

Characterization of Fuels and Asphalts

for

Oregon Department of Transportation

by

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1. Summary

This report describes a study of thirteen samples of fuel oil, original asphalt, and recovered asphalt received in 1983 May. Some additional work on a set of three samples received in 1982 October was also done.

1. The May fuel samples all volatilized completely at 100°, but the October fuel sample was only 43% volatilized.
2. Development of better gas chromatographic (GC) procedures was a major part of this study. The improved procedures give us a much better characterization of the fuels and asphalts.
3. The fuels are complex mixtures in which the predominant detectable components are n-paraffins in the C10 to C20 range. The n-paraffins were identified by comparison with known reference standards. The proportion of n-paraffins in the October fuel sample is only 10-15% of what it is in the May fuel samples. A large part, probably over 50%, of the October fuel sample appears to be undetected by our GC procedures.
4. The 1983 May fuel samples are all quite similar, based on GC analyses. Likewise the May original asphalt samples are all very similar, and the May recovered asphalts are all very similar.
5. The May original asphalts contain traces of C12 to C22 n-paraffins. The May recovered asphalts also contain detectable concentrations of C12 to C22 n-paraffins. The levels of C12-C16 paraffins in the recovered asphalts are somewhat lower than in the original asphalts. The levels of the C17 to C22 paraffins are about the same in both original and recovered asphalt. The paraffins present in largest concentration in both original and recovered May asphalt are C20 to C23. There is no indication that the 1983 May asphalts are contaminated with fuel.

6. No C12 to C22 n-paraffins were detected in the October original asphalt sample. C12 to C20 n-paraffins were observed in the October recovered asphalt. The n-paraffin concentration in the October recovered asphalt, relative to the n-paraffin concentration in the October fuel, increased from about 1% for C12 to 10% for the C17 compounds. Thus the October recovered asphalt contains n-paraffins that most likely originated in the fuel oil.
7. At high (350°C) GC temperatures, n-paraffins up to C34 could be observed in samples or reference standards, but no additional information relating to asphalt contamination was developed.
8. The chromatographic investigation of asphalts and fuels used a variety of chromatographic conditions, but only one column was used. Possibly other column materials or procedures would give improved results, but that is speculation. Any further work should be preceded by obtaining information from literature on asphalt characterization, or directly from those experienced in the area.
9. Other methods of asphalt characterization may be more appropriate. Liquid chromatography, thermogravimetric analysis, and differential thermal analysis should be considered.
10. The acceptability of an asphalt mixture is, in the final analysis, a function of its performance. Subjecting recovered asphalts to the same kinds of performance tests as are used for original asphalts would reveal unsatisfactory properties that develop during processing - from fuel contamination or other causes.

2. Introduction

Some asphalt aggregate mix used for highway construction or maintenance in 1982 was not performing properly. The problem was suspected to be contamination of the asphalt with fuel oil. The asphalt aggregate mix is heated by direct contact with the fuel combustion products. If combustion is incomplete, unburned fuel could mix with the asphalt and alter the composition and performance of the asphalt.

In 1982 October we received a sample of recovered asphalt suspected of being contaminated, a sample of the original asphalt, and a sample of the fuel oil. We were asked by the Department of Transportation to examine the suspect recovered asphalt by gas chromatographic (GC) analysis. We hoped that comparison of the recovered asphalt with original asphalt and with the fuel oil would answer the question: How much fuel oil, if any, is present in the recovered asphalt?

In October, after a very limited study of GC conditions, we observed some compounds which were present in the fuel oil and in the recovered asphalt but not in the original asphalt. Based on a comparison of relative amounts of these compounds in the recovered asphalt and in the fuel oil, it appeared that the recovered asphalt contained about 8% fuel oil.

In 1983 May we received in all 13 samples: fuel oil (4), original asphalt (4), and recovered asphalt (5). Again the question was whether or not fuel oil was present in the recovered asphalt.

Both fuel oils and asphalts are very complex mixtures, and development of a better procedure for GC analysis was important. Considerable time and effort was spent in finding GC conditions that would satisfactorily characterize the fuel oils and asphalts. Although it's not certain the final GC procedure is optimal, it is far superior to the procedure used in October, and comparisons of

recovered asphalts with original asphalts and fuel oils are much more clear cut and definitive. The preparation of a known n-paraffin standard mixture permitted the actual identification of the n-paraffins as the predominant components of the fuel oils and of n-paraffins in the original and recovered asphalts. The 1982 October samples of fuel oil and asphalt were reanalyzed to take advantage of the improved GC procedures, and to allow a direct comparison with the 1983 May samples.

In addition to the GC studies, a gravimetric comparison of the volatility of the fuels and asphalts at 100°C was made.

3. Procedure and Results

3.1 Volatilization at 100°C

Volatilization of fuel and asphalt samples at 100°C was determined by heating one gram samples in aluminum dishes for 3 days. The results are shown in Table 1. All the fuel oil samples received 1983 May completely volatilized in three days at 100°C. This shows that these fuels did not contain any significant components of very low volatility. That is, there were no significant components that were higher boiling than diesel fuel. The fuel oil sample received in 1982 October (3532) was very different. It was only 43% volatilized at 100°C. Thus a large fraction of this sample was higher boiling than diesel fuel, or was nonvolatile.

3.2.a. Gas Chromatographic Characterization of Fuels and Asphalts

Approximately 2% mixtures of fuel or asphalt in trimethylpentane (TMP) were prepared by weighing 0.10 g samples into 2 dram vials. Then 5.0 ml TMP was added to each vial with a syringe. The mixtures were warmed to 50°C for several hours and then left to stand overnight. The 1983 May fuel oil samples dissolved completely, but fuel sample 3532 (October) did not all dissolve. None of the asphalt samples dissolved completely. The sample numbers of the 2% solutions

are correlated with the Department of Transportation Laboratory identification in Table 1.

