



INLAND WATERS BRANCH

DEPARTMENT OF ENERGY, MINES AND RESOURCES



Identification of Petroleum Products in Water

ADRIAN DEMAYO

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INLAND WATERS BRANCH
DEPARTMENT OF ENERGY, MINES AND RESOURCES
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Abstract

This report describes an extraction method used in the Water Quality Division laboratory to analyze water samples, and activated carbon samples through which water has been passed, for the presence of crude oil or other petroleum products.

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INTRODUCTION

The contamination of surface and ground waters by petroleum products, for example, gasoline, diesel oil, or crude oil, is an important problem in the field of water pollution.

The analyst is faced with two problems: (1) to detect the presence of a petroleum product in water, and if present, (2) to identify the source of the petroleum product.

A number of recently published papers deal with the analysis of petroleum products in water ¹⁾²⁾³⁾⁴⁾⁵⁾⁶⁾¹¹⁾. The analytical technique used most often is gas-liquid chromatography, using flame ionization detectors. The specific types of gas chromatographs used, columns, detectors, etc., depend very much on their availability in a given laboratory. Other techniques have also been used ⁶⁾⁷⁾⁸⁾⁹⁾¹⁰⁾¹¹⁾. Recently a review of this subject was published ¹²⁾.

EQUIPMENT AND CHEMICALS

A Hewlett-Packard 5750B gas chromatograph was used in this work. It was equipped with a dual flame ionization detector. The columns used were of stainless steel, 1/4 inch outside diameter and 6 feet long.

The packing used was 10 per cent (w/w), DC-200 on Chromosorb W, DMCS 80-100 mesh.

The conditions for each chromatogram are given on the respective charts (Figures 1 to 14). Generally the gas chromatographic parameters had the following values:

Hydrogen pressure: 15 psi (corresponds to a flow of 45cc/min.)

Air pressure: 28-33 psi (corresponds to a flow of 400-500cc/min.)

Carrier gas: nitrogen (certified high purity; oxygen content less than 20 ppm, moisture content less than 5 grains/1000 cf; Union Carbide Canada Limited)

Nitrogen pressure: 40 psi

Nitrogen flow: 60cc/min.

Injector temperature: 255-265°C

Detector temperature: 290-310°C

Column temperature: temperature programmed from 100 to 240°C at a rate of 15°C/min.

Post injection interval: 1 min.

Upper limit interval: as necessary (usually 10 min.)

Sample size: 4 or 8 µl

Range and attenuation: variable, depending on the sample injected.

Extraction solvent: The main characteristics of a good solvent for extracting hydrocarbons from water are (i) good preferential solvent properties for hydrocarbons, (ii) retention time outside the range of the sought product, and (iii) high purity²⁾. Because, generally, in the extraction procedure, the ratio of solute/solvent is very small, the solvent should not show any extra peaks when the sensitivity of the gas chromatograph is increased. Any extra peaks shown by the solvent will, most likely, interfere with the peaks of the compound which is being analyzed. Straight chain hydrocarbons are suitable solvents when they fulfill the purity conditions. When an analysis for gasoline (C₅-C₁₁) is required, a good solvent would be any C₁₂ or higher, normal alkane; hexadecane has been successfully used in some trial runs in the laboratory. When analyzing for diesel oil, a low-molecular weight hydrocarbon (C₅-C₇) will not interfere with the oil; in the present work n-heptane was used with good results. The large peaks at the beginning of each of the chromatograms (Figures 5 to 14) reflect the n-heptane.

The n-heptane (Eastman Organic Chemicals, Cat. No. 2215) was used without any further purification. Its chromatogram is given in Figure 14.

The activated carbon used in this work was of the type Nuclear C-190-N, 10 x 40 mesh, West Virginia Pulp & Paper Co., New York, N.Y.

The sodium sulphate (Anachemia Chemical Limited, Cat. No. AC-8515) was maintained at 600°C for at least 12 hours before use.

METHODS, RESULTS AND DISCUSSION

In a complete gas chromatographic analysis, each peak on a chromatogram is associated with one or more specific compounds. In the simplest gas chromatographic analysis of petroleum products in water, one looks for a specific pattern of peaks rather than positive identification of each peak on the chromatogram. In a sense this operation resembles the spectroscopic technique, in which one compares the spectrum of an unknown compound with the spectra of a series of known pure compounds, one of which is suspected of being identical to the unknown compound.

Figure 1 gives the chromatogram of a mixture of a series of hydrocarbons which was used to check the performance of the gas chromatographic system at various times. The performance of the system was constant over the period of time during which this work was carried out.

Figure 2 contains the chromatogram of a diesel oil and Figure 3 that of a gasoline. The two chromatograms are very different in their patterns. Obviously the range of the carbon number is also different; in gasoline it ranges from C_6 to C_{11} while in a diesel oil the range is from C_{10} to C_{18} . Another point worthy of mention is the closer similarity between the chromatograms of a diesel oil and that of a crude oil (Figure 4) as compared to a gasoline.

Analysis of Water Samples by an Extraction Method

Figure 5 gives the chromatograms of two mixtures of diesel oil and tap water. Separation of the two components was not very successful with the type of packing used in this work (see Equipment and Chemicals). At a concentration of 0.1 per cent (v/v) of diesel oil in water, some of the peaks characterizing the oil are present (see Figure 5A); however, they are not very well resolved. At a lower concentration (0.01 per cent v/v) the characteristic peaks of the diesel oil disappear completely (see Figure 5B). Actually, the chromatogram of Figure 5B is almost identical to the chromatogram of Figure 6, which was obtained by injecting a sample of tap water. Another fact worth mentioning at this point is the deterioration in performance of the columns used, which was observed after a series of aqueous injections. This is shown in the chromatogram of Figure 7 which represents a sample of diesel oil injected after a series of aqueous injections. Comparing Figure 2 with Figure 7, it can be seen that the resolution in the former is much better.

The analytical procedure is as follows: Measure one litre of water in a 1-litre volumetric flask or, better still, extract the water sample directly in its container, provided that the container has a proper shape. It was found that 40-ounce whisky bottles are very good for sampling, shipping, and extracting operations. Using a syringe or pipette, add 500 μ l of heptane (see Equipment and Chemicals) and shake the flask, or stir with a magnetic stirrer, for approximately five minutes. Then allow the flask to stand for at least one hour. Remove the heptane with a 100 μ l syringe and place it in a 300 μ l Microflex tube. Examine the tube after all the solvent which can be removed from the extraction flask has been placed in the Microflex tube. If an aqueous layer is observed, it can be removed with the same 100 μ l syringe. After adding a very small amount of anhydrous sodium sulphate, cap the Microflex tube and allow it to stand for about one-half hour. Then, the extract is ready for injection in the gas chromatograph. Note that the extract should not be left overnight since loss of the solvent due to evaporation may change the concentration of the extract.

Note: So far, only tap water and lake water have been analysed. No clean-up of the extract was necessary in these cases.

Standards - For the purpose of identifying the source of the petroleum product present in water from among several suspected sources and/or for quantitative analysis of the gas chromatographic results, standard solutions must be run.

The standard solutions are prepared by adding known amounts of the petroleum product(s) being sought to a known amount of distilled water. The concentration of the petroleum products in water must cover the entire working range of the analysis. The distilled water is measured in a 1-litre volumetric flask or a bottle similar to the ones which are used for sampling.

The petroleum product is added using a syringe of proper size. The contents of the flask are stirred with a magnetic stirrer for one hour, and then 500 μ l of heptane is added. Thereafter, the procedure is identical to that described above for water samples.

For a qualitative analysis the chromatograms of the unknown samples are compared visually with those of the standard solutions. The peaks of the gas chromatograms for the standard solution and the unknown water sample are compared for: (i) shape, (ii) relative intensity, and (iii) retention time. If they are identical, it is probable that the petroleum products in the two extracts are the same. If the chromatograms differ in one or more of these points, it is most likely that the extracts contain different petroleum products.

For 90 percent of the samples, this visual comparison is sufficient for assessing the presence of a petroleum product in a water sample and/or for matching it with a sample from one of several suspected sources. This visual inspection will also render an approximate quantitative estimate of the amount of petroleum product in the water sample.

For quantitative analysis, the concentration range is divided into 10 equal intervals and a standard solution prepared for each of the eleven resultant points. For example, assume that the concentration range for analysis is 0 to 50 μ l/l; then the eleven standard solutions must contain 0, 5, 10, ..., 50 μ l/l of the respective petroleum product. These standard solutions are used in the procedure already described. The total area of the chromatogram is measured and then plotted against concentration. A "standard curve" implicitly containing an efficiency factor, results.

Figure 8A shows such a standard curve for a concentration range of 0-90 ppm (v/v) of diesel oil in water. The points were fitted to a straight line by the least squares method using program AD0001¹³⁾.

The points of line 1, Figure 8A, represent the area under the chromatogram of the diesel oil, as it is given by the integrator. The points of line 2, Figure 8A, represent the area of the diesel oil normalized with respect to the solvent peak¹⁴⁾. This second method is probably better because it will implicitly take care of any change in the sensitivity of the detector.

Figures 8B to 8E represent the chromatograms of some of the extracts of the standard solutions. Notice that even at low levels of diesel oil in water, the characteristic pattern of the diesel oil is well defined. The y axes of chromatograms 8D and 8E are logarithmic. By using a logarithmic y axis, all peaks are kept on scale. Notice that on a logarithmic scale, the peaks appear to be less sharp and not as well separated when compared to those of a linear scale.

In the Water Quality Division an electronic integrator, Hewlett-Packard Model 3360A is used at the present time to integrate the chromatograms. Two examples of the integrator output can be seen in Figures 8D and 8E.

