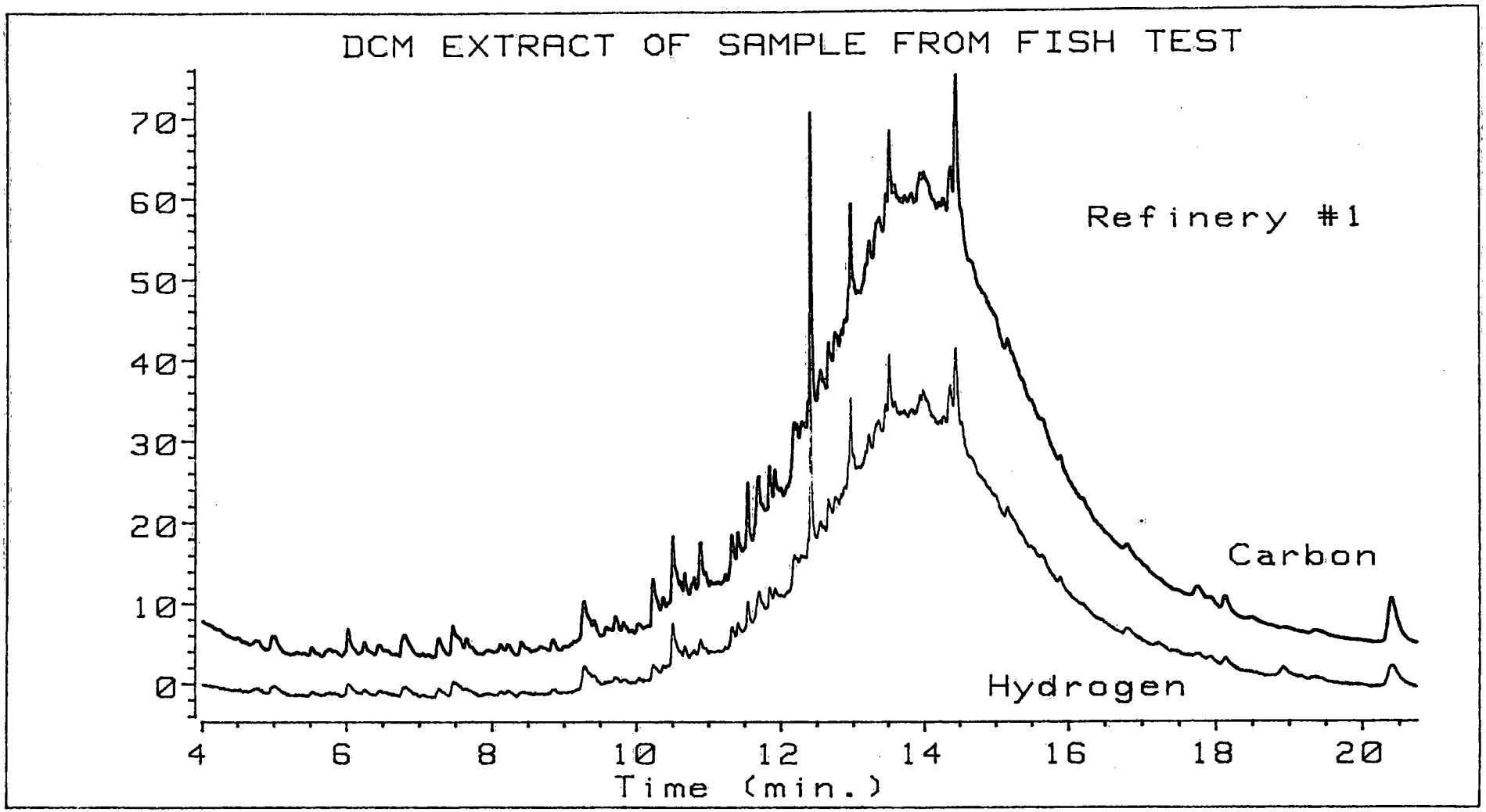

DCM EXTRACT OF SAMPLE FROM FISH TEST
70
60
50
40
30
20
10
0
Refinery #1
Carbon
Hydrogen
4
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 25.