The GC system was a Perkin Elmer Sigma 2 with flame ionization detector. The column was 10 ft x 1/8 in stainless steel packed with 10% SP 2100 (methyl silicone) on 100/120 Sulpulcoport. Flow rate for nitrogen carrier gas was 20 cc/min. Column temperature was immediately programmed from 160°C to 250° C at 6°/min, then held at 250°C. Samples injected were 2 ul. This procedure would detect components in the normal paraffin range of about C12 to C22, but would not characterize complex high boiling fractions such as lubricating oil.

Copies of 8 GC recorder chart tracings will be referred to in this report (Figures 1-8). For all traces, the chart speed was 0.5 in/min for the first 10 minutes, and then 0.1 in/min. Detector attenuation depended on the sample and is indicated on the bottom of the trace. For fuels the attenuation was 256X. For asphalts, the attenuation between about 2 min and 10 min was 8X; after 10 min, attenuation was 16x.

A chromatogram of solvent (TMP) alone is shown in Figure 1. The initial large peak is the solvent. Tailing from this peak continues until about 3 minutes. At about 5 minutes, the baseline begins to gradually rise, and this rise continues, with acceleration, until about 15 minutes, at which time the column has reached 250°C, and remains at that temperature. The rising baseline between 5 and 15 minutes is caused by bleed of the column fixed phase which increases as the temperature increases. Note that this solvent chromatogram contains minor peaks between 8 and 9 minutes and at about 20 to 25 minutes which should be discounted in chromatograms of asphalt mixtures.

Figure 2 is a chromatogram of known n-paraffins C12, C13, C15, C16 continuing through C23 (at lower detector attenuation, peaks of paraffins up to C33

Table 1: Identification and Volatilization of
Fuel and Asphalt Samples

OSU # for Volatilization	ODOT I.D.		Fraction Volatilized (100°, 3day)	OSU # For 2% Solution Used for GC
1983 - May Samples				
144-1	24015	fuel oil	.998	148-1
144-2	24015	orig asp	.024	148-2
144-3	24015	redc asp	.011	148-3
144-4	24016	fuel oil	.998	148-4
144-5	24016	orig asp	.015	148-5
144-6	24016	recd asp	.012	148-6
144-7	24017	fuel oil	1.000	148-7
144-8	24017	recd asp	.010	148-8
144-9	24019	fuel oil	1.000	148-9
144-10	24019	orig asp	.017	148-10
144-11	24019	recd asp	.010	148-11
144-12	83-5120	orig asp	.012	148-12
144-13	83-5121	recd asp	.019	148-13
1982 - October Samples				
144-14	3532	fuel oil	.431	148-14
144-15	Witco W2	orig asp	.001	148-15
144-16	Witco W2	rec'd asp	.021	148-16

were seen.) This standard paraffin mixture, prepared from Aldrich Chem. Co. n-paraffins, contained 1.21 mg/ml C12, 2.09 mg/ml C13, 1.03 mg/ml C15 and 1.89 mg/ml C16. The standard also contained 2.71 mg/ml of a paraffin labeled "eicosane" (C20), origin unknown, which actually contained n-paraffins from C17 to at least C33. By comparing retention times of the known paraffins with the retention times of the components of fuels and asphalts, n-paraffins in the fuels and asphalts were identified. The correlation of GC retention time with carbon number of n-paraffin is given in Table 2. (Retention times of paraffins C10, C11, and C14 were determined from fuel oil mixtures.)

TABLE 2

Correlation of n-paraffin carbon number with GC retention time.

(GC conditions as described.)

C-number	10	11	12	13	14	15	16	17	18	19	20	21	22	23
Retention Time (min)	(1.9)	(2.6)	3.6	4.8	(6.2)	7.8	9.4	11.1	12.8	14.4	16.1	18.0	20.4	23.4

3.2.b. Characterization of Fuels

The gas chromatograms of the 4 fuels received 1983 May were very similar. One that is representative (148-4) is shown in Figure 3. It exhibits a series of predominant peaks with retention times of 1.9, 2.6, 3.6, 4.8, 6.2 min, etc. that correspond to the n-paraffin series C10, C11, C12, C13, C14, etc. (cf Fig 2). Between consecutive major components are minor components that were not identified. The chromatogram (Fig. 4) of October fuel sample 3532 (148-14) exhibited many of the same components as the other fuels, but the proportion of fuel represented by the major detectable constituents is much less. Comparing C14, C15 and C16 paraffins in sample 148-14 with the same constituent in sample

148-4 we find that the concentrations of these constituents in sample 148-14 are only 10-13% of the concentration of the same constituent in sample 148-4. Much of sample 3532 (148-14) is unaccounted for by the chromatograph. Since it was found that most of 3532 is less volatile than diesel fuel the unaccounted for material is probably higher boiling fractions that would not be detected by with the chromatographic procedure.

3.2.c. Characterization of Asphalts

The 2% asphalt mixtures were chromatographed at the same conditions used for the fuels. All the 1983 May original asphalts were very similar. Figure 5 (148-5) is representative. Traces of n-paraffins are detectable (4.7 min C13, 6.2 min C14; 7.8 min, C15; 9.4 min C16, etc). The largest n-paraffin component appears to be C20 (16.1 min).

All of the 1983 May recovered asphalts were also very similar. Figure 6 (148-6) is representative. The recovered asphalts also contain traces of some of the n-paraffins, but the concentrations of the C12 to C16 paraffins in the recovered asphalt is slightly lower than in the original asphalt. The concentrations of the C20 and C21 paraffins (16.1 and 18.0 min) are about the same in both original and recovered May samples. There is no evidence of contamination of the recovered asphalts with fuel.

