Naval Submarine Medical Research Laboratory

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# FINAL REPORT
# ANALYSIS OF HYDRAULIC FLUIDS AND LUBRICATING OILS FOR THE FORMATION OF TRIMETHYLOLPROPANE PHOSPHATE (TMP-P)

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PREPARED FOR:

SEA 05R23

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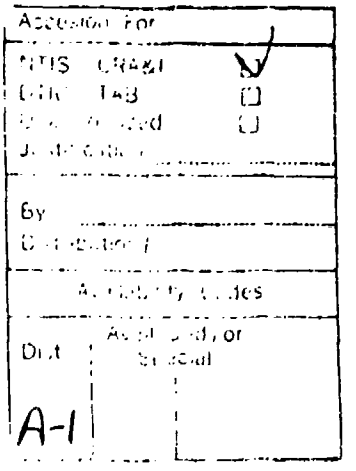

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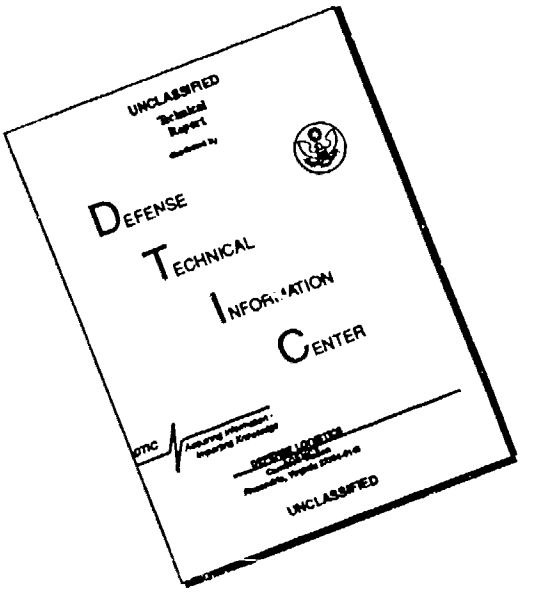


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## PREFACE

This document constitutes the final report on the Analysis of Hydraulic Fluids and Lubricating Oils for the Formation of Trimethylolpropane Phosphate (TMP-P). The research covered a period from August 1985 through April 1987.

The work was sponsored by the U. S. Navy (SEA 05R23) and was performed at Naval Submarine Medical Research Laboratory, Naval Submarine Base New London, Groton, CT under Program Element 63514N.

ACKNOWLEDGEMENT

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# EXECUTIVE BRIEF

Twenty-six different oils, hydraulic fluids and lubricants in the U.S. Navy inventory were screened for yield of the neurotoxin Trimethylolpropane phosphate (TMP-P) in order to obtain an estimate of safety hazard potential.

A commercially available synthetic aircraft engine oil (Exxon 2380) with a demonstrated yield of TMP-P was studied to establish the optimal temperature and pyrolysis time conditions for TMP-P production.

Results of the analysis indicate that in the Exxon 2380 synthetic oil, TMP-P is formed very rapidly (within 5 minutes) with formation beginning in a temperature range of 350 to 400°C. The yield of TMP-P increases as a function of temperature and achieves a maximum yield at 450-500°C. Above this temperature, the TMP-P yield decreases rapidly to zero at 600°C probably due to thermal decomposition. At optimal temperature for TMP-P production (450°C) the yield of TMP-P increases as a function of temperature, reaching a maximum between 30 and 60 minutes. After 60 minutes, the yield of TMP-P decreases, attributable to a competition between TMP-P formation and thermal decomposition. At 90 minutes the yield of TMP-P is only 40% of the maximum yield at 60 minutes.

Only one of the twenty-six oils from the U. S. Navy inventory gave evidence of TMP-P formation. The maximum TMP-P yield of oil (MIL-L-23699C) was only 1.9% (120 ug/g) of the maximum yield (6241 ug/g) for the Exxon 2380 synthetic engine oil.

Results obtained in the Naval Submarine Medical Research Laboratory (NSMRL) study for Exxon 2380 have been found to be in good agreement with results obtained at National Transportation Safety Board and University of Colorado. Results reported from these three laboratories have been applied to an assessment of the hazard potential of pyrolyzed oils and lubricants assayed in this study.

The conclusions and recommendations resulting from this study are as follows:

CONCLUSIONS

1. It is possible to generate large quantities of TMP-P from Exxon 2380 oil under laboratory conditions.
2. Of the 26 oils which were analyzed and which were actually found in the U.S. Navy inventory, only one, MIL-L-23699C, demonstrated evidence of formation of TMP-P. It appeared to produce only 1/30 the TMP-P of Exxon 2380.

Recommendations

1. Research should be initiated for overall toxicity of combined, combustion byproducts rather than for any individual combustion product present.
2. All polyol ester based synthetic oils in the U.S. Navy inventory should be tested for toxic byproduct production.
3. The Exxon 2380 formulation for MIL 23699 should not be included in the U.S. Navy inventory because of its high potential for producing TMP-P on pyrolysis.

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## BACKGROUND

Fires are a serious problem for the U.S. Navy as well as the civilian community. In an established fire scenario, the well-known combustion products common to fires, i.e., irritants and narcotic gases such as CO, $CO_2$, and HCN, present a substantial hazard to shipboard operational effectiveness and integrity as well as to the safety crew personnel.

In addition to the common combustion products there are serious concerns as to whether extremely toxic materials can be produced by certain materials that are carried aboard ships. One of these potentially "super-hazardous" materials is trimethylopropane phosphate (TMP-P).

Petajan et al. (23)* and Voorhees et al. (25) have demonstrated that TMP-P can be formed during the combustion of polyurethane foams, the formulation of which is based on trimethylol propane polyols and phosphorus containing fire retardants. Kalman et al. (14) have demonstrated the production of TMP-P during the thermal decomposition of an aircraft engine oil containing fatty acids of trimethylol propane (TMP) and tricresylphosphate (TCP). Their data show small quantities of TMP-P produced in an open tube combustion device at temperatures from 400 to 645°C. Larger quantities of TMP-P were produced at 432°C when the oil was pyrolyzed in sealed glass tubes. Aircraft turbo oil lubricants with the designation MIL-L-23699 are in common usage throughout the military and may have TMP and TCP in the base stock.

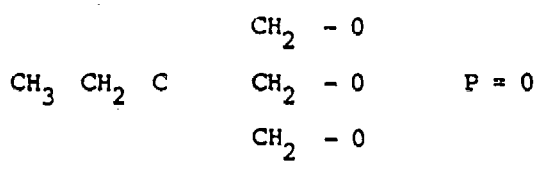
Since TMP-P has been demonstrated to be a potent neurotoxic chemical (29), the following study was initiated in order to determine the potential for pyrolytic TMP-P formation in a variety of oils and lubricants used by the U.S. Navy.

* references appear in Appendix A.

Physical Chemical Properties of TMP-P (19, 25, 26)

Trimethylolpropane Phosphate (TMP-P) is a white micro-crystalline solid which is not explosive, not an oxidizing agent and is relatively inflammable and non-corrosive.

It has the following structure:



The formal chemical name is 4-ethyl-1-oxo-2,6,7-trioxa-1-phospha-bicyclo (2.2.2) octane.

The formula and molecular weight are: $C_6H_{11}O_4P$ ; MW = 178

Vapor Pressure

The vapor pressure for TMP-P has been reported as follows:

| TEMP | VAPOR PRESSURE (mmHg) |
|---|---|
| 22°C | $4 \times 10^{-8}$ |
| 60°C | $7 \times 10^{-7}$ |
| 108°C | $1 \times 10^{-5}$ |
| 140°C | $1 \times 10^{-4}$ |

TMP-P solid is not directly a source of hazardous vapor. The room temperature vapor pressure is such that an equilibrium content of TMP-P in air is 0.00005 ppm.