Analysis of Activated Carbon

To assess the possibility of extracting a sorbed diesel oil from an activated carbon, 100 μ l of diesel oil were added to 500 ml of tap water

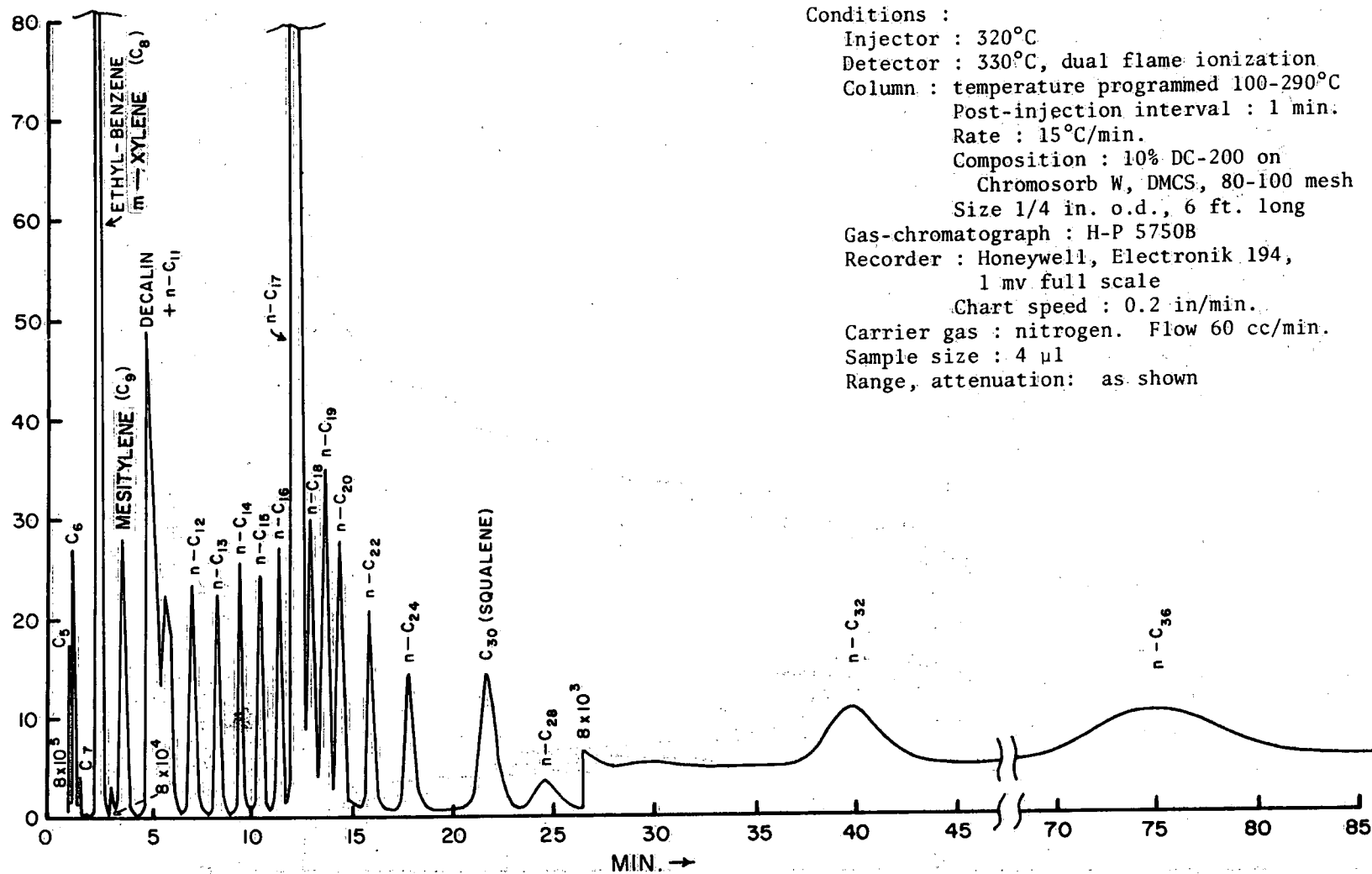
in an erlenmeyer flask and stirred for 10 minutes with a magnetic stirrer; then, 50 g. of activated carbon were added and the mixture stirred for 2½ hours, after which a sample of the liquid was filtered, and 25 ml of the filtered liquid was extracted with 250 µl of n-heptane. The extract was dried over anhydrous sodium sulphate and then analyzed by gas chromatography. The results are shown in Figure 9. It can be seen that the extract did not contain any diesel oil, and therefore the 100 µl of diesel oil added initially to the water was completely sorbed by the activated carbon. The stirring was continued for another 70 hours and then the mixture was filtered through a Buchner funnel. The carbon was extracted with 100 ml of heptane (in two portions: 80 ml and 20 ml, respectively) by shaking the mixture in an erlenmeyer flask. The heptane extract was dried over anhydrous sodium sulphate and then analysed by gas chromatography. The chromatogram obtained is shown in Figure 10. The presence of diesel oil in this extract is clear. Concentration of the extract by a factor of approximately 40 (evaporation in air) improved the resolution of the chromatograms. The chromatogram obtained after concentration is given in Figure 11.

A blank sample identical to the reference sample with the exception of the diesel oil which was omitted, was run in parallel with the reference sample. The results obtained with the blank sample are shown in Figures 12 and 13. Figure 12 gives the chromatogram of the heptane extract of the water after stirring it for 2½ hours with activated carbon. Figure 13 gives the chromatogram of the heptane extract of the activated carbon from the blank sample. This chromatogram is practically identical to that of the solvent used for extraction, that is, heptane, which is given in Figure 14.

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Conditions :

Injector : 320°C

Detector : 330°C, dual flame ionization

Column : temperature programmed 100-290°C

Post-injection interval : 1 min.

Rate : 15°C/min.

Composition : 10% DC-200 on

Chromosorb W, DMCS, 80-100 mesh

Size 1/4 in. o.d., 6 ft. long

Gas-chromatograph : H-P 5750B

Recorder : Honeywell, Electronik 194,

1 mv full scale

Chart speed : 0.2 in/min.

Carrier gas : nitrogen. Flow 60 cc/min.

Sample size : 4 µl

Range, attenuation: as shown

Figure 1. Hydrocarbons mixture.

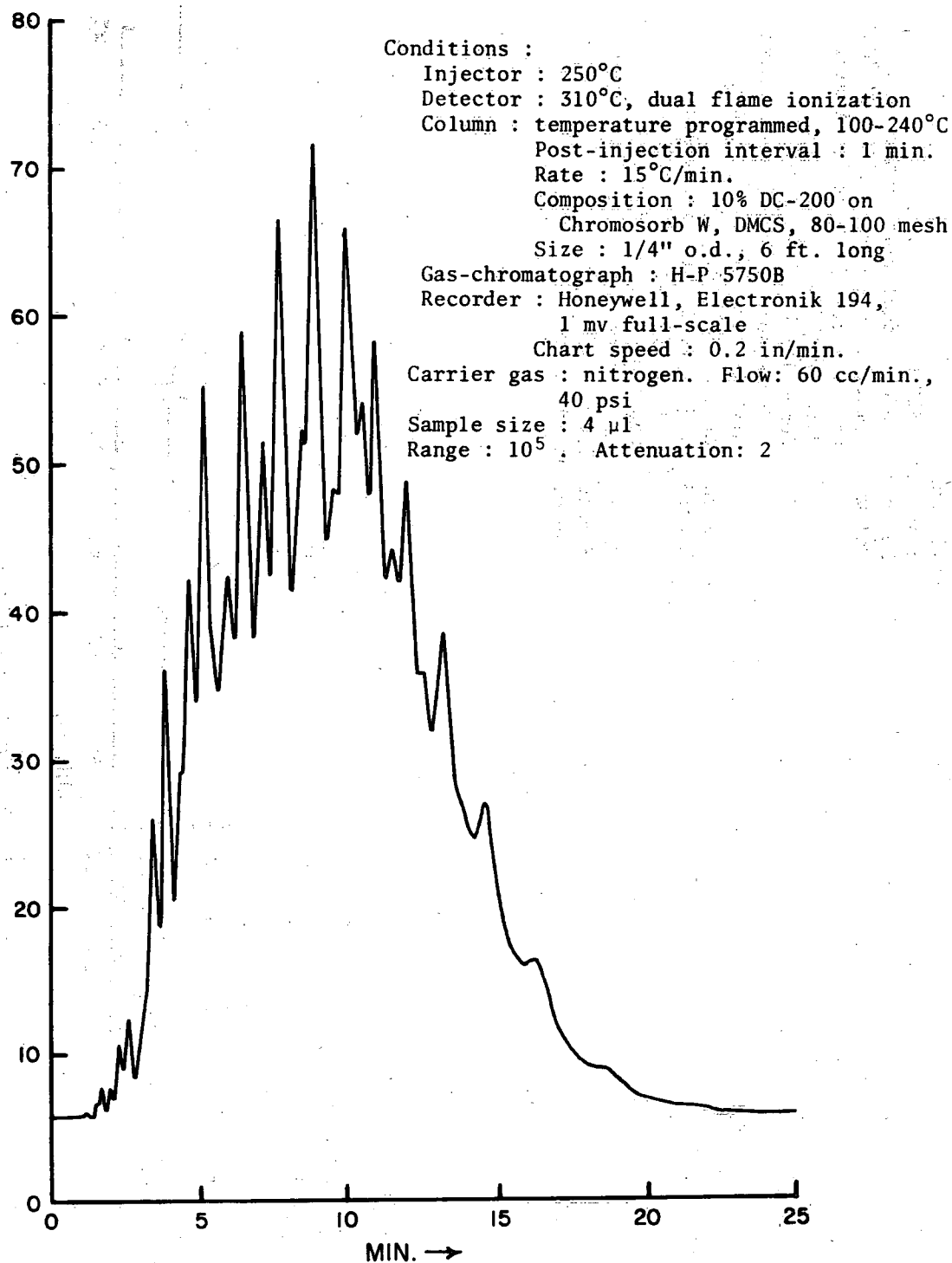


Figure 2. Diesel oil.