The chromatogram of the 1983 October original asphalt (Witco W2) is shown in Fig. 7. No n-paraffin peaks are detectable. (The peaks between 8 and 9 minutes are undoubtedly spurious and were sometimes seen in the solvent blank. In any event, their retention times do not correlate with n-paraffins). This sample has lower n-paraffin content than any of the 1983 May asphalts.

The chromatogram of the October recovered asphalt is shown in Figure 8. All of the n-paraffins from C12 to C20 (3.5 to 16.1 min) are easily detectable, as well as some intermediate, unidentified components.

Since the October original asphalt did not contain detectable quantities of these n-paraffins, it is probable that the fuel oil is the source of the n-paraffins in the recovered asphalt.

The absolute amount of n-paraffins in the October recovered asphalt was not determined. But it was possible to compare the concentration of individual n-paraffins in the recovered asphalt with the concentration of the same n-paraffin in the fuel oil (3532). This is done on Table 3.

Table 3

Concentration of n-paraffin in October recovered asphalt, relative to the concentration of the same paraffin in October fuel 3532.

n-Paraffin (Carbon number)	12	13	14	15	16	17
%	0.8	2.0	2.9	4.7	7.9	9.8

These numbers give some indication as to the contamination of the October recovered asphalt on a component by component basis. But since over half of the October fuel is not detected by GC analysis, an overall integral estimate of the degree of contamination of the October recovered asphalt cannot be given. It would be possible to calculate an approximate absolute concentration of the C12, C13, C15, and C16 n-paraffins in the various fuels and asphalts, but it's doubtful that this would be meaningful.

3.2.d. Characterization of Fuels and Asphalts At Different GC Conditions

Further characterization of fuel and asphalt samples by GC analysis at higher temperature was explored. My hope particularly, was to better characterize the October fuel material. Isothermal chromatography at 250°, 300°, and 350° was tried, but no more information on the nature of the October fuel (or other samples) was developed.

4. Discussion

To examine asphalt for the possible presence of fuel oil, some measurable property of fuel oil must be found which is very different from the same property of asphalt. The property of the fuel oil must be measurable in the presence of asphalt, or some way of separating the oil and asphalt must be developed. One property in which the two differ is volatility. Asphalt is the residue remaining after the volatile materials are removed from petroleum; fuel oil is one of the volatile fractions. Thermal gravimetric analysis is a procedure that measures sample weight loss as temperature increases. This should detect volatile materials in an asphalt. Differential thermal analysis measures heat uptake or release as temperature increases. Since volatilization is endothermic, it should also be detected by DTA.

Chromatographic analysis reveals differences in volatility or solubility in a moving fluid phase relative to adsorption or solubility in a fixed phase. In liquid chromatography solubility is the critical factor that allows components to be separated and identified. L.C. may be well suited for characterization and comparison of fuel oils and asphalts. In gas chromatography, volatility is the critical factor for separation and identification. With suitable standards, individual components can be identified. The Diesel type fuel oils in the May set of samples appeared to be well characterized by GC, but the much less

volatile October fuel sample was less completely characterizable. Only a very small fraction of an asphalt is volatile enough to be observed by GC.

Another property in which fuel oil and asphalt differ is in their chemical nature. Fuel oil is largely aliphatic while asphalt is largely aromatic. Infrared and nuclear magnetic resonance spectroscopy can distinguish aliphatic hydrogen from aromatic hydrogen and therefore may be able to detect fuel oil contamination in asphalt.