## Solubility

The following solubilities have been reported for TMP-P:

| | Approximate Solubility (% w/v) |
|---|---|
| Ethanol | 3 |
| Pehroleum Ether 60-80 | <1 |
| Toluene | <1 |
| Ethyl Acetate | 2 |
| Methyl Ethyl Ketone | 5 |

## Thermal Stability

Thermal decomposition curves for TMP-P have been determined by passing the material through a heated zone in both air and nitrogen streams and measuring TMP-P recovery. Temperatures in a range of 350°C to 850°C were used with a residence time of 25 seconds. Recovery data is reported to be

| Temperature | Recovery (%) (approx) |
|---|---|
| 350°C | 88% |
| 450°C | 78% |
| 500°C | 67% |
| 650°C | 3-7% |

Thus above 500°C, TMP-P is quickly decomposed.

Spectroscopic Data

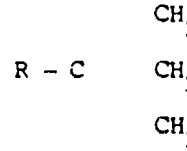
The following predominant ions have been reported for TMP-P using conventional electron impact mass spectrometry

| M/Z | 68 | 67 | 79 | 150 | 151 | 80 | 178 |
|---|---|---|---|---|---|---|---|
| Intensity (%) | 100 | 56 | 50 | 32 | 25 | 25 | 11 |

Toxicity of Bicyclophosphate Esters

Acute toxic effects have been reported to have been caused by certain 4-alkyl derivatives of 4-ethyl-1-oxo-2,6,7-trioxa-1-phospha-bicyclo(2.2.2) octane (1, 14, 15, 27). Bellet and Casida (1) have reported that these compounds after intraperitoneal injection into mice, produced convulsive seizures and death within a few minutes. They showed that the bicyclophosphates, phosphites and thiophosphates with the same 4-alkyl substituents are of similar toxicity, but the potency is dependent on the nature of the 4-alkyl substituent. Maximum toxicity was obtained with the isopropyl group substitution. Phosphates of the 4-isopropyl or 4-n-propyl compounds are slightly more toxic than phosphites or thiophosphates.

The values reported for toxicity of bicyclophosphate esters with various 4-alkyl substituents are (1):



| R | $LD_{50}$ mg/kg body weight |
|---|---|
| $CH_3-$ | - |
| $CH_3CH_2$ | 1.10 |
| $CH_3CH_2CH_2$ | .39 |
| $(CH_3)_2$ CH- | .22 |

The $LD_{50}$ is defined as the dose that is lethal for 50 percent of the test subjects.

An indication of the toxicity of TMP-P can be demonstrated by comparing its $LD_{50}$ with a familiar, highly toxic substance such as strychnine. This substance has a reported $LD_{50}$ of 1.4-2.3 mg/Kg while TMP-P has a reported $LD_{50}$ of 1.0 mg/Kg. TMP-P therefore is slightly more toxic on a weight basis than strychnine when injected intraperitoneally.

The bicyclophosphate esters have reported to produce convulsive seizures and death in mice within a few minutes. The definitive mechanism by which TMP-P produces its toxic effect has not been fully elucidated, but it is thought to act as an antagonist of the GABA neurotransmitter substance at the nerve endings. A short review of the literature on the mechanism of action of TMP-P is presented in Appendix A.

## MATERIALS AND METHODS

### 1. Open pyrolysis system

In this system, apparatus similar to that employed by Kalman, et al. (14) was used. 40 ul of oil was placed in each of 4 ceramic boats for a total sample of 160 ul of oil. The boats were pushed into a pyrex combustion tube of a Lindberg Single Zone Tube Furnace (Model 59344). The pyrex combustion tube was 20 cm long, 3 mm I.D. with a constriction at one end. A Teflon tube, 20 cm long (I.D. = 3 mm) was fitted over the constriction on the pyrex combustion tube. This tubing led into a 5 ml vial which was filled with 2 ml methanol (MeOH) and served as a trap for pyrolysis products. An air flow of 20 ml/min was maintained through the combustion tube to carry the pyrolysis products into the MeOH trap.

For the open tube pyrolysis, the oven was preset to selected temperatures and after the temperature stablized, the combustion tubes containing the samples were heated in the oven for 10 minutes. The oil samples in the ceramic boats flash pyrolyzed rapidly and condensed in the cool part of the combustion tube outside of the oven. The majority of the pyrolysate condensed on the upstream side of the Teflon transfer tube. After pyrolysis the apparatus was lifted out of the oven and allowed to cool. Air flow was stopped, and the MeOH trap was removed. The combustion tube and Teflon tube were flushed with 4 ml MeOH to remove the condensed pyrolysate. Samples from both the MeOH trap and from the combustion tube were analyzed by GC/MS for TMP-P.

Two temperatures were selected for the open tube pyrolysis; 390°C and 470°C. These temperatures were selected on the basis of the results reported by Kalman, et al as producing effective detectable yields of TMP-P. Experiments using open tube pyrolysis were performed on Exxon 2380 with Trimethylolpropane (TMP) and Tricresylphosphate (TCP) in the base stock.

Sealed Tube Pyrolysis - Pasteur Pipets

Pyrolysis tubes were fashioned from 5 3/4 inch Pasteur bacteriological soft glass pipets which were flame sealed at the tip. 40 ul of oil were pipeted into the tube and the open end of the tube was flame sealed. Total internal volume of the resulting pyrolysis tube was 2 ml. These tubes proved to be adequate for pyrolysis at temperatures below 480°C. Above that temperature the tubes failed due to internal gas pressure buildup resulting from pyrolysis of the sample.

The sample material used in this experiment was Exxon 2380 engine oil.

Following pyrolysis of the oil sample, the pyrolysis tube was removed from the combustion tube in the tube furnace and allowed to cool. The pyrolysis tube was opened and 100 ul of MeOH were pipeted into the tube. The tube was tilted manually and rotated to bring the MeOH solvent for TMP-P into contact with the wall surface. Following this procedure, the MeOH solvent containing the pyrolysate was decanted into a 5 ml glass vial, capped with a Teflon screw cap and retained for GC/MS analysis.

In order to determine effects of combustion temperature and combustion time on TMP-P formation, the following pyrolysis conditions were established. Samples were pyrolyzed at temperatures of 140°C, 165°C, 190°C, 215°C, 240°C, 265°C, 290°C, 315°C, 340°C, 365°C, 390°C, 415°C, and 440°C. At each temperature, samples were pyrolyzed for time periods of 1, 5, 10, 20, and 30 minutes.

3. Heavy walled, Sealed Tube Pyrolysis - Qualitative Assay

Because of repeated structural failure of the soft glass pyrolysis tubes at temperatures above 440°C, a modified pyrolysis procedure was established. Pyrolysis tubes were fashioned of annealed pyrex glass by a professional glass blower. The internal diameter of these tubes was 1 cm with a wall thickness of 3 mm. A small section of thick walled pyrex glass tubing 8 mm O.D. was sealed to the main body of the tube to facilitate flame closure of the tube after the oil sample had been added. The length of the sealed heavy-walled pyrolysis tube was 12.5 cm with an internal volume of 10 ml. 100 ul of oil was used as a pyrolysis sample in this series of experiments.

The sample materials used in this procedure were the Exxon 2380 and 26 additional oils and lubricants. These additional oils, fluids and lubricants which are in general use in the U. S. Navy are listed in Appendix B, along with the source location, type, and description.