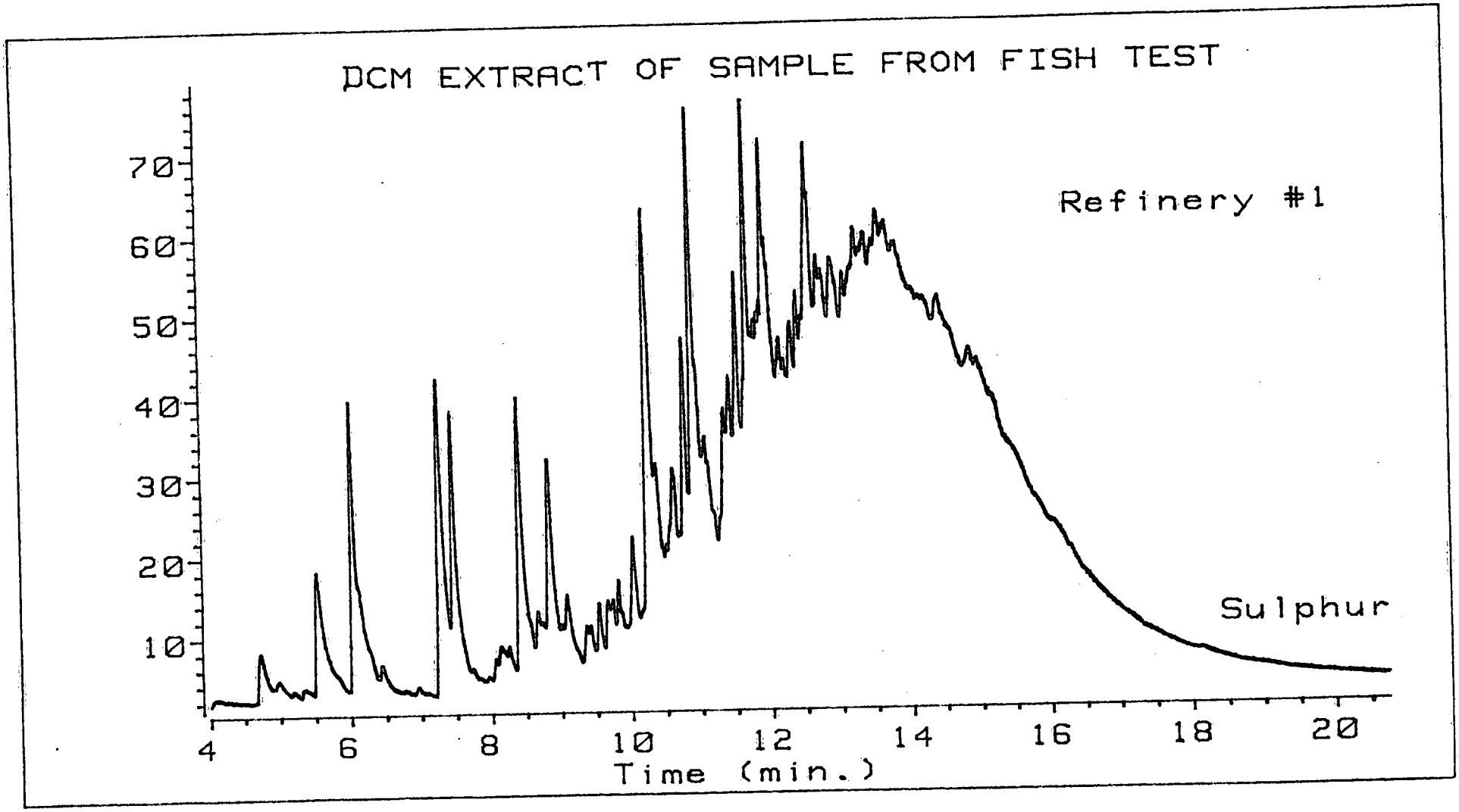

DCM EXTRACT OF SAMPLE FROM FISH TEST
Refinery #1
Sulphur
70
60
50
40
30
20
10
4
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 26.