26.0

15.8

Fig 1 TMP Trimethylpentane

10.0 min
0.1 min
10 min

20 min

8 min

6 min

4 min

8.2 =

16x

8x

TMP

2nd

54.5

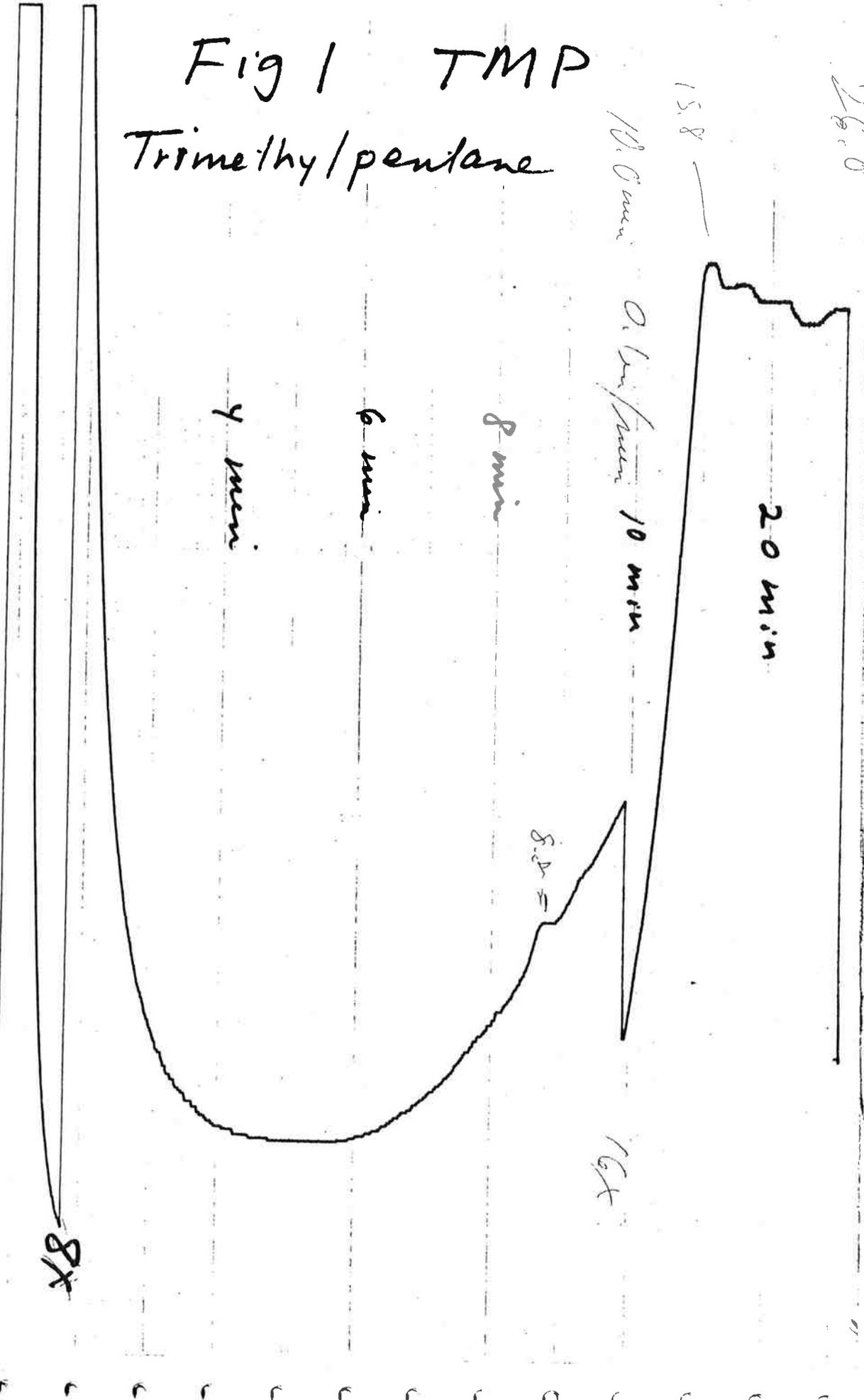
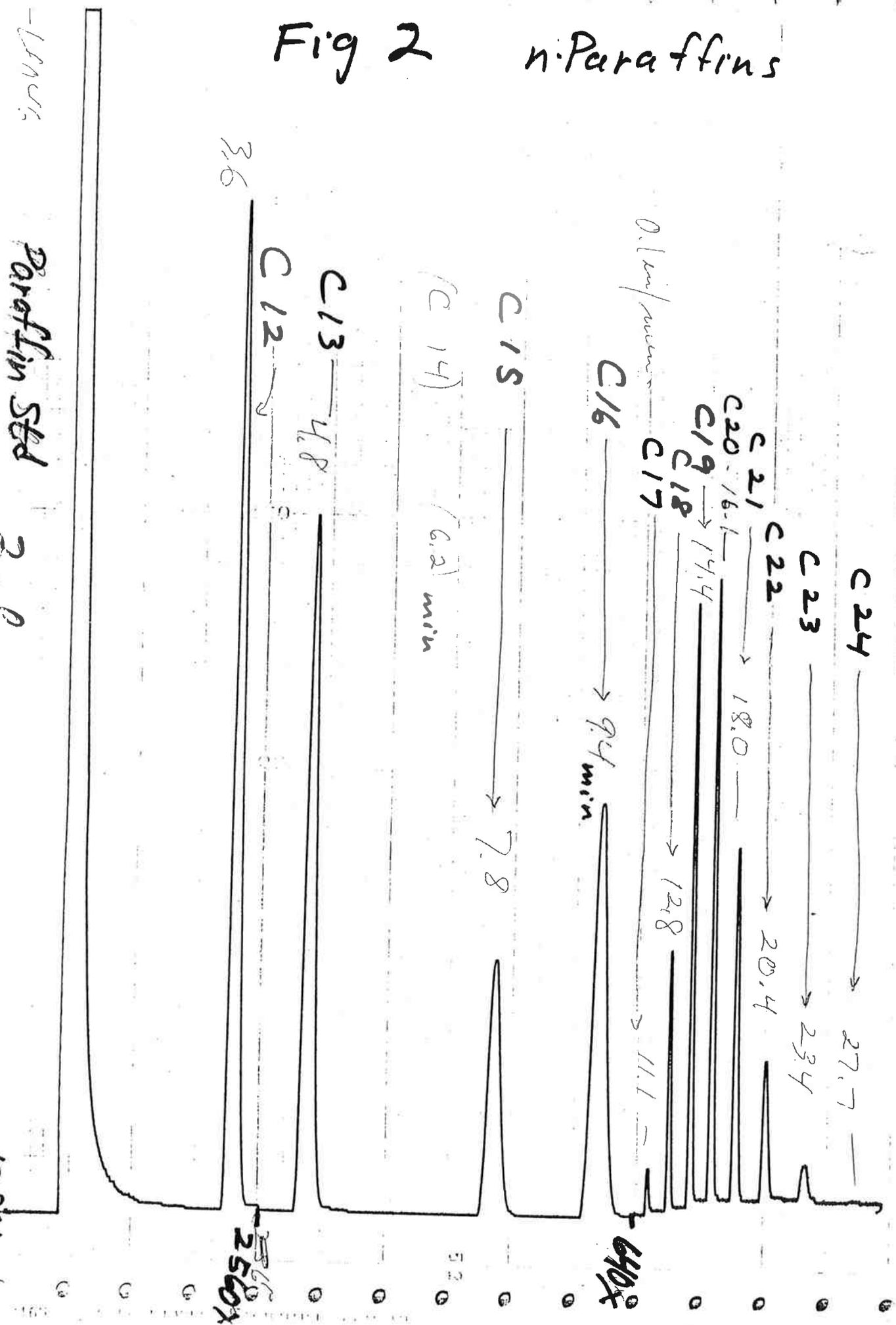