The temperatures at which Exxon 2380 samples were pyrolyzed in the thick-walled tubes were 440°C, 450°C, 460°C, 470°C, 475°C, 480°C, 490°C, 515°C, 540°C, 565°C, and 590°C,. Single samples in the temperature range 440°C to 490°C were pyrolyzed for 30 minutes. Single samples in the temperature range 515°C to 590°C were pyrolyzed for periods of 5, 10, 20 and 30 minutes.

Single samples of the 26 additional oils and lubricants were screened for TMP-P production at a temperature of 540°C for 30 minutes.

Following pyrolysis in the Lindberg Tube Furnace, the pyrolysis tubes were allowed to cool to room temperature for 30 minutes, then to 4°C in a freezer to minimize gas pressure in the tube. The neck of each tube was scratched with a file and broken off under an exhaust hood. 200 ul of methanol were added into the pyrolysis tubes with a pipetter. As in previous analysis the tube was tilted and rotated manually to insure that the MeOH fully contacted the length of the interior of the tube. The pyrolysate solution was decanted into a 5 ml glass vial, capped with a Teflon cap and set aside for GC/MS analysis.

4. Heavy Walled Sealed Pyrolysis-Quantitative Assay

In order to obtain better data from a more quantitative TMP-P recovery, the pyrolysis and sample extraction procedures were modified as follows.

Pyrolysis tubes were of the constructed as in (3. above). 200 ul of oil was used as sample volume. Tubes were pyrolyzed in a muffle furnace (Precision Scientific Co., temperature range 0-2000°C). Four tubes were pyrolyzed in the oven at each selected temperature ir order to obtain more statistically accurate data on TMP-P yield.

The wash procedure was also modified in order to provide a more standardized procedure and to insure, as much as possible, equal recovery in each tube.

After removal from the muffle furnace, the tubes were allowed to cool to room temperature and then were placed in a freezer. After sufficient time (1/2 hour minimum) had elapsed for the tubes to reach freezer temperature (4°C), the tubes were opened, and allowed to come to room temperature. Four (4.0) ml of methanol were pipetted into each tube. The tubes were vigorously shaken on a Vortex mixer for approximately 1 minute until the charred material coating the inside of the tube was removed. Oily material that had not been charred was readily or dissolved in the methanol. The tubes were centrifuged for three (3) minutes at 1500 rpm (Safeguard Centrifuge) to remove particulate matter. The pyrolysate was decanted from the tube by means of a 4.0 ml syringe, placed in 5.0 ml vial and capped with a Teflon cap.

Using these modified procedures, the following studies were performed:

Time Constant-Temperature Varied

a. In order to evaluate effect of temperature on TMP-P production, four (4) tubes were pyrolyzed at each of the following temperatures for 30 minutes: 300°C, 400°C, 425°C, 450°C, 500°C. 525°C, 550°C and 600°C. The recovery of the pyrolysate was accomplished as described above and the samples were set aside for GC/MS analysis.

Temperature Constant-Time Varied

b. The effect of pyrolysis time at a single temperature was also evaluated. In this procedure, fourteen (14) 200 ul samples of Exxon 2380 oil in the heavy walled pyrolysis tubes were placed in the muffle furnace which had been stablized for one (1) hour at 450°C. The tubes were rapidly placed into the muffle furnace in order to minimize heat loss. Two pyrolysis tubes were removed at each of the following time intervals: 5, 10, 15, 20, 30, 60, and 90 minutes. The pyrolysate was recovered as previously described.

INSTRUMENTATION

Two different GC/MS instruments were used in this study.

For the initial studies, open pyrolysis system and sealed tube pyrolysis (Pasteur pipettes, and Qualitative Assay), analysis was performed at the U.S. Coast Guard Research and Development Center using a Hewlett-Packard 5890 Gas Chromatograph with a Nitrogen-Phosphorus Detector (NPD), and a Hewlett-Packard 5970 Mass Selective Detector (MSD). The column used was a 10 meter, wide bore (.530 mm) fused silica 50% phenyl-methylsilicone (Hewlett-Packard #19095-1). Two microbore transfer tubes were fitted into the end of the megabore column and acted as a splitter with one half of the effluent going to the NPD and the other half going to the MSD.

For screening purposes utilizing GC with NPD analysis, the instrument operating conditions were set for rapid analysis of pyrolysates. The injection temperature was set at 250°C and the NPD was set at 300°C. The initial oven temperature was 170°C and was held for 1 minute. The oven temperature then increased at a rate of 10°C/min to a final temperature of 275°C. Total run time was 15 minutes.

For GC/MS analysis, the initial oven temperature was set at 60°C with a temperature increase of 20°C/min to a temperature of 200°C which was held for 1 minute. The temperature then increased 10°C/min to a final temperature of 275°C which was held for 30 minutes. Total run time for GC/MS run was 45 minutes.

Injection volume for all samples was 2 ul.

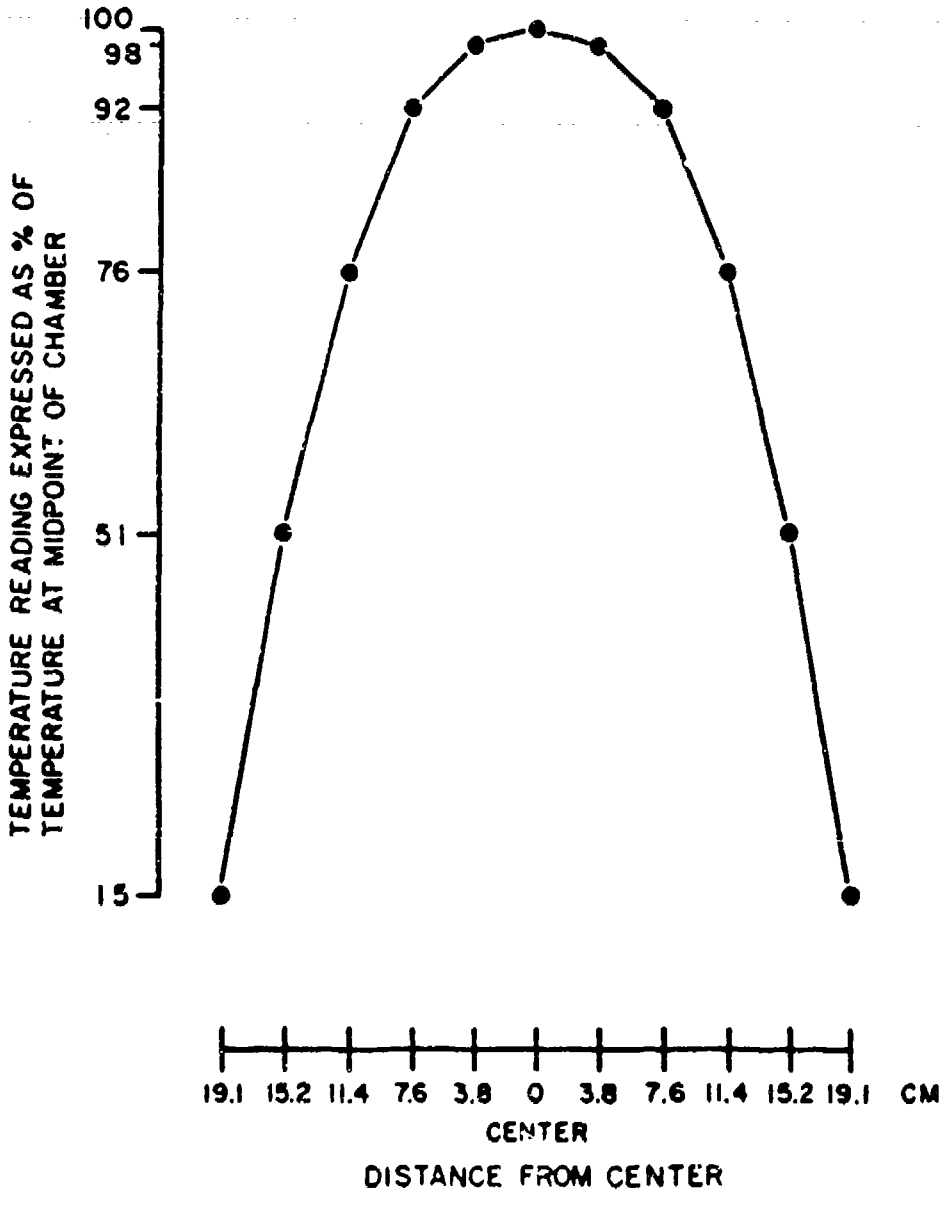
For the Quantitative studies(Time Constant-Temperature Varied, Temperature Constant-Time Varied), the GC/MS at the Naval Submarine Medical Research Laboratory was used. This apparatus consisted of a Hewlett-Packard 5880A Gas Chromatograph with a Nitrogen-Phosphorus Detector and Hewlett-Packard 5970 Mass Selective Detector. The column used was a Hewlett-Packard fused silica capillary column, crosslinked 50% phenylmethylsilicone; film thickness 0.17 micron, 0.20 ID, 25 meters in length. The operating conditions for this instrument were: initial oven temperature 150°C, held for 1 minute with an increase of 20° per minute to a final temperature of 275°C which was held for 45 minutes. Injection volume for all samples was 2 ul and the splitless injection mode was used.