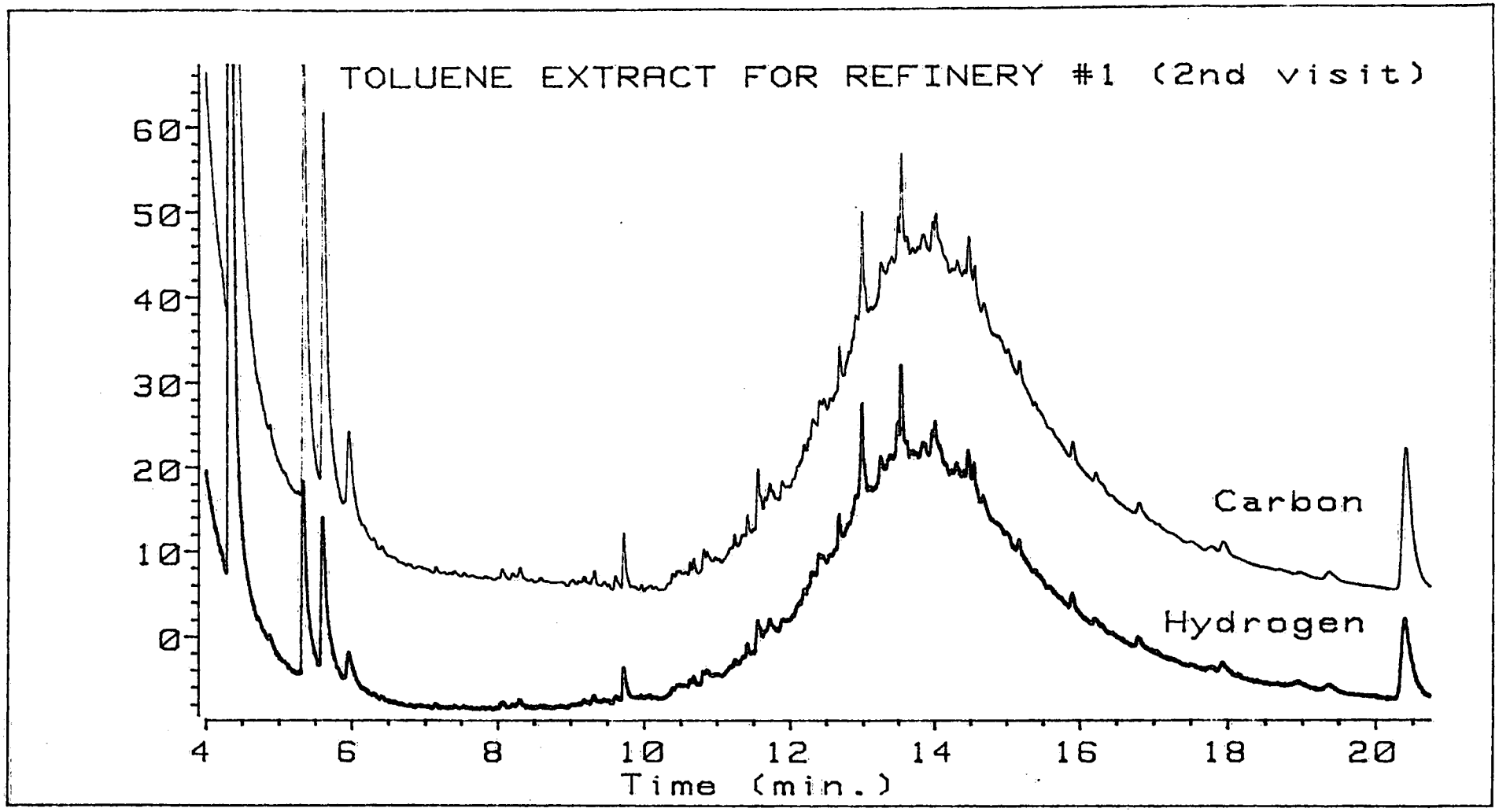

TOLUENE EXTRACT FOR REFINERY #1 (2nd visit)
60
50
40
30
20
10
0
Carbon
Hydrogen
4
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 27.