Fig 2 n-Paraffins



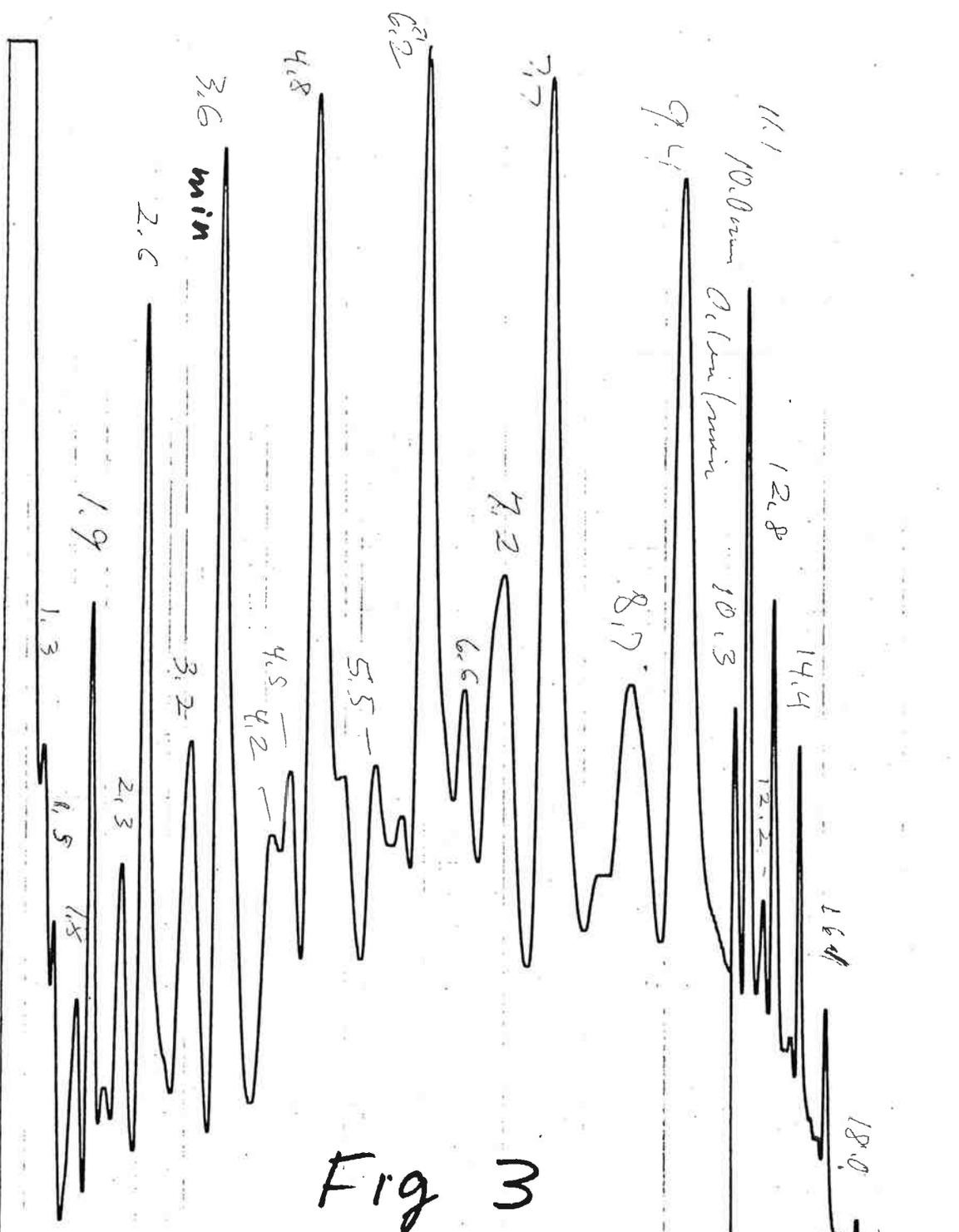


Fig 3

Fuel oil 24016
(148-4)

110412

148-4

2nd

256x

Fig 4

Fuel oil 3532

(148-14)