Pyrolysis of Samples

The pyrolysis of the oil samples in these studies presented an experimental problem. Ideally the sample tubes should be placed in a thermal environment which is constant during the whole time of pyrolysis. In the present study, it was impossible to avoid variability in the pyrolysis temperature.

One source of this variability is due to the fact that the Lindberg Tube Furnace has a temperature gradient across the length of the combustion cavity. Figure 2 illustrates the temperature profile of the combustion cavity. A displacement of only 3.0 cm form the center of the combustion

FIGURE 2, TEMPERATURE PROFILE
IN COMBUSTION CHAMBER
OF LINDBERG TUBE FURNACE



cavity where the temperature is highest can result in a temperature decrease of nearly 25%. Displacement at 6 cm from the center of the cavity can result in a 51% difference in temperature. Considering the fact that the pyrolysis tubes were 12.5 cm long is is obvious that after volatilization, the oil was dispersed over a wide temperature range.

Small displacements in the positioning of individual tubes in the Lindberg furnace could subject the contained oil to a larger gradient of pyrolysis temperatures.

In order to avoid this problem, we adopted the procedure of using a muffle furnace which could hold multiple tubes. In this way all tubes would at least be subjected to the same thermal environment. This approach did not completely solve the problem however. After the furnace was brought to a stable pyrolysis temperature, opening of the furnace door to insert the tubes undoubtably reduced the furnace temperature. The thermoprobe available for temperature calibration and measurement had a response time which was too long to accurately monitor the furnace temperature. The furnace temperature returns to its set value faster than the thermoprobe indication. Our best indication was that the furnace temperature dropped by 50-60$^{o}$C and the temperature was restored to its set value within 3-4 minutes.

Since no solution was found for this problem, it was decided to use the stabilized temperature value measured for the muffle furnace prior to inserting the tubes and accept the fact that there was an initial temperature drop. Therefore it should be pointed out, that in view of the situations discussed above, the temperature reported in these studies should be considered as <u>indicated temperatures</u> rather than actual temperatures.

Data Collection and Analysis

For studies involving qualitative determinations, the GC/MS was operated in the scanning mode. This mode of operation considers all ions with M/Z values of 50-200.

For quantitative determinations, the GS/MS was operated in the selected ion mode (SIM). This alternative mode of operation considers only the ion masses designated by the operator. Figures (1 and 1a) show a topographical comparison of GC/MS output for an oil sample pyrolyzed at 450°C for 30 minutes in the scan (Fig. 1) and SIM (Fig. 1a) modes and demonstrates the simplification introduced by employing the SIM.

It is the presence of specific, characteristic ions at the proper retention time which determines whether TMP-P is present or absent. The application of the selected ion mode for data collection, considering only the characteristic ions for TMP-P, avoids the inclusion of extraneous ion masses in the total ion peak for TMP-P and results in a better quantitative estimate of TMP-P content.

TMP-P standards (100 ppm) were run before and after every two oil pyrolysate samples. Baseline time intervals for the total TMP-P standard peaks were determined automatically by the GC/MS internal program and the peak area was integrated over this time interval. Retention time was taken as the time of the maximum value for peak amplitude. Values for retention time, integration interval and peak area for the standard were retained in program memory.

Retention time of the TMP-P standard and the time interval over which this peak was integrated were subsequently applied to the sample pyrolysate spectrographic analysis. Peak area integrals for the sample pyrolysate were