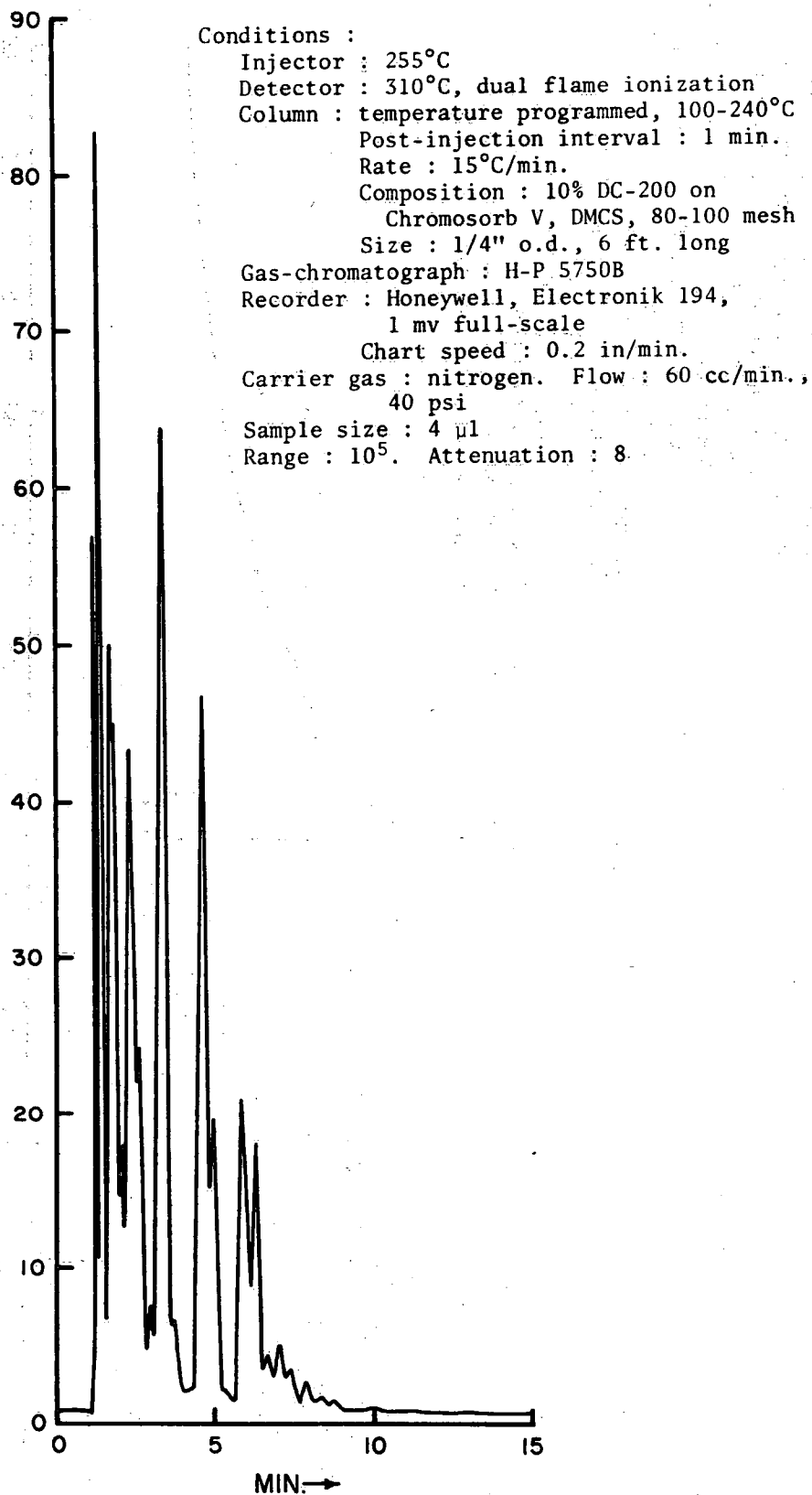


Figure 3. Premium gasoline.

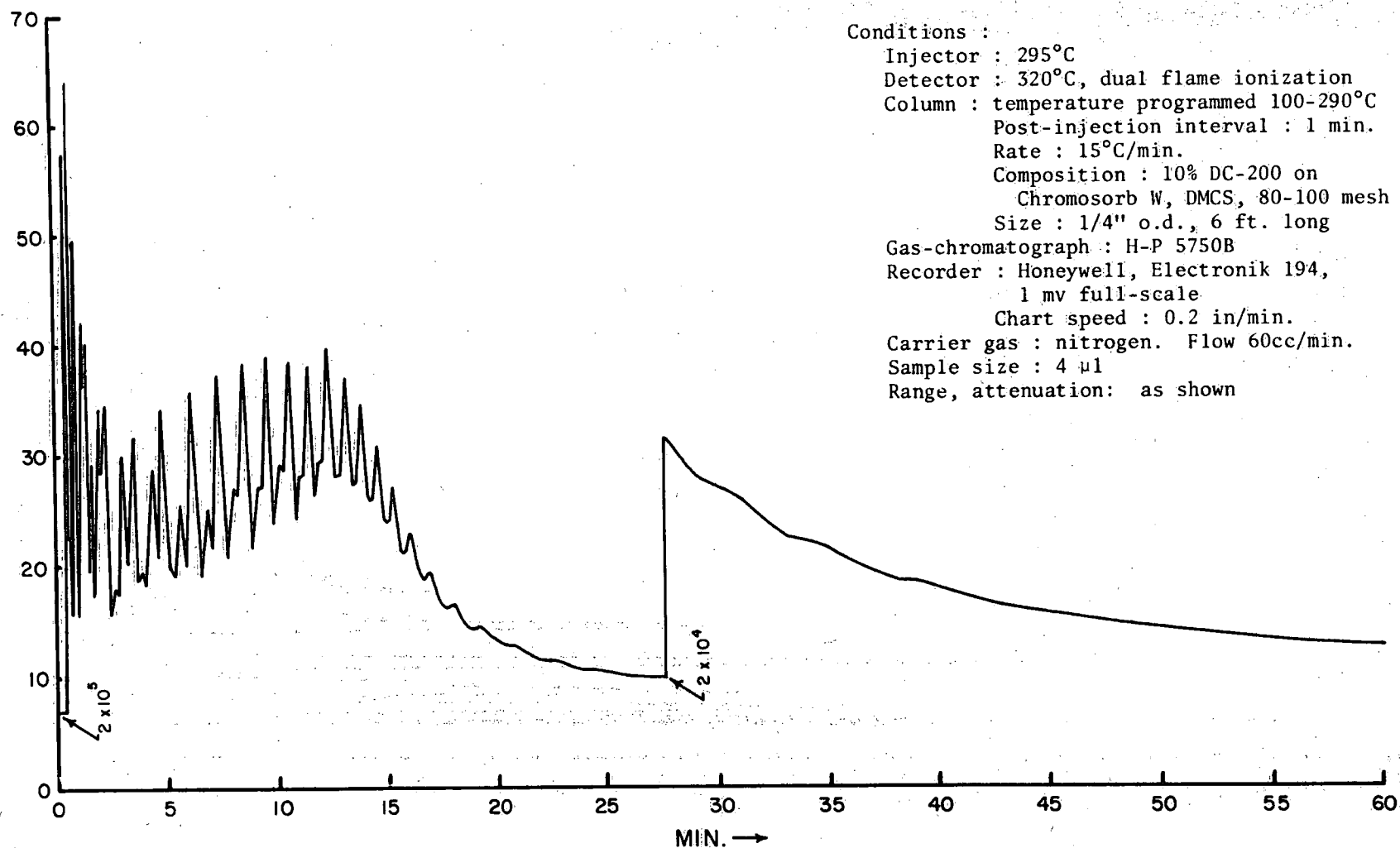


Figure 4. Crude oil (Lake Erie).

Conditions :

Injector : 245°C

Detector : 308°C, dual flame ionization

Column : temperature programmed, 100-240°C

Post-injection interval : 1 min.

Rate : 15°C/min.

Composition : 10% DC-200 on

Chromosorb W, DMCS, 80-100 mesh

Size : 1/4" o.d., 6 ft. long

Gas chromatograph : H-P 5750B

Recorder : Honeywell, Electronik 194,

1 mv full scale

Chart speed : 0.2 in/min.

Carrier gas : nitrogen. Flow : 60 cc/min.,

40 psi

Sample size : 4 µl

Range : 10². Attenuation : A=8, B=4.