4044

7 MP

2nd

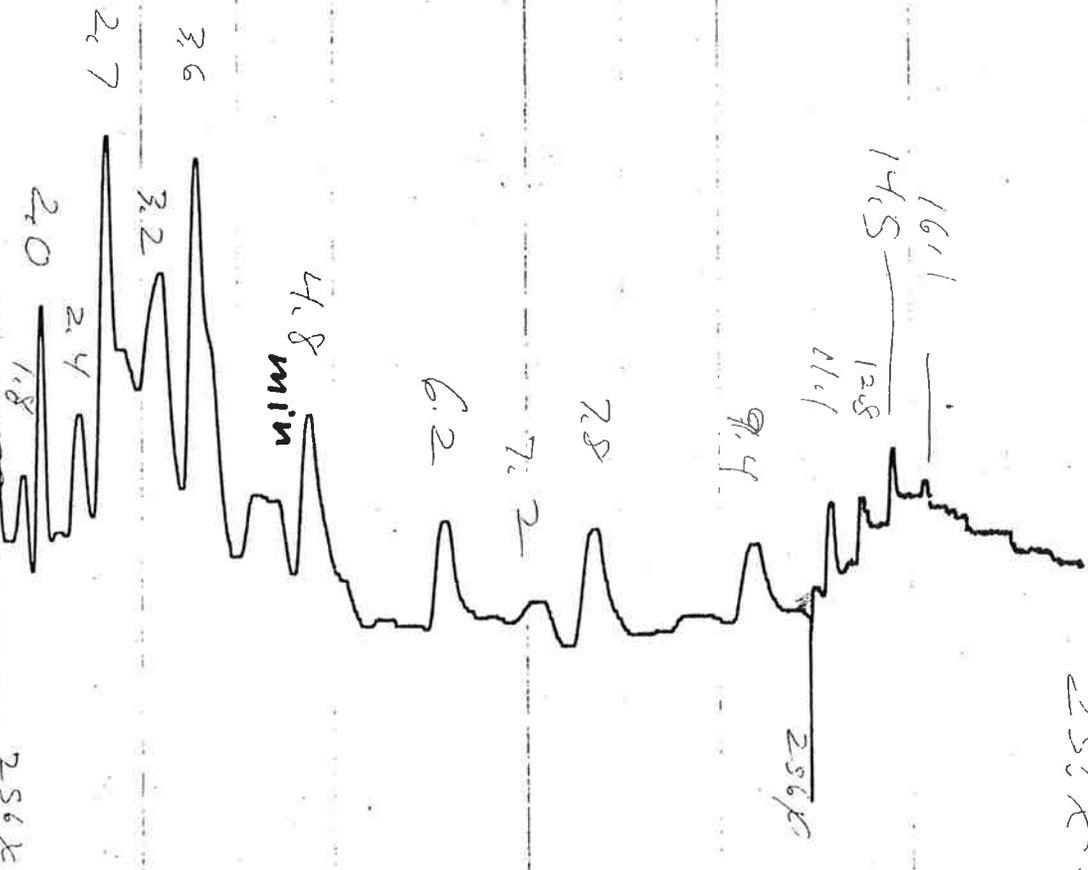
10.0 oil surface

4043

148-14

2nd

1.2



Ether peaks

256X

256X

256X

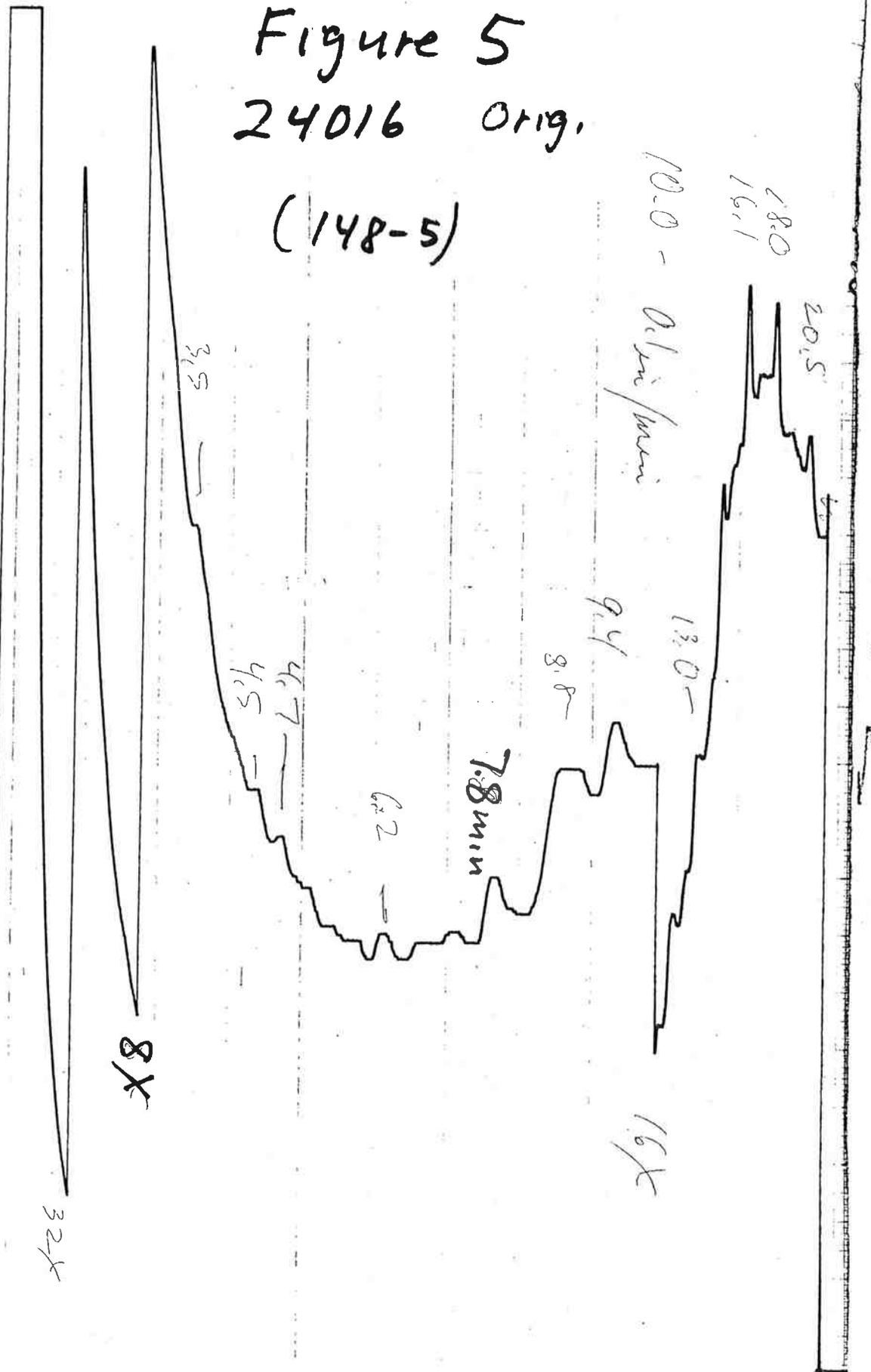
256X

Figure 5
 24016 Orig.
 (148-5)

4034- 148-5
 200

Slow expansion ?