FIGURE 1

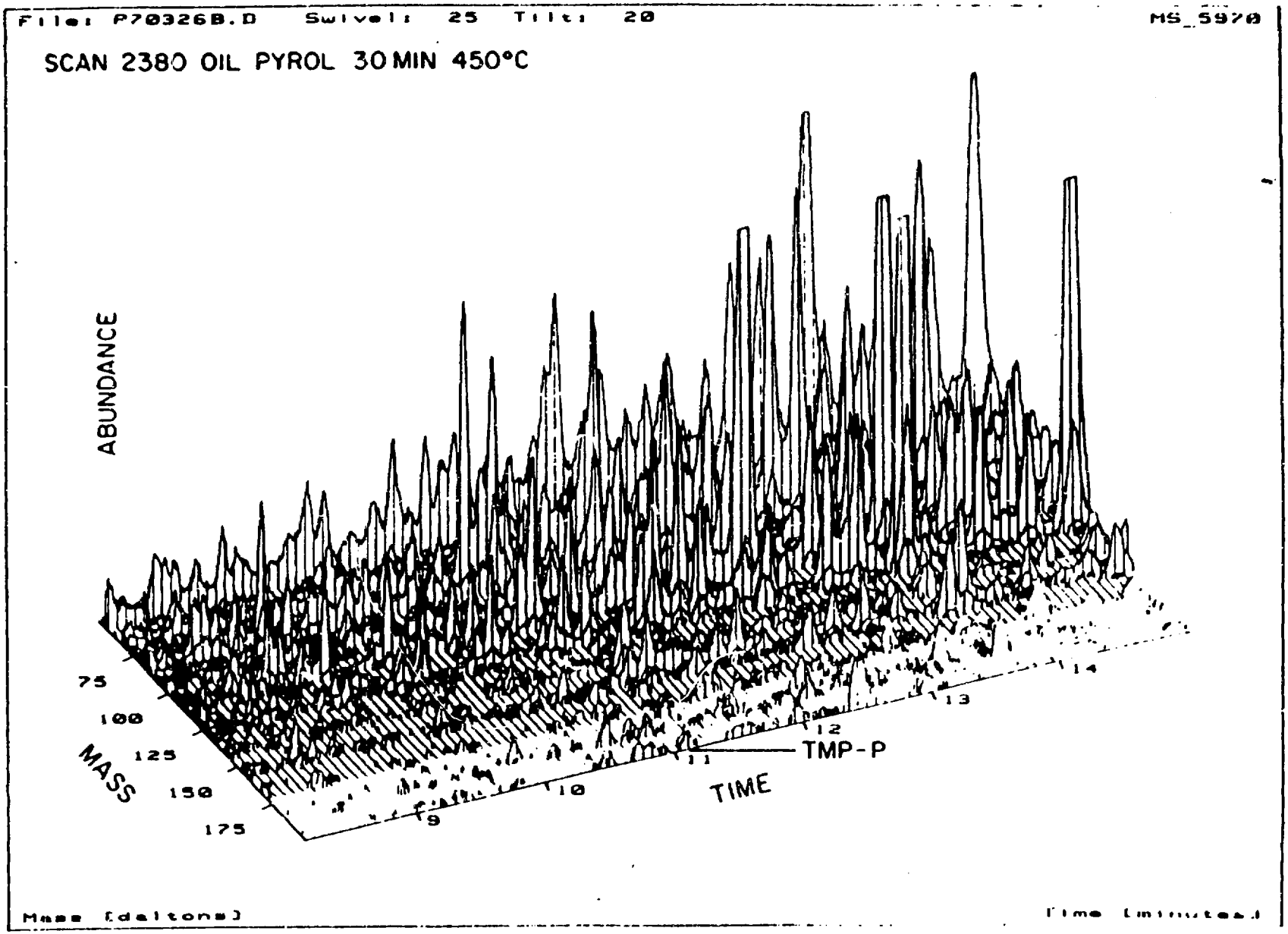
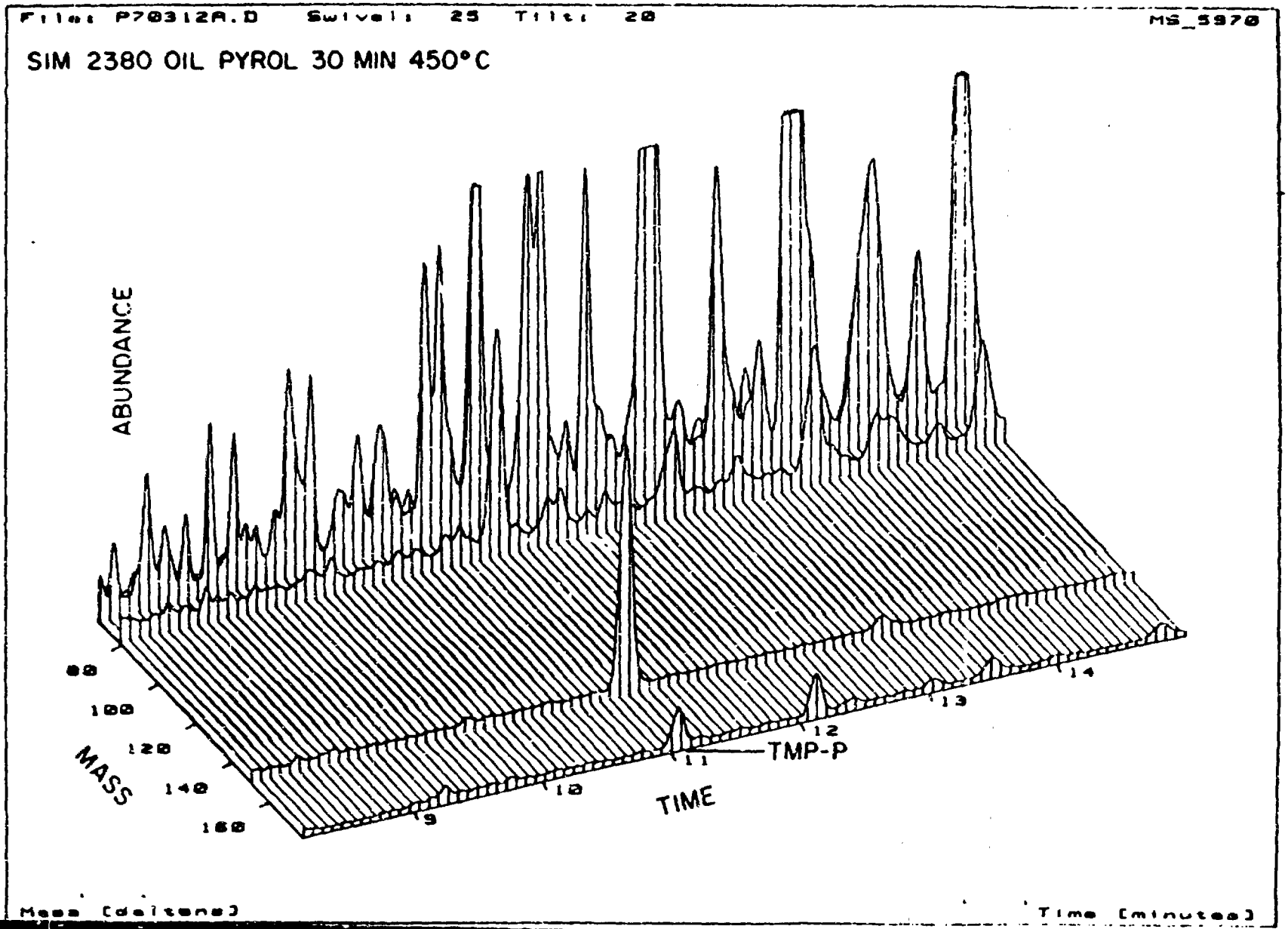

File: P70326B.D Swivel: 25 Tilt: 20
MS_5970
SCAN 2380 OIL PYROL 30 MIN 450°C
ABUNDANCE
MASS
75
100
125
150
175
9
10
11
12
13
14
TIME
TMP-P
Mass (daltons)
Time (minutes)

FIGURE 1a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MS_5970
SIM 2380 OIL PYROL 30 MIN 450°C
ABUNDANCE
MASS
80
100
120
140
160
TIME
9
10
11
12
13
14
TMP-P
Mass [daltons]
Time [minutes]

obtained for the total ion peak and for peaks of individual ion fragments: M/Z = 67, 68, 79, 150 and 178.

The TMP-P content of the sample pyrolysate was determined on the basis of the ratio of the peak area of the ion fragment, M/Z = 150, of the sample to the peak area obtained for the ion of the same mass in the TMP-P standard. The TMP-P content of each oil sample was adjusted for the dilutions introduced during the analysis according to the calculation details shown in Appendix C.

Accuracy of the GC/MS was determined on the basis of four sequential injections of 2 ul TMP-P (100 ppm) standard. Data consistently gave a mean retention time of 11.077 minutes with a standard deviation of .029 and a coefficient of variation of .026%. These data were based on unadjusted times.

Since the determination of TMP-P was accomplished by comparison of the sample to the TMP-P standard, it was necessary to evaluate the linearity of the TMP-P standard response.

A calibration curve for seven concentrations of TMP-P was determined. The TMP-P concentrations used were 15, 30, 60, 120, 240, 480 and 960 ppm. Three determinations were made at each concentration.

The plot of the calibration curve data is presented in Figure 10a. The data has a correlation coefficient of .9667.