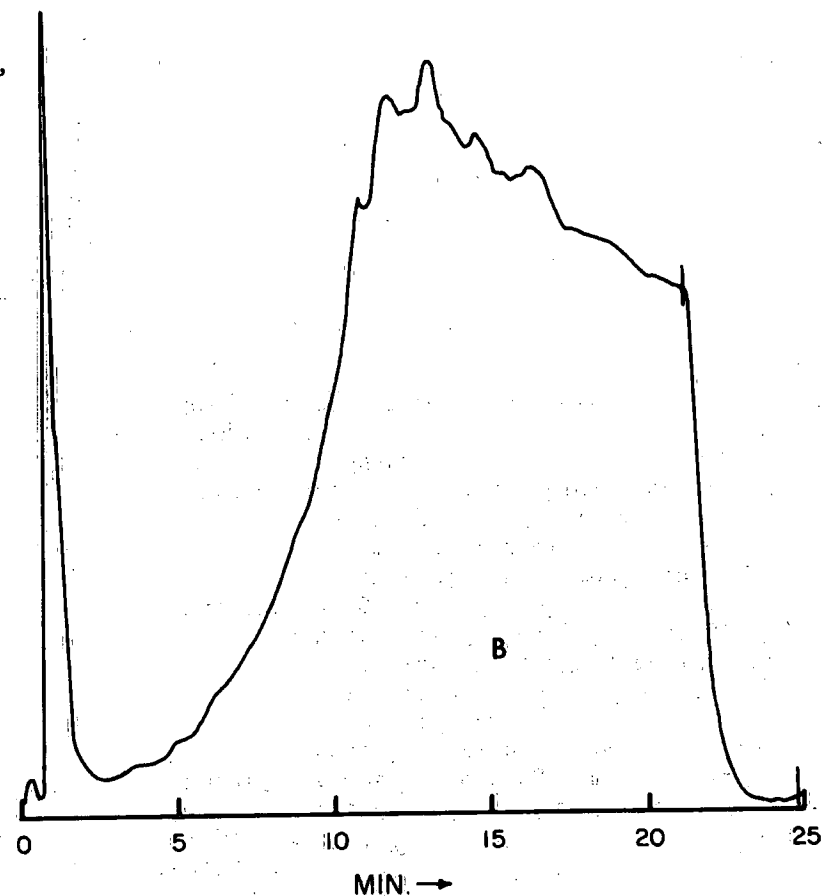
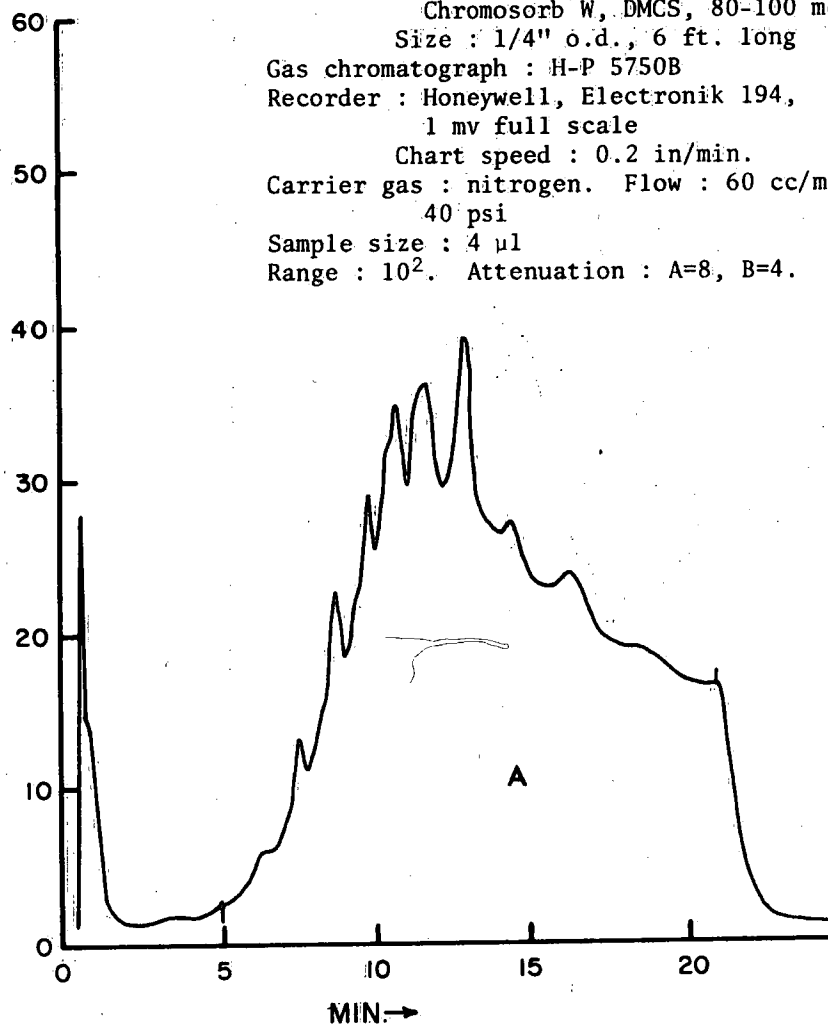
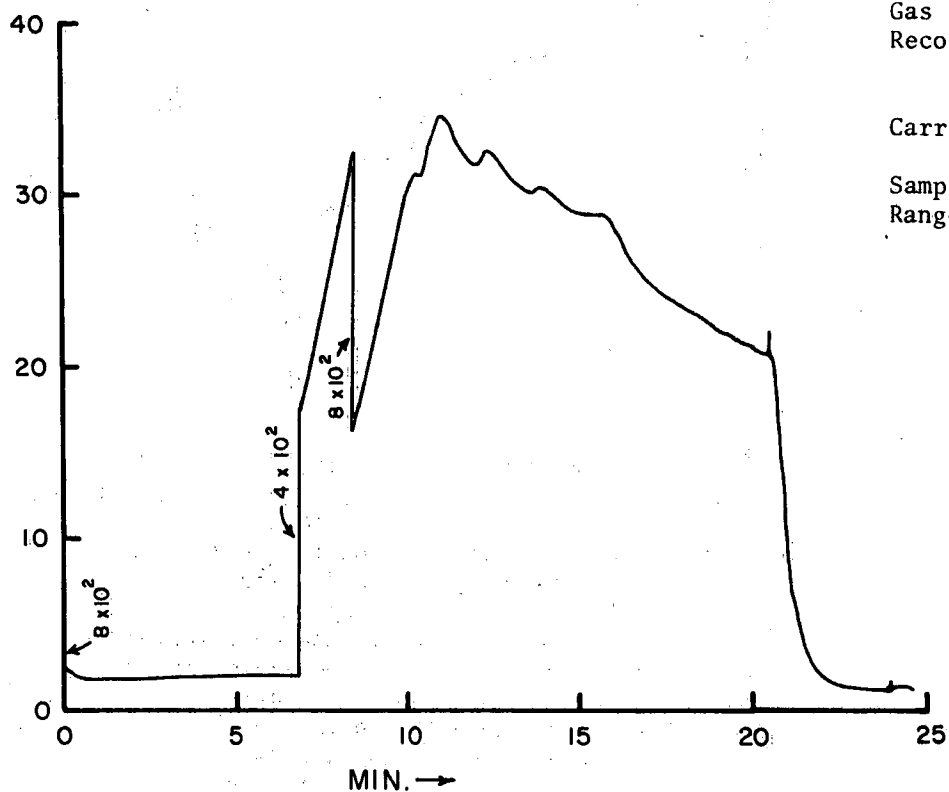


Figure 5, A and B: 100 µl diesel oil and A (100 ml tap water, City of Ottawa, stirred overnight) and B (1000 ml tap water stirred overnight).



Conditions :

Injector : 245°C

Detector : 308°C, dual flame ionization

Column : temperature programmed, 100-240°C

Post-injection interval : 1 min.

Rate : 15°C/min.

Composition : 10% DC-200 on
chromosorb W, DMCS, 80-100 mesh

Size : 1/4" o.d., 6 ft. long

Gas chromatograph : H-P 5750B

Recorder : Honeywell, Electronik 194,
1 mv. full scale

Chart speed : 0.2 in/min.

Carrier gas : nitrogen. Flow : 60 cc/min.,
40 psi

Sample size : 4 μ l

Range, attenuation : as shown

Figure 6. Tap water (City of Ottawa).

Conditions:

Injector : 245°C

Detector : 310°C, dual flame ionization

Column : temperature programmed, 100-240°C

Post-injection interval : 1 min.

Rate : 15°C/min.

Composition : 10% DC-200 on

Chromosorb W, DMCS, 80-100 mesh

Size : 1/4" o.d., 6 ft. long

Gas Chromatograph : H-P 5750B

Recorder : Honeywell, Electronik 194,

1 mv full scale

Chart speed: 0.2 in/min.

Carrier gas: nitrogen. Flow : 60 cc/min.

40 psi

Sample size : 4 μ l

Range : 10^5 . Attenuation : 4

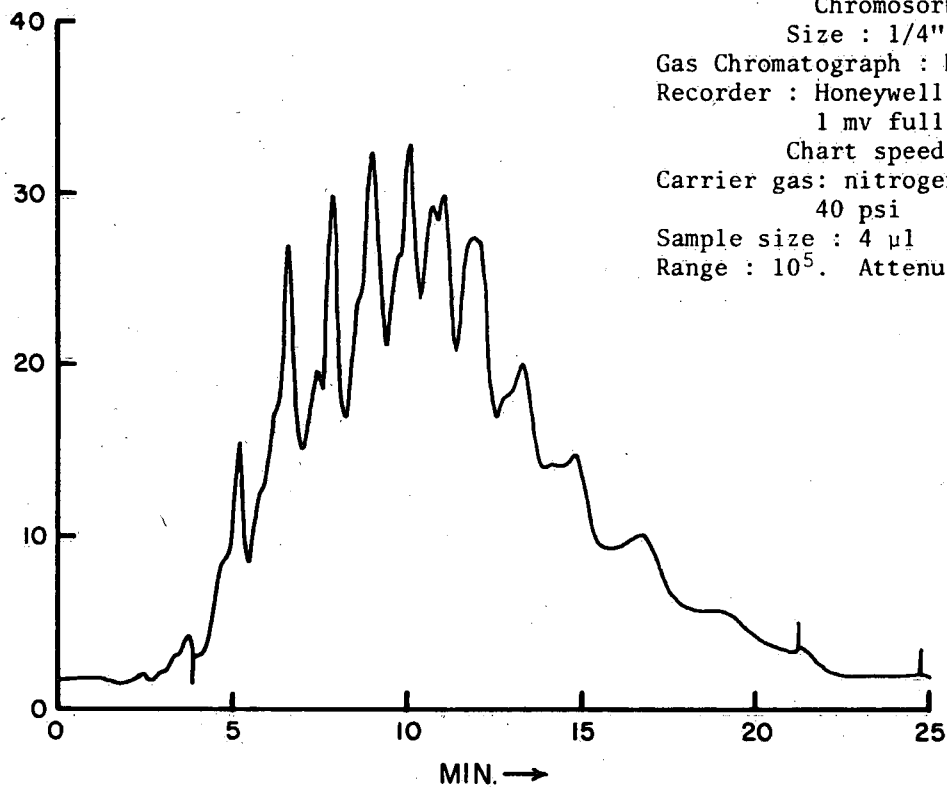


Figure 7. Diesel oil injected after a series of aqueous injections.