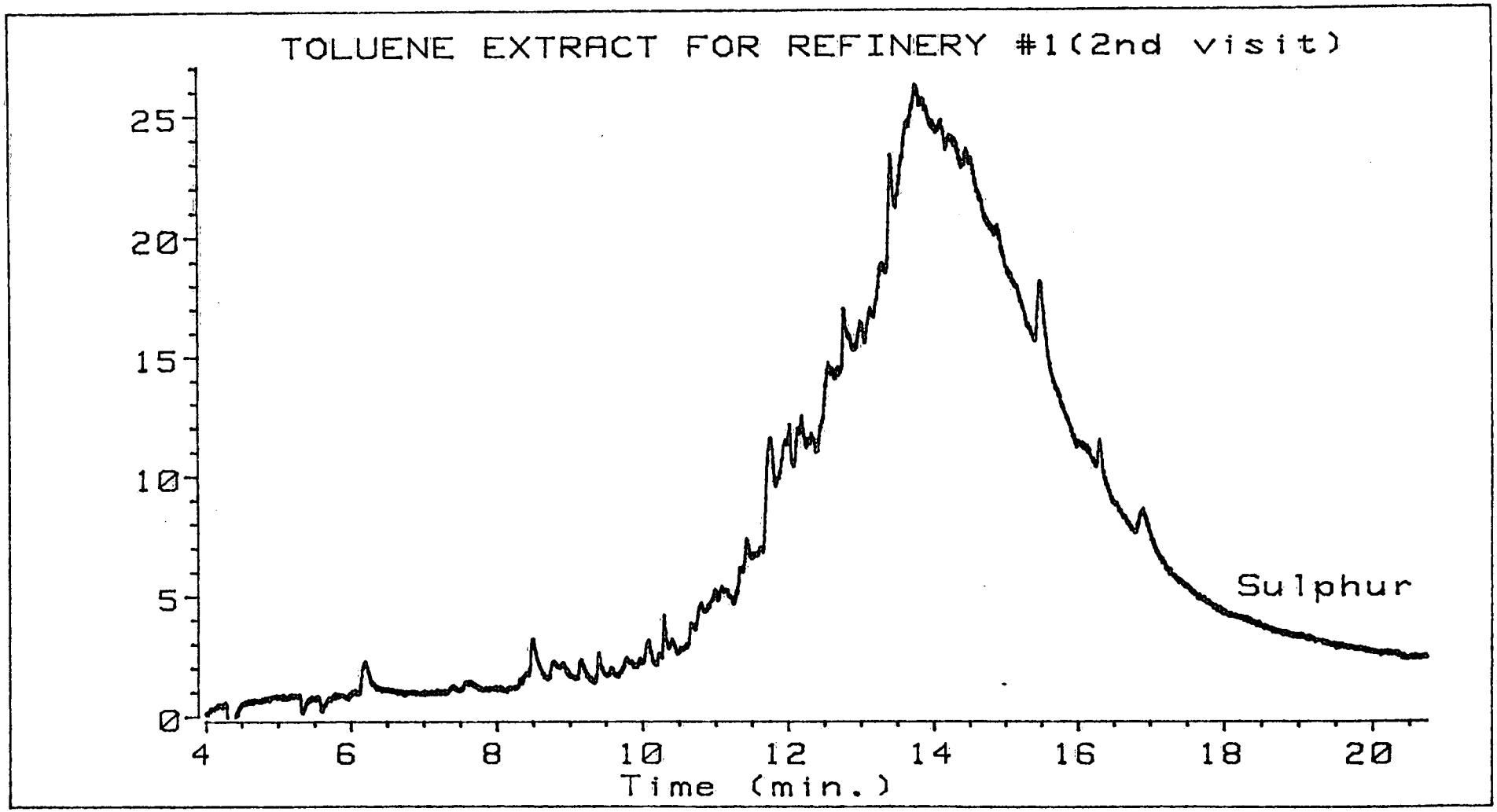

TOLUENE EXTRACT FOR REFINERY #1(2nd visit)
25
20
15
10
5
0
4
6
8
10
12
14
16
18
20
Time (min.)
Sulphur

FIGURE 28.