## RESULTS

### QUALITATIVE ASSAYS

#### Open Tube Studies

We were unsuccessful in reproducing the results of TMP-P formation reported by Kalman, et al (4) using Exxon 2380 oil. The levels of TMP-P reported by Kalman using open tube combustion ranged from 16 PPM to 734 PPM in

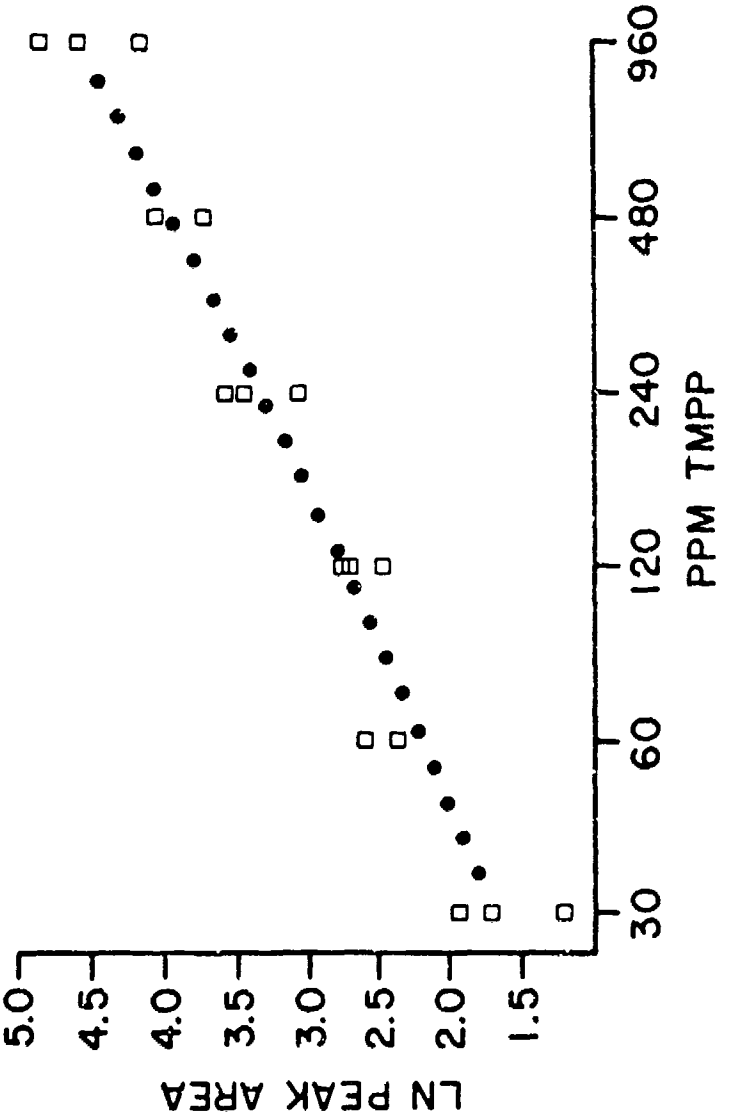



FIGURE 10A

a linear fashion over a temperature range of 400°C to 650°C. Results obtained at this laboratory did not demonstrate the consistency of recovery or linear response with temperature that Kalman reported. Of the 26 samples analyzed, 9 showed peaks which co-chromatographed with the TMP-P standard. Subsequent analysis on the Mass Selective Detector (MSD) failed to confirm unequivocally the presence of TMP-P. The nature of the discrepancies were non-agreement of sample retention time (RT) with standard RT and/or absence of one or more of the characteristic ions at the proper RT. Subsequent experience with the behavior of the oil under various pyrolysis conditions have provided an explanation for these results (see discussion). At the time it was decided to terminate the open tube pyrolysis system and revert to a sealed tube pyrolysis system also described by Kalman, et al (14). With the sealed tube system Kalman reported that 400 ul of oil pyrolyzed at 432°C produced a TMP-P yield of 9000 PPM. We elected to adopt the sealed tube pyrolysis system in order to bring our results into qualitative and quantitative agreement with the literature since maximal quantities of TMP-P would be generated in the sealed tubes.

Sealed Tube Experiments

The initial study using the sealed tube pyrolysis technique was intended as a qualitative screening for TMP-P. The purpose was to obtain information on the effects of temperature o TMP-P production.

Exxon 2380 oil was used as the test sample because of reports in the literature that it contained the requisite compounds, tricresylphosphate (TCP) and trimethylol propane (TMP), for the production of TMP-P. Results of this study were to be used to establish the optimal pyrolysis conditions for the analysis of the oils and lubricants selected for assay.

A (5 x 24) time-temperature matrix protocol was established (see Materials and Methods: Sealed Tube Pyroloysis, p. 6-7) and 120 assays were performed. The results of this study are presented in Table 1. Although trace contents of TMP-P are reported as low as 265°C, it is conjectural as to whether TMP-P was actually present, or whether the result represented only a compound which co-chromatographed at the same retention time as TMP-P. The doubt as to whether this material was TMP-P arises from the condition that either the retention time differed from the TMP-P retention time by more than 0.26% of the retention time of the TMP-P standard or an absence of one or more characteristic ions, usually M/Z = 178.

In order to complete the temperature-time profile, it was necessary to change to the heavy-walled pyrex glass tubes to avoid pyrolysis tube failure due to gas pressure. The time-temperature matrix using heavy-walled pyrex tube is presented in Table 2. Although the matrix is incomplete, the available data shows definite formation of TMP-P in the range of 440°C to 565°C. At 590°C only two of eight samples show the presence of TMP-P indicating an apparent loss of TMP-P due to the higher temperature.

Attempts to quantitate the results of this study were not particularly successful. Quantitative results varied over a wide range and detection of TMP-P in samples within the 400-500°C temperature range was not consistent.

A review of the data at this point demonstrated that the chance of missing the presence of TMP-P was substantial under the experimental conditions. The sample size (40 and 100 ul) was smaller than necessary, requiring very sensitive detection settings on the GC/MS. Pyrolysis conditions and pyrolysate recovery procedures introduced additional potential

TABLE 1

SCREENING RESULTS FOR TMP-P

| TEMP (°C) | 1 | 5 | 10 | 20 | 30 |
|---|---|---|---|---|---|
| 140 | N | N | N | N | N |
| 165 | N | N | N | N | N |
| 190 | N | N | N | N | N |
| 215 | N | N | N | N | N |
| 240 | N | N | N | N | N |
| 265 | N | N | T | N | T |
| 290 | N | N | N | N | N |
| 315 | N | N | N | N | N |
| 340 | N | N | N | N | N |
| 365 | N | N | N | N | N |
| 390 | N | Y | N | Y | T |
| 415 | Y | T | - | N | N |
| 440 | N | T | N | N | T |

N - no TMP-P Detected
T - Trace Amount
Y - TMP-P Detected

40 ul samples 2380 oil - one determination per point 1.0 ml volume soft glass pyrolysis tubes

TABLE 2

SCREENING RESULTS FOR TMP-P

TIME (MIN)

| TEMP (°C) | 1 | 5 | 10 | 20 | 30 |
|---|---|---|---|---|---|
| 440 | - | - | - | - | Y (1) |
| 450 | - | - | - | - | Y (2) |
| 460 | - | - | - | - | Y (2) |
| 570 | - | - | - | - | Y (4) |
| 480 | - | - | - | - | Y (3) |
| 490 | - | - | - | - | Y (5) |
| 515 | - | Y (1) | - | Y (2) | Y (1) |
| 540 | - | Y (1) | Y (1) | Y (2) | Y (2) |
| 565 | - | - | - | - | Y (1) |
| 590 | - | - | N (2) Y (1) | Y (1) | N (4) |

( ) = number of samples analyzed
- = number of determinations performed

100 ul samples 2380 oil - 10.0 ml volume thick-walled pyrex glass pyrolysis tubes

errors which could confuse the detection of TMP-P. A single determination at a single time/temperature did not provide enough data for statistical treatment or redundancy. Because of high probability for false-negatives, it was decided to introduce changes in the experimental procedure which would correct these problems and consequently the time-temperature matrix was not completed.

This time-temperature data did however provide a adequate qualitative determination of the presence or absence of TMP-P. This qualitative screening served substantially to establish the effective temperature range of TMP-P formation and determined the design of the quantitative studies which follow.