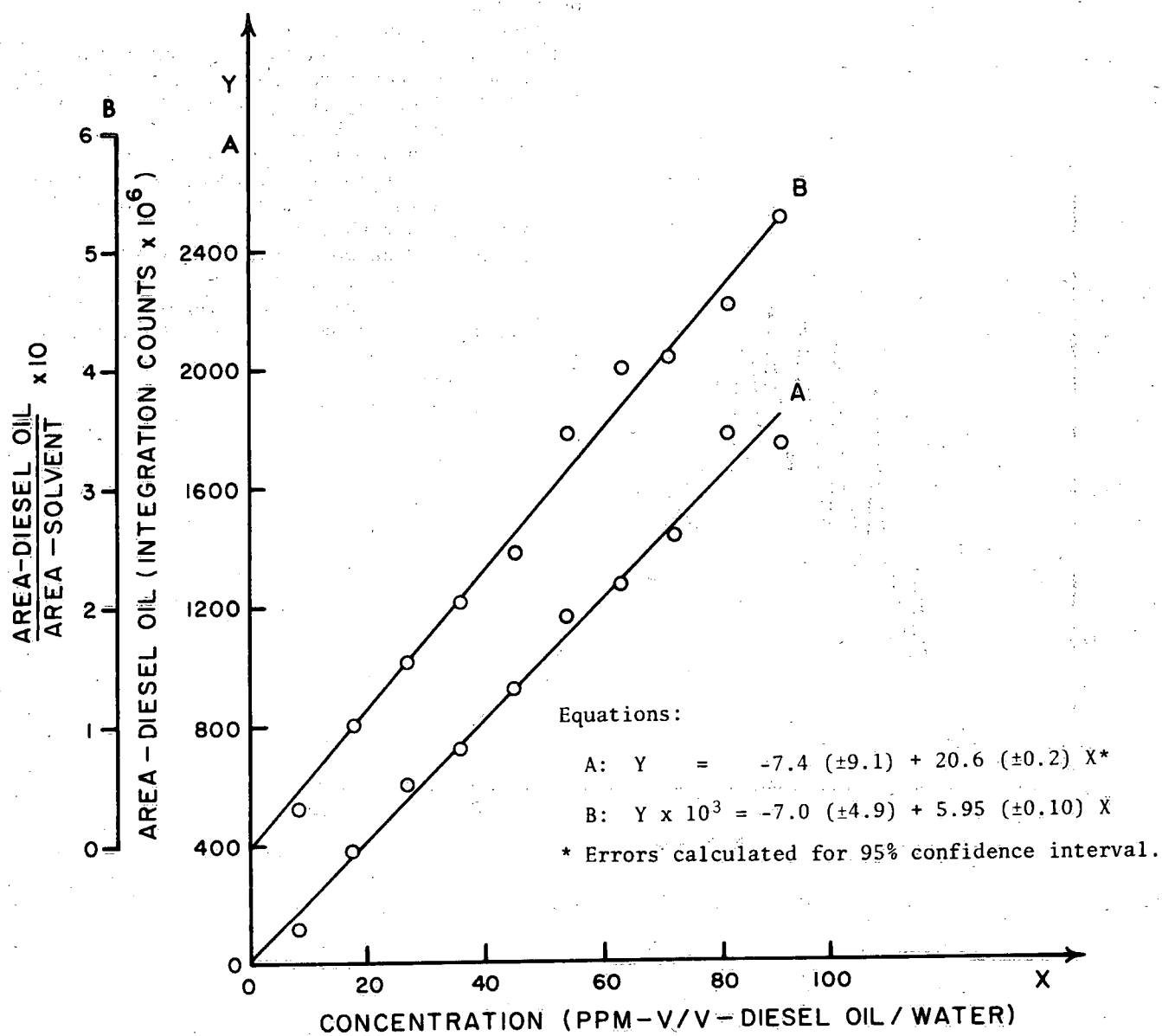


Figure 8A. Standard curve - diesel oil in water.

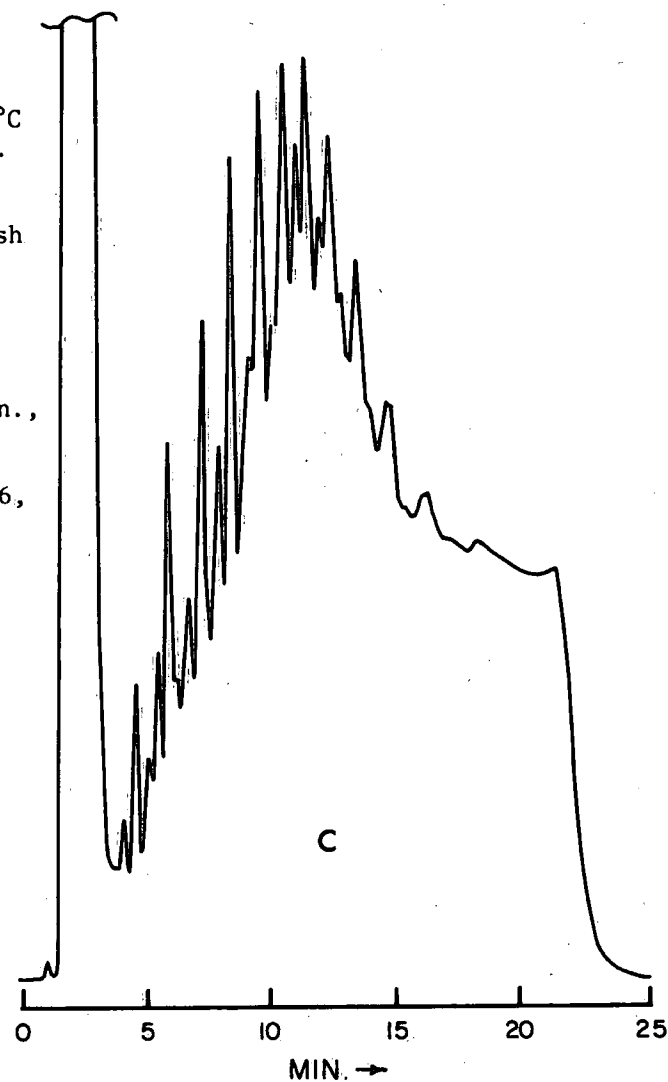
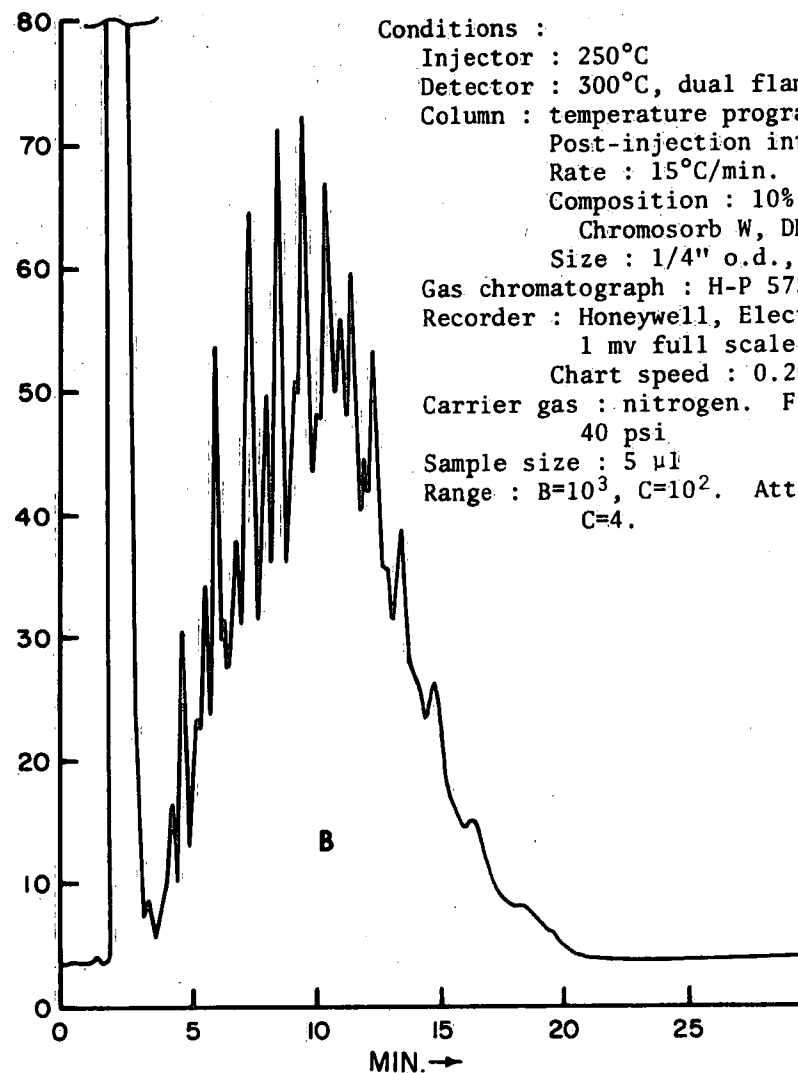