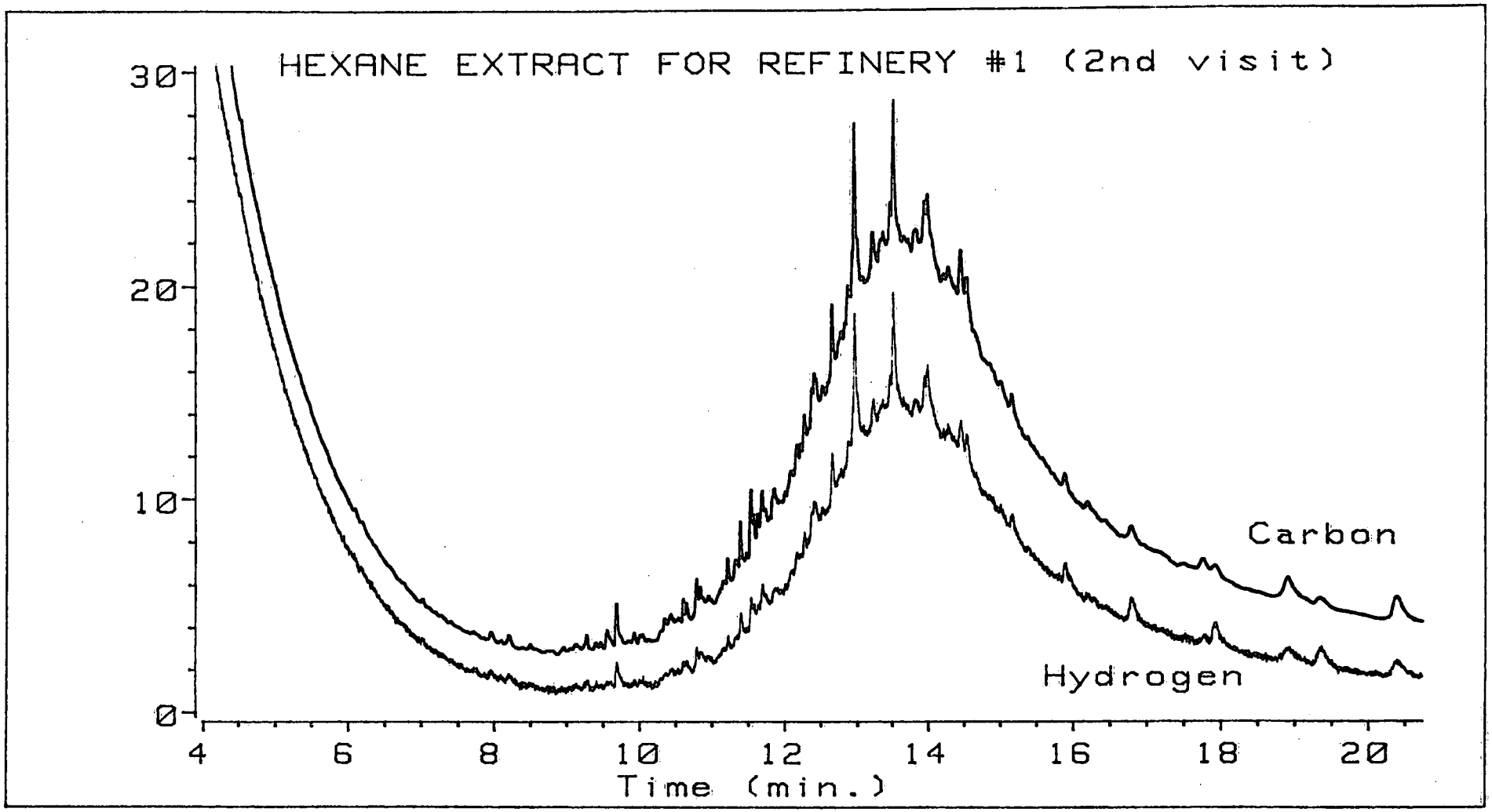

HEXANE EXTRACT FOR REFINERY #1 (2nd visit)
30
20
10
0
4
6
8
10
12
14
16
18
20
Time (min.)
Carbon
Hydrogen

FIGURE 29.