256



*
Fig 6

24016 recovered
(148-6)

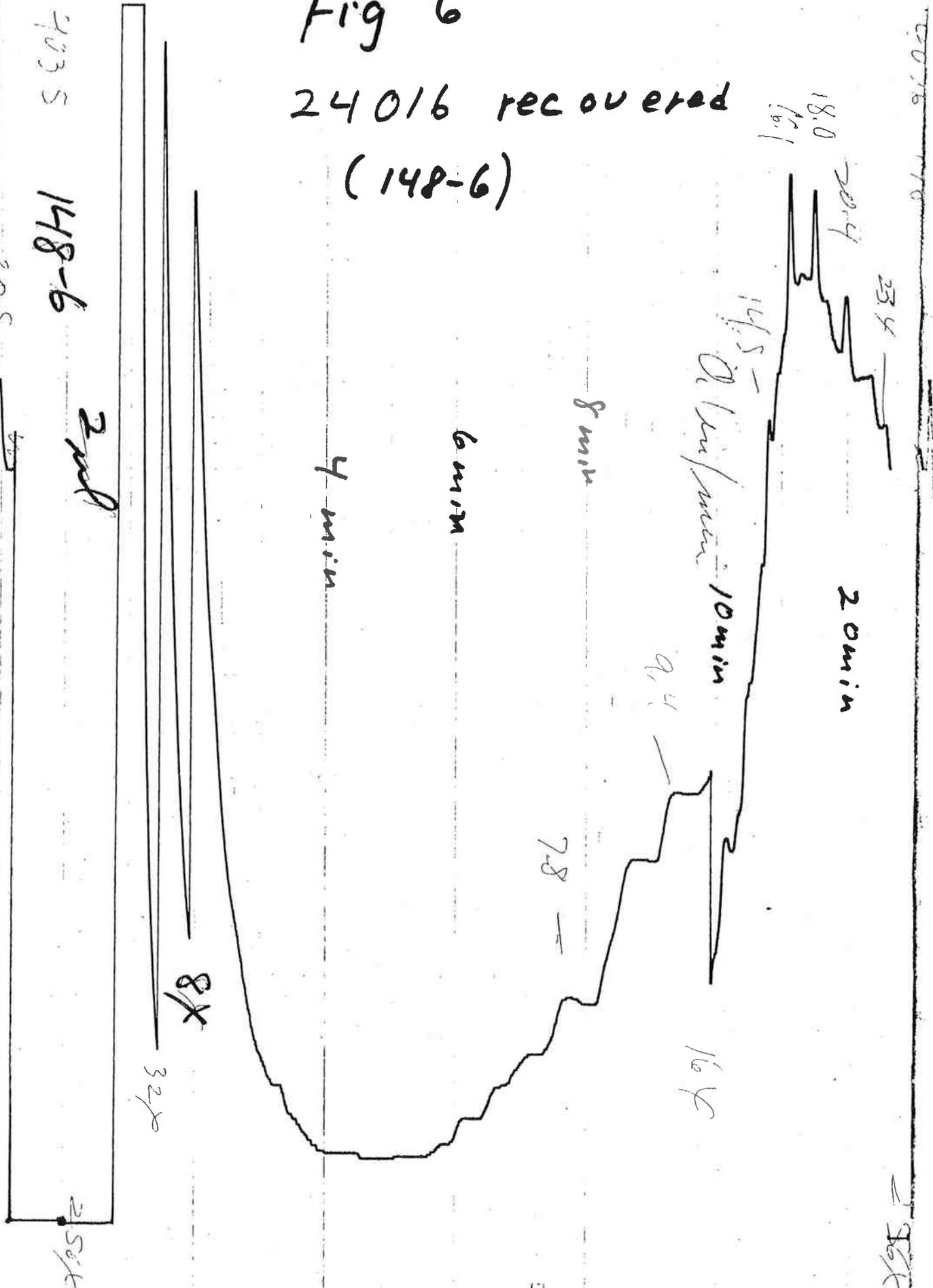


Fig 7

Witco W 2 Orig.

(148-15)