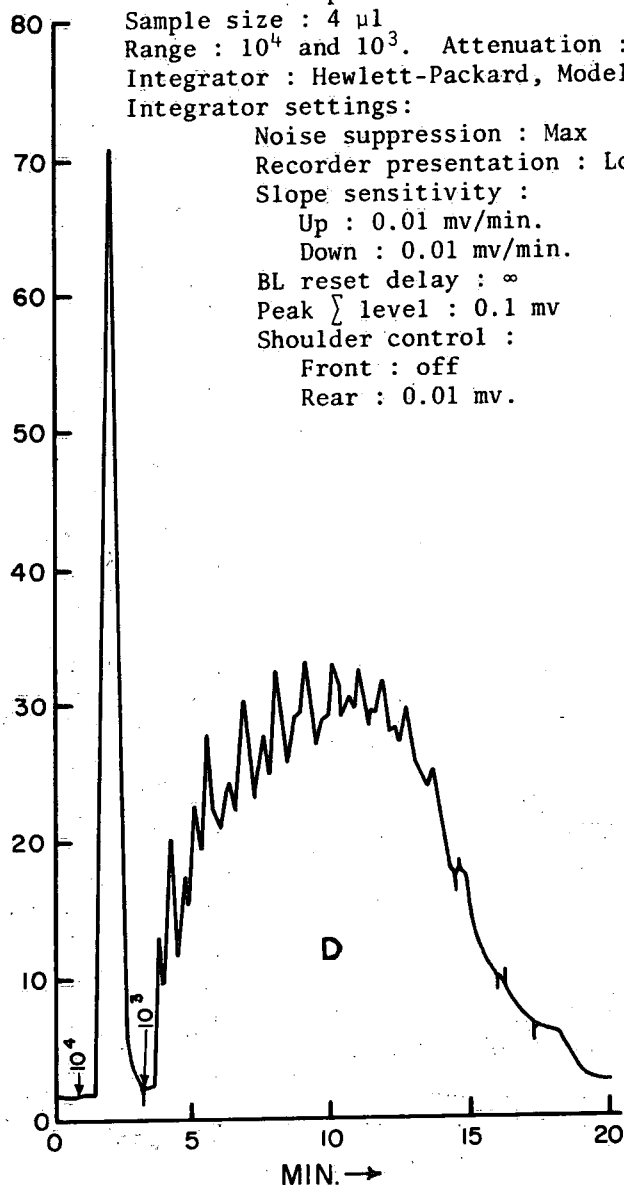
Figure 8, B and C: Diesel oil B: (25 μ l), C: (1 μ l) + 1000 ml water, extracted with 500 μ l heptane, dried over anhydrous sodium sulphate.

Conditions :

Injector : 260°C
 Detector : 300°C, dual flame ionization
 Column : temperature programmed, 100-250°C
 Post-injection interval : 1 min.
 Rate : 15°C/min.
 Composition : 10% DC-200 on
 Chromosorb W, DMCS, 80-100 mesh
 Size and material : 1/4" o.d.,
 6 ft. long, stainless steel
 Recorder : Honeywell-Electronik 194,
 1 mv full scale
 Chart speed : 0.2 in/min.
 Carrier gas : nitrogen. Flow: 60 cc/min.,
 40 psi

Sample size : 4 µl
 Range : 10⁴ and 10³. Attenuation : Log
 Integrator : Hewlett-Packard, Model 3360A
 Integrator settings:

Noise suppression : Max
 Recorder presentation : Log
 Slope sensitivity :
 Up : 0.01 mv/min.
 Down : 0.01 mv/min.
 BL reset delay : ∞
 Peak \int level : 0.1 mv
 Shoulder control :
 Front : off
 Rear : 0.01 mv.



D	E
0116,8	0075,8
3713,2	0000,0
0224,8	0102,8
0230,0	2980,2
0249,8	0150,8
2650,0	0596,0
0281,8	0199,8
1894,0	2421,0
0302,8	0224,8
0320,8	3563,0
0378,8	0278,8
0406,8	0306,8
0449,8	0359,8
0476,8	0387,8
0522,8	0431,8
0541,8	0460,8
0602,8	0507,8
0634,8	0527,8
0657,8	0590,8
0689,8	0622,8
0709,8	0645,8
0736,8	0678,8
0762,8	0698,8
0820,8	0726,8
1237,2	0752,8
0883,8	0808,8
4516,0	1573,2
0658,0	0870,8
0000,0	3331,0
1103,8	0000,0
1105,6	1167,6
0001,0	0001,0

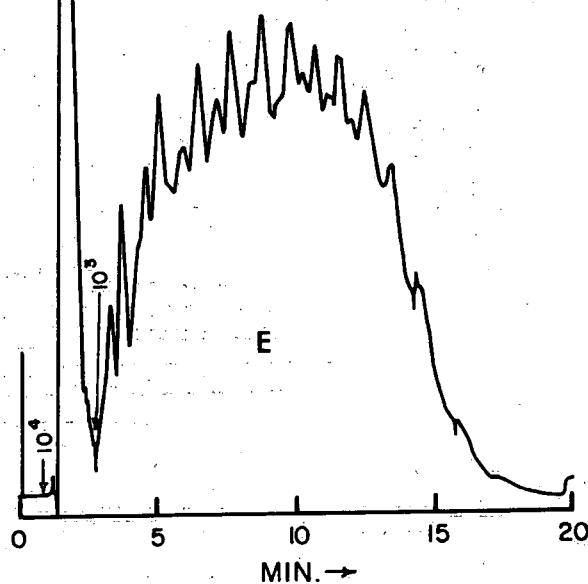


Figure 8, D and E: Diesel oil, D (9 µl), E (90 µl) + 1100 ml distilled water, extracted with 500 µl heptane, dried over anhydrous sodium sulphate.

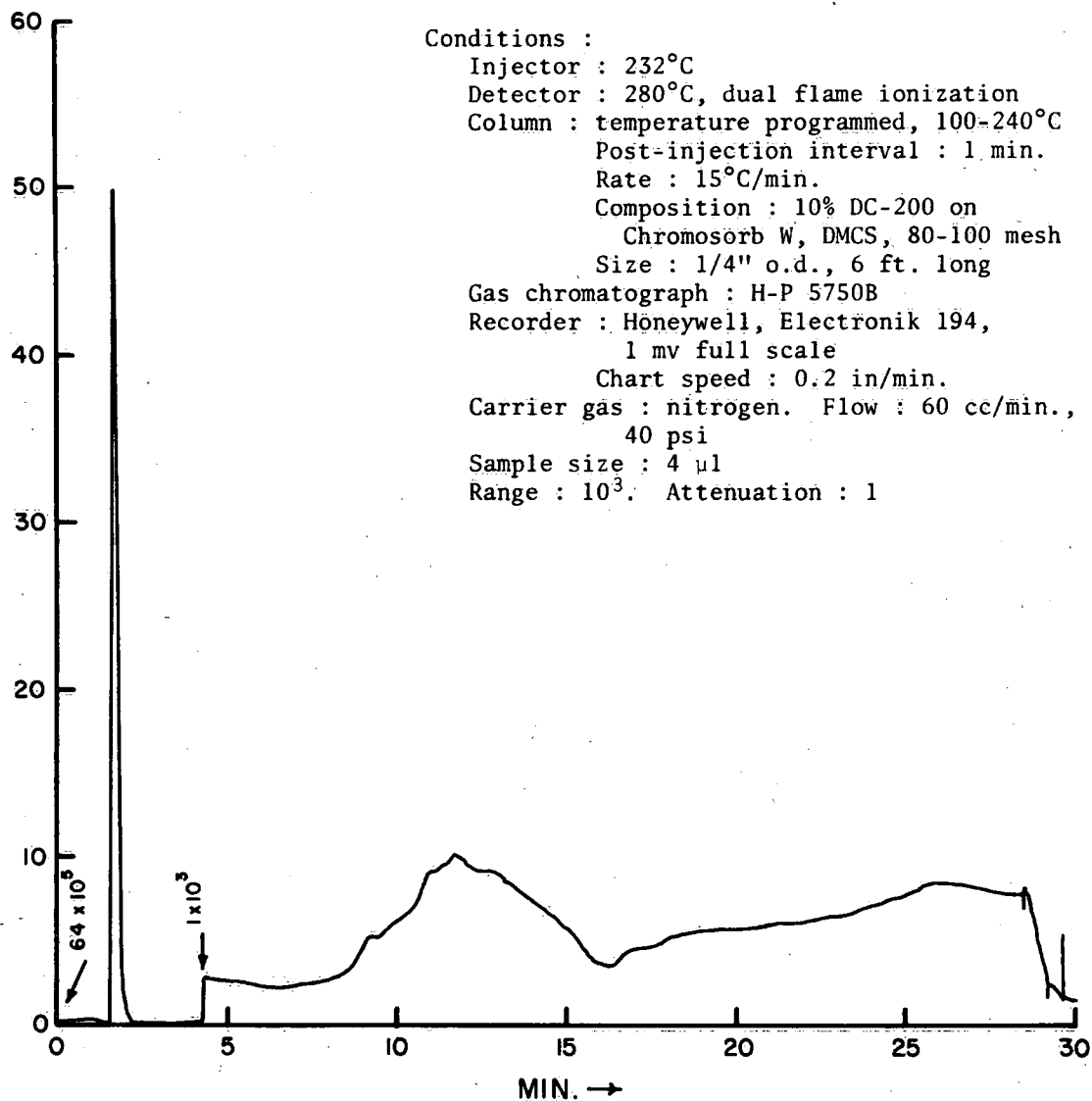


Figure 9. 100 μ l diesel oil + 500 cc tap water + 50 g activated carbon, stirred for 2 1/2 h.; 25 cc of the filtered liquid was extracted with 250 μ l heptane and then dried over anhydrous sodium sulphate.