QUANTITATIVE STUDIES

The modified pyrolysis and recovery procedures used in the qualitative studies are described in Materials and Methods, Heavy walled, Sealed Tube Pyrolysis-Quantitative Studies, p. 7.

Two sets of experimental conditions were examined: (a) Time constant-Temperature varied and (b) Temperature constant-Time varied.

A. Time Constant-Temperature Varied

In this study the pyrolysis time was held constant at 30 minutes and the temperature varied over a range of 300-600°C.

The results of this quantitative study are shown on Graph #1 and the data obtained are presented in Table 3. TMP-P was detected over a range of 400°C to 550°C. No TMP-P was detected either at 300°C or 600°C. Graph 1 shows a rapid rise in TMP-P content of the oil sample, reaching a peak content at 450°C and then falling sharply. TMP-P levels were not only low at both 400°C and 550°C, but in one sample at 400°C and two samples at 550°C, no TMP-P

GRAPH I, TMP-P YIELD 2380 OIL
TIME CONSTANT - TEMPERATURE VARIED

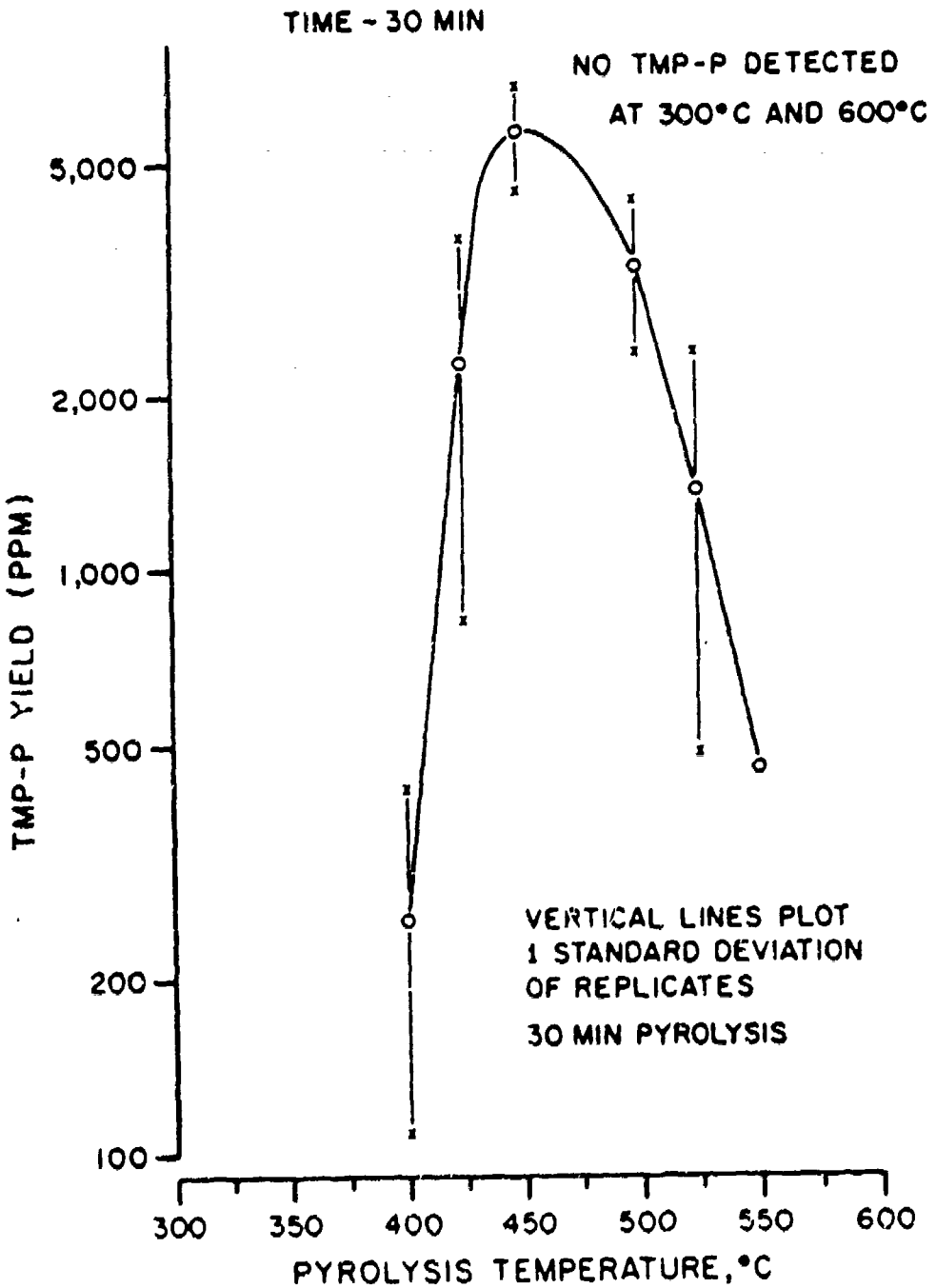


TABLE 3
TMP-P YIELD
TIME CONSTANT - TEMPERATURE VARIED

30 Minutes EXXON 2380

| Temp | Sample # | Aliquot yield ppm | Oil Sample yield ppm | Mean $\bar{X}$ | Standard Deviation | Coefficient Variation (C.V.) |
|---|---|---|---|---|---|---|
| 300°C | #1,#2,#3,#4 | N.D.* | - | - | - | - |
| 400°C | 1 | N.D. | - | | | |
| | 2 | 7.4 | 148.0 | | | |
| | 3 | 21.7 | 434.0 | | | |
| | 4 | 10.0 | 200.0 | | | |
| | | | | 261 | 152 | 58.2 |
| 425°C | 1 | 187.8 | 3756 | | | |
| | 2 | 157.9 | 3158 | | | |
| | 3 | 40.3 | 806 | | | |
| | 4 | 63.0 | 1260 | | | |
| | | | | 2245 | 1433 | 63.8 |
| 450°C | 1 | 330.9 | 6618 | | | |
| | 2 | 215.9 | 4304 | | | |
| | 3 | 293.2 | 5864 | | | |
| | 4 | broken | | | | |
| | | | | 5595 | 1180 | 21.1 |
| 500°C | 1 | 165.8 | 3316 | | | |
| | 2 | 200.8 | 4016 | | | |
| | 3 | 98.7 | 1974 | | | |
| | 4 | 194.1 | 3882 | | | |
| | | | | 3297 | 933 | 28.3 |
| 525°C | 1 | 53.7 | 1074 | | | |
| | 2 | 141.0 | 2820 | | | |
| | 3 | 44.6 | 892 | | | |
| | 4 | 34.1 | 682 | | | |
| | | | | 1367 | 982 | 71.8 |
| 550°C | 1 | 11.8 | 236 | | | Overall C.V. |
| | 2 | 33.6 | 672 | | | 48.6 |
| | 3 | N.D. | - | | | |
| | 4 | N.D. | - | | | |
| | | | | 454 | - | - |
| 600°C | #1,#2,#3,#4 | N.D. | - | - | - | - |

* N.D. (not detected)

was detected. The plot of the standard deviations for the various temperature groups are shown in Graph 1. Although the error bars are large, the separation of the mean values and lack of significant overlap of the error bars lend statistical confidence to the presence of an actual maximum.

The quantitative results presented in Table 3 show the variability in yield of the oil samples within each temperature group.

B. Temperature Constant-Time Varied

Based on previous study (A above) the optimal temperature for TMP-P production in the oil sample under the experimental conditions used is 450°C. In order to evaluate the effect of pyrolysis time on production of TMP-P at a given temperature, samples were pyrolyzed at a constant temperature of 450°C for time periods of 5, 10, 15, 20, 30, 60 and 90 minutes. The precision in replicability obtained in the previous study of the effects of temperature on TMP-P formation was sufficiently high that for each time point in this study only duplicate oil samples were analyzed.