4039
148-15
278

256A

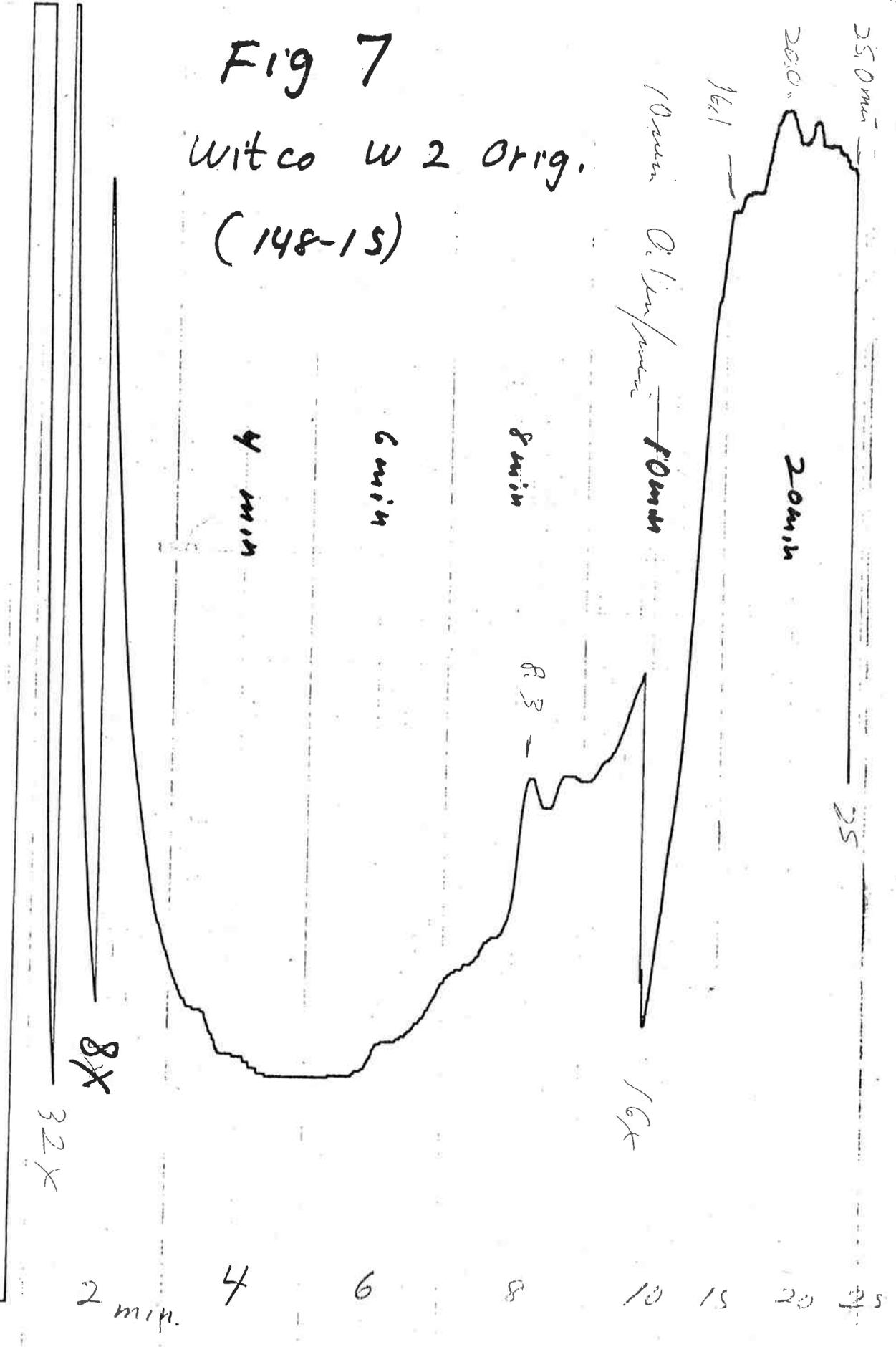
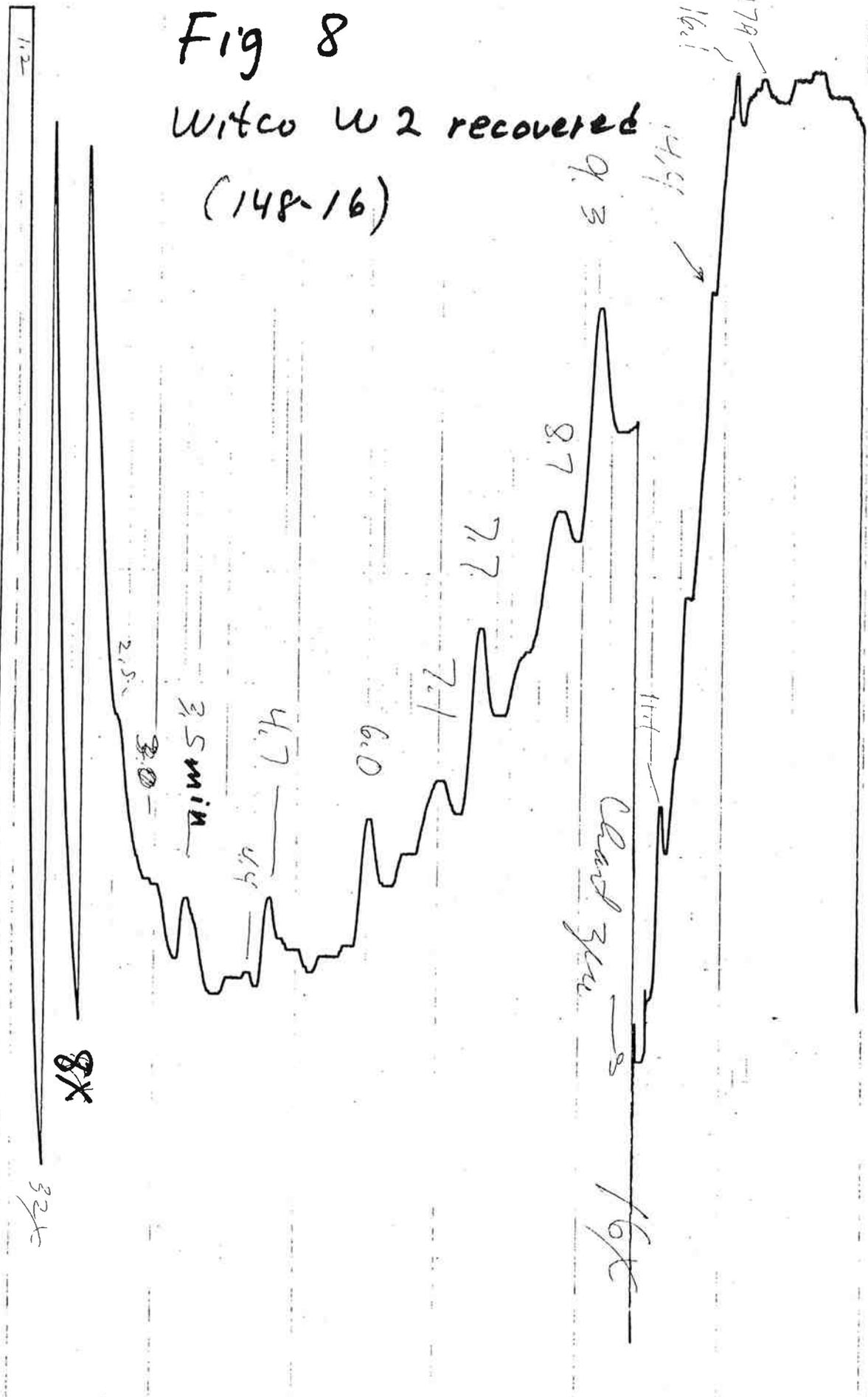


Fig 8

Witco W2 recovered
(148-16)



4040

148-16

2nd