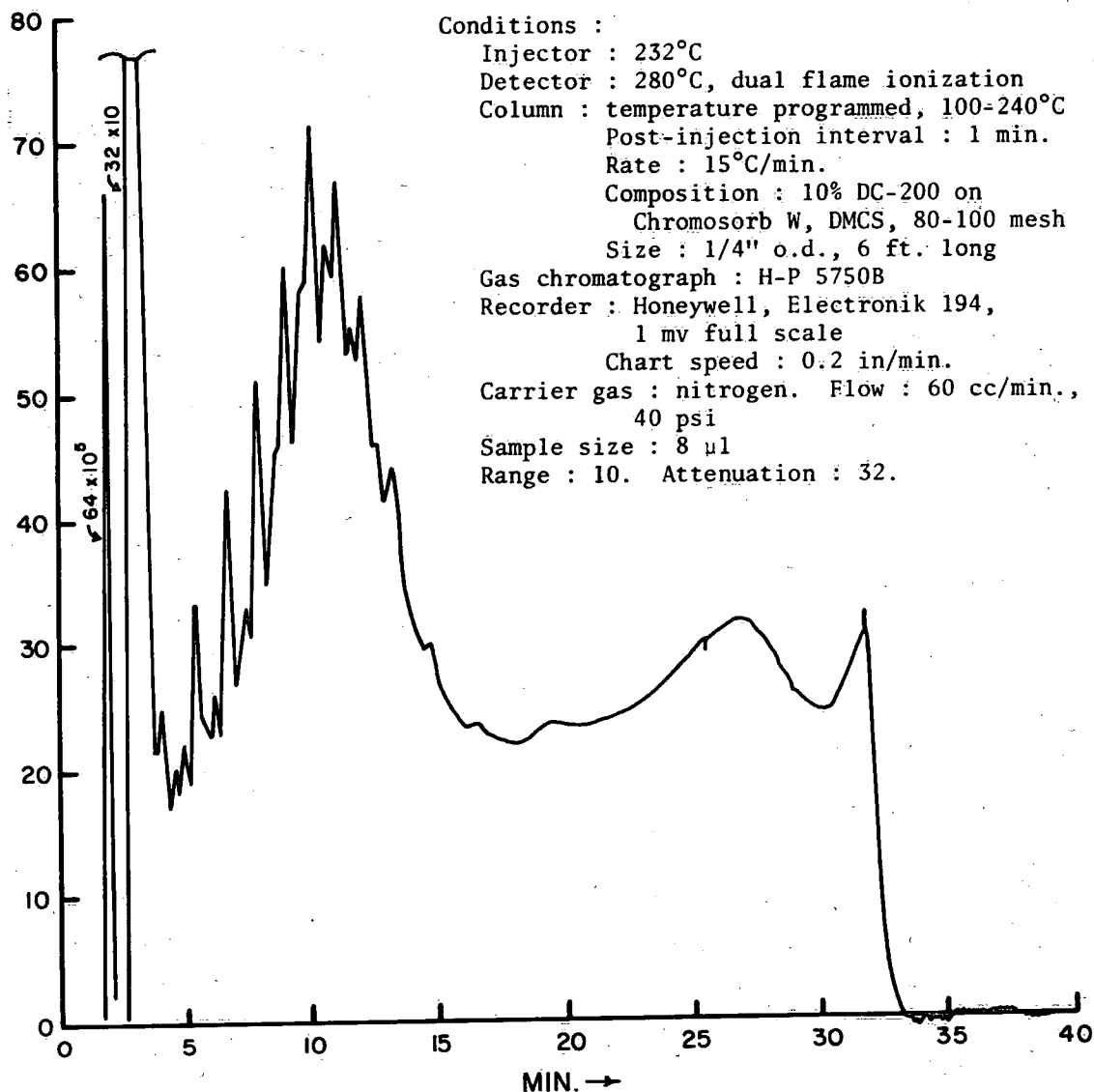


Figure 10. 100 μ l diesel oil + 500cc tap water + 50g act. carbon, stirred for 72h, filtered. The carbon extracted with 100cc (80+20) heptane. The extract dried over anhydrous sodium sulphate.

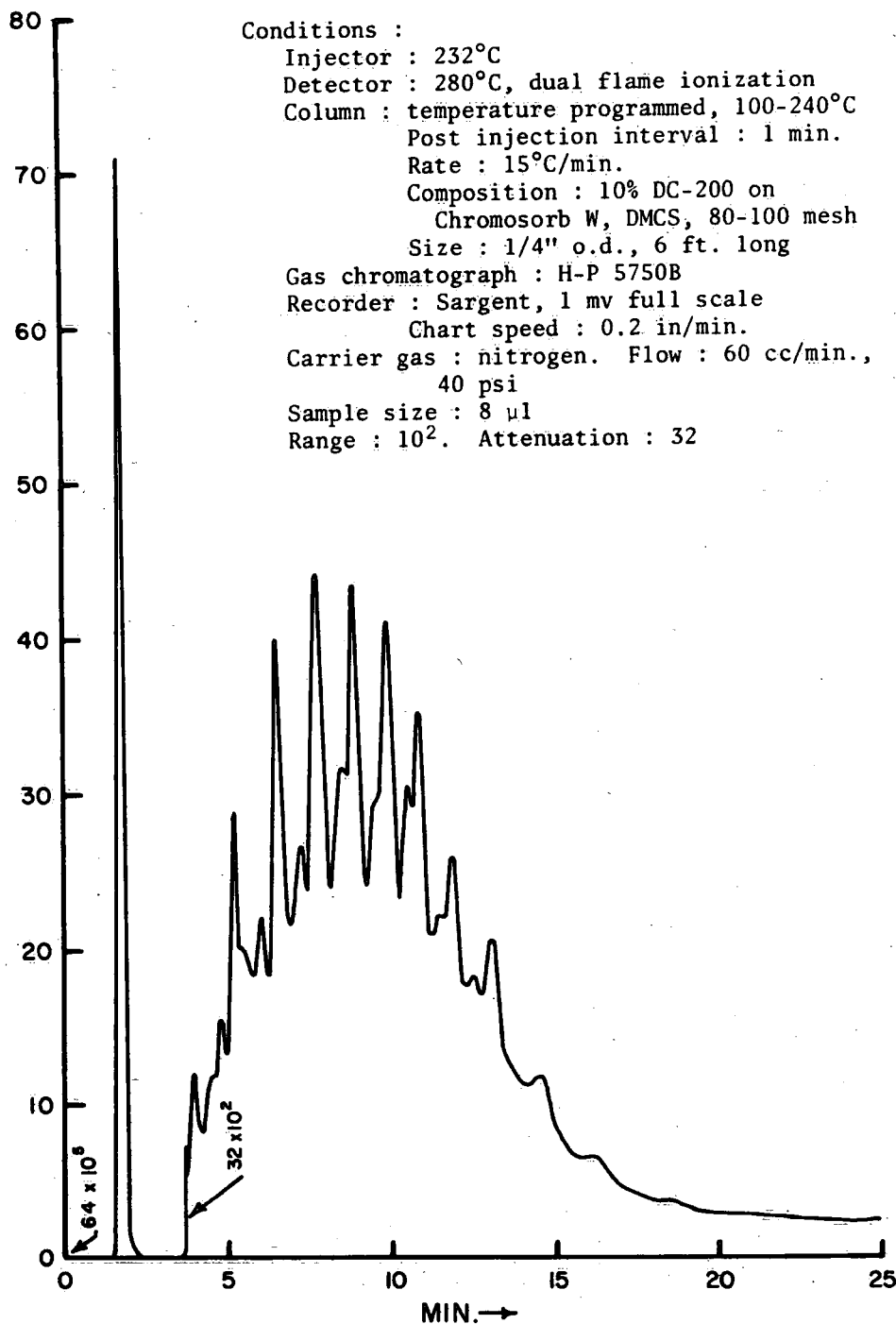


Figure 11. Sample of Figure 10 after concentration in air.

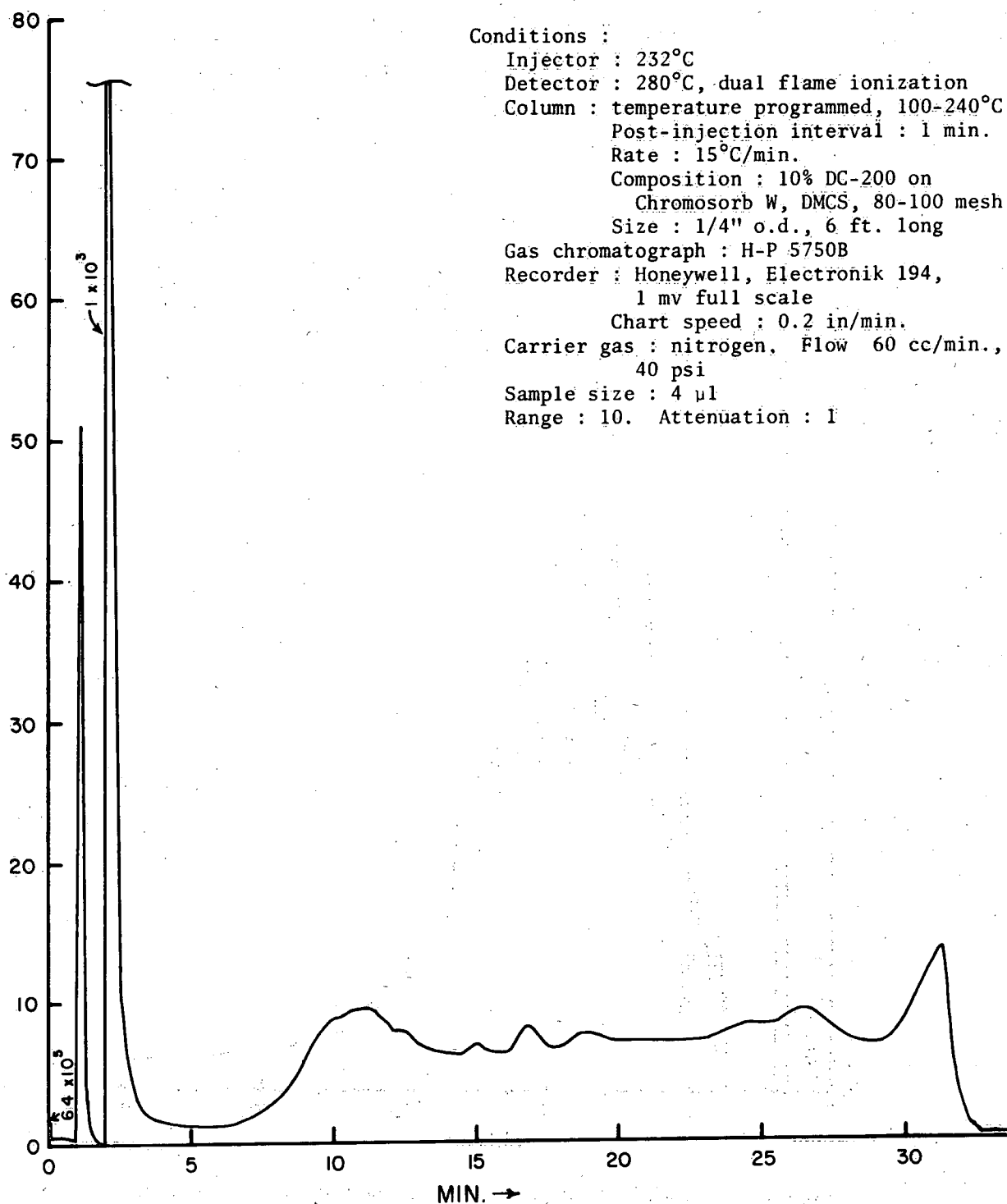


Figure 12. 500cc tap water + 50g activated carbon stirred for 2 1/2 h.; 25 cc of the filtered liquid extracted with 250 μ l heptane. The extract dried over anhydrous sodium sulphate.