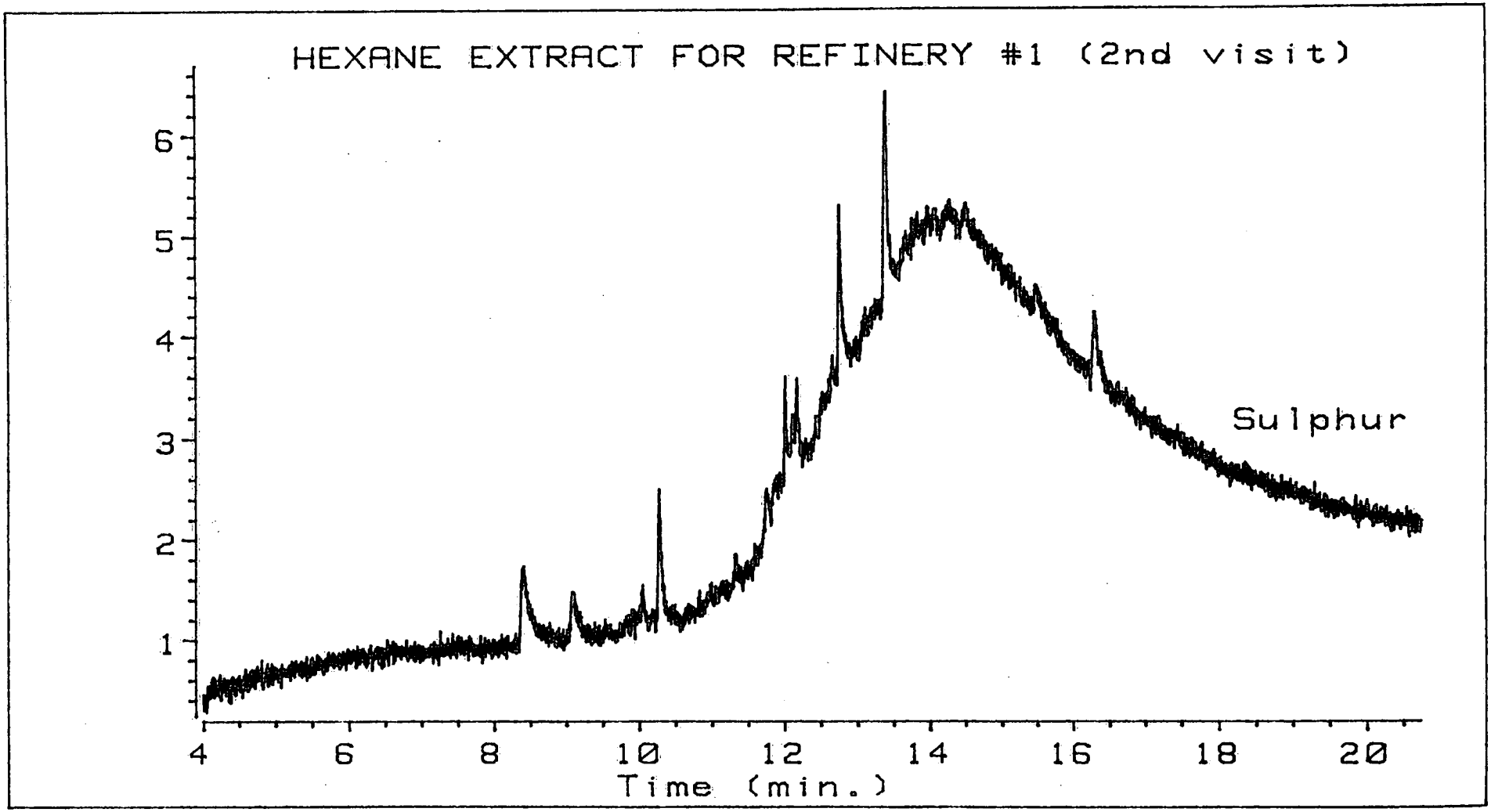

HEXANE EXTRACT FOR REFINERY #1 (2nd visit)
6
5
4
3
2
1
Sulphur
4
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 30.