The results for the effects of pyrolysis time are presented in Graph #2. This graph plots the data and the average value for the duplicates pyrolyzed at 450°C at each time period. The overall coefficient of variation for results of the constant temperature study is also included on the graph in order to indicate that the scattering of the duplicate points in the time study did not exceed the magnitude of error encountered in the temperature study. The variability is small enough to support statistically a peak in yield at an intermediate time (30-60 run time period). These data show an increasing formation of TMP-P starting at 5 minutes and reaching an apparent maximum during the 30-60 minute period. After thirty minutes the TMP-P content begins to decrease.

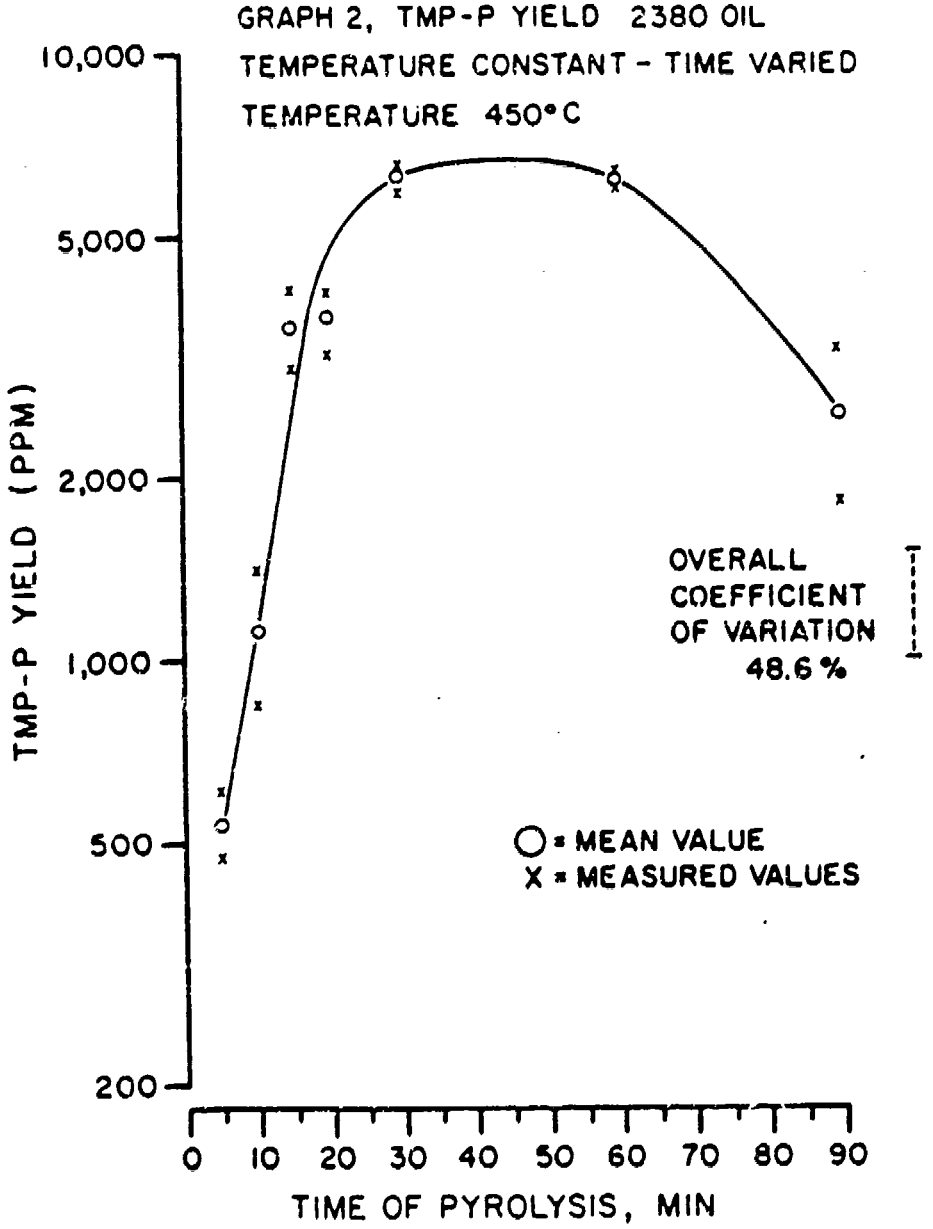

GRAPH 2, TMP-P YIELD 2380 OIL
TEMPERATURE CONSTANT - TIME VARIED
TEMPERATURE 450°C
10,000
5,000
2,000
1,000
500
200
TMP-P YIELD (PPM)
OVERALL
COEFFICIENT
OF VARIATION
48.6 %
○ = MEAN VALUE
X = MEASURED VALUES
0 10 20 30 40 50 60 70 80 90
TIME OF PYROLYSIS, MIN

TABLE 4

TMP-P YIELD
TEMPERATURE CONSTANT - TIME VARIED
450°C EXXON 2380

| TIME (MIN) | SAMPLE # | ALIQUOT YIELD ppm | OIL SAMPLE YIELD ppm | MEAN $\bar{X}$ |
|---|---|---|---|---|
| 5 | 1 | 26.4 | 528 | |
| | 2 | 30.6 | 612 | 570 |
| 10 | 1 | 42.2 | 844 | |
| | 2 | 70.9 | 1418 | 1131 |
| 15 | 1 | 150.0 | 3000 | |
| | 2 | 206.0 | 4120 | 3560 |
| 20 | 1 | 158.1 | 3162 | |
| | 2 | 220.5 | 4010 | 3586 |
| 30 | 1 | 330.9 | 6618 | |
| | 2 | 293.2 | 5864 | 6241 |
| 60 | 1 | 310.0 | 6200 | |
| | 2 | 306.4 | 6128 | 6164 |
| 90 | 1 | 90.9 | 1818 | |
| | 2 | 160.1 | 3202 | 2510 |

The value for TMP-P production at 450°C at 30 minutes pyrolysis time is 6241 PPM which agrees quite well with the value of 5595 PPM obtained in the time constant-temperature varied study for a temperature of 450°C and 30 minutes pyrolysis time. This agreement indicates a quite satisfactory reproducibility in the experimental techniques employed in the quantitative study.

Mass Spectral Data

Mass spectrograms for the two quantitative studies, i.e. time constant-temperature varied and temperature constant-time varied demonstrated some interesting characteristics. Representative mass spectra are presented here for purposes of illustration (Figures 3 and 4). Although only one mass spectrogram is presented for each experimental condition, it should be emphasized that all mass spectra within an experimental group were very similar with respect to numbers of peaks, retention time for peaks, and peak heights.

Figure 3 illustrates the mass spectral output for the quantitative study with time constant and temperature varied. The arrow indicates the position of the TMP-P peak.

Figure 4 is a similar presentation for the quantitative study in which the temperature was kept constant at 450°C and the pyrolysis time varied.

Inspection of the series of spectrograms in Figure 3 shows an increase in the number and amplitude of peaks with increasing temperature. Three major peaks at retention times of 12.4, 13.5 and 14.8 minutes are retained up to a temperature of 450°C and then rapidly disappear above 450°C. The TMP-P peak at a retention time of 11.09 minutes represents the TMP-P peak

FIGURE 3
REPRESENTATIVE MSD OUTPUT
TIME CONSTANT - TEMPERATURE VARIED
2380 OIL 30 MINUTE PYROLYSIS