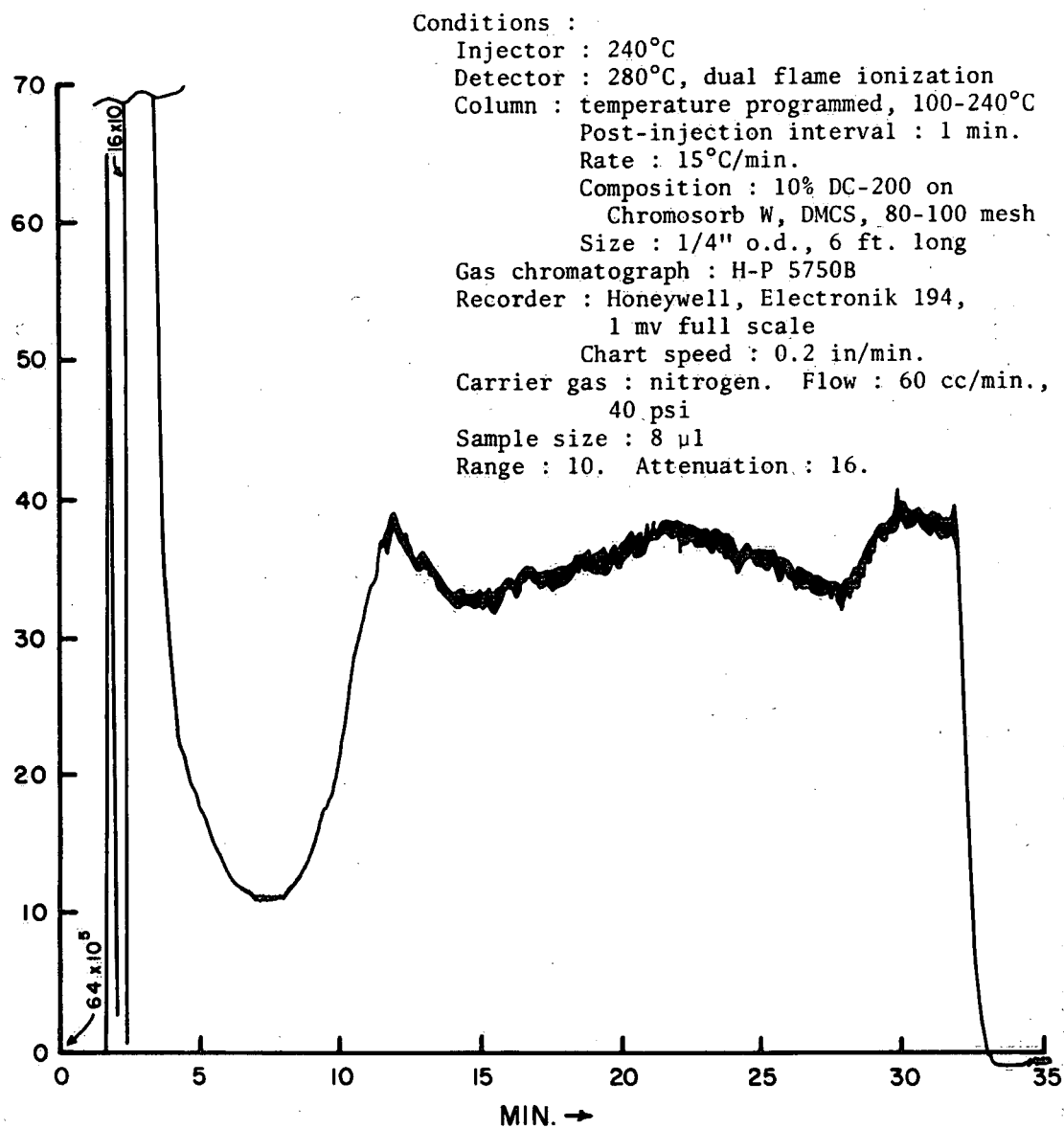


Figure 13. 500cc tap water + 50g act. carbon stirred for 96h, then the carbon extracted with 100cc(50,25,25) heptane.

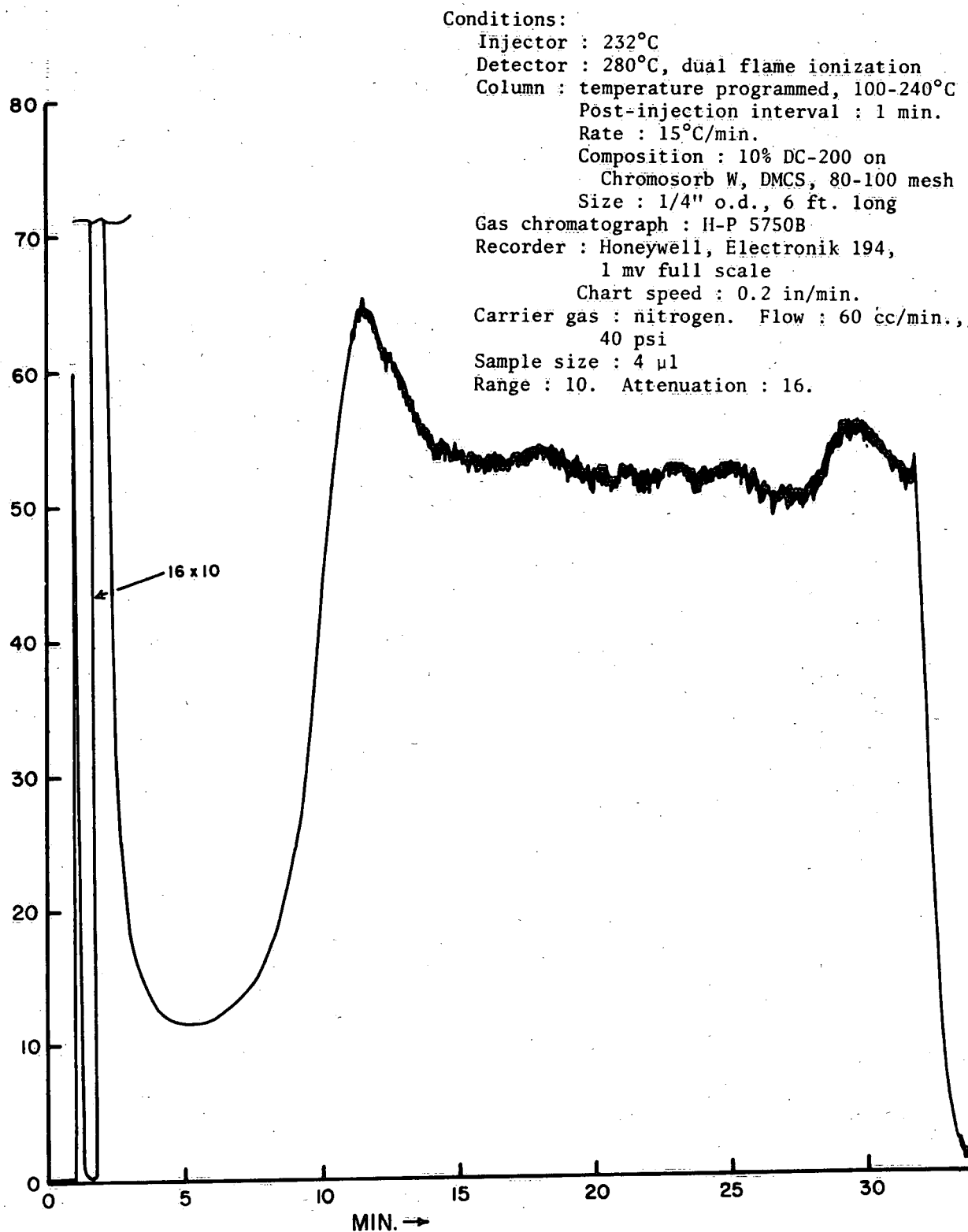


Figure 14. Heptane used for extractions.



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A discussion of the results obtained from a model study of wave action in the small boat basin at the Canada Centre For Inland Waters, Burlington, Ontario.
- No. 29 Measurement of Discharge Under Ice Conditions. P.W. Strilaeff and J.H. Wedel, 1970.
An outline of the difficulties encountered in the measurement of discharge under ice cover and a discussion of a possible technique for estimating river discharge using a single velocity in a cross-section.
- No. 30 Prediction of Saturation Precipitation of Low Solubility Inorganic Salts from Subsurface Waters under Changing Conditions of Total Concentration, Temperature and Pressure. R.O. van Everdingen, 1968.
A report containing graphs that enable the determination of the degree of (under- or over-) saturation of aqueous solutions with respect to BaSO₄, CaSO₄, SrSO₄, BaF₂, CaF₂ and MgF₂ under a variety of conditions of temperature, pressure, and total salt concentrations. Also presented are examples of the influence of temperature changes, dilution, evaporation, addition of common salt, and mixing, on the degree of saturation of the above solutions.
- No. 31 A Hydrologic Model of the Lake Ontario Local Drainage Basin. D. Witherspoon, 1970.
A discussion of a hydrologic model proposed for the Lake Ontario local drainage area. The basic principles used in the model are those of water and energy balances. Using estimates of actual evaporation, realistic values of the regional moisture are obtained which, when routed, simulate the measured outflow.