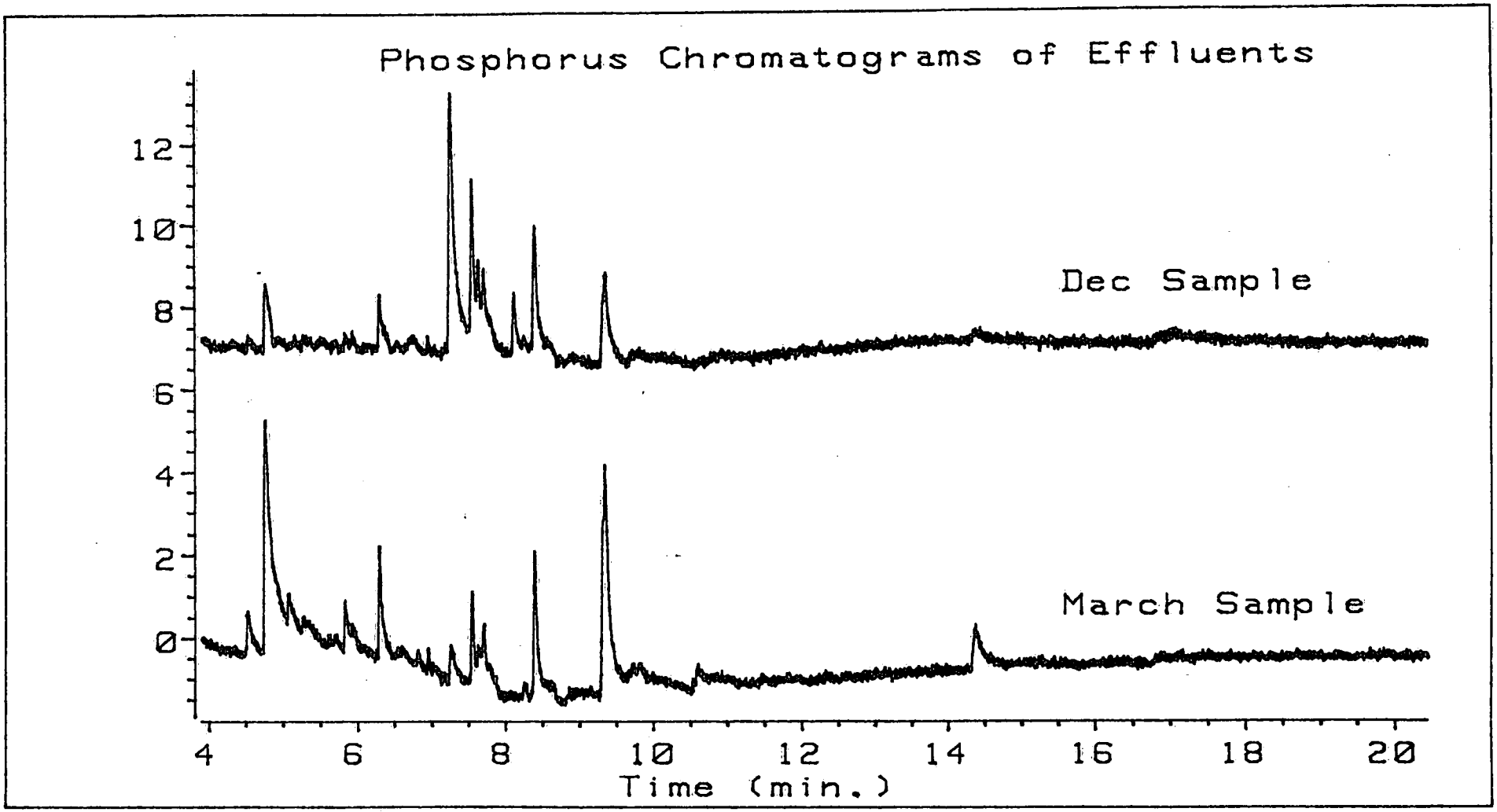
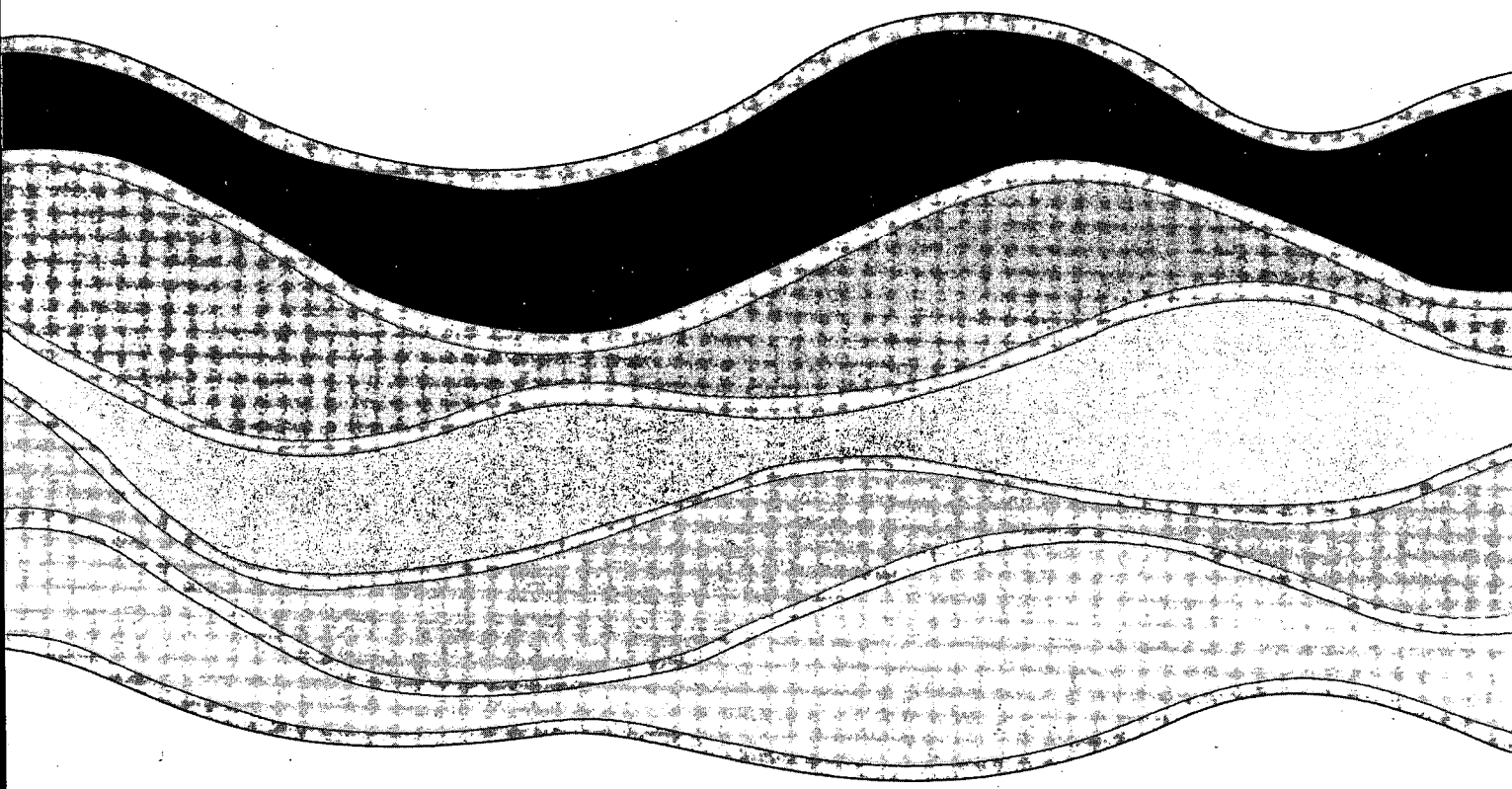

Phosphorus Chromatograms of Effluents
Dec Sample
March Sample
12
10
8
6
4
2
0
4
6
8
10
12
14
16
18
20
Time (min.)

FIGURE 31.



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P.O. BOX 5050, BURLINGTON, ONTARIO L7R 4A6

Environment Canada Environnement Canada

Canada

INSTITUT NATIONAL DE RECHERCHE SUR LES EAUX
C.P. 5050, BURLINGTON (ONTARIO) L7R 4A6

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Pensez à recycler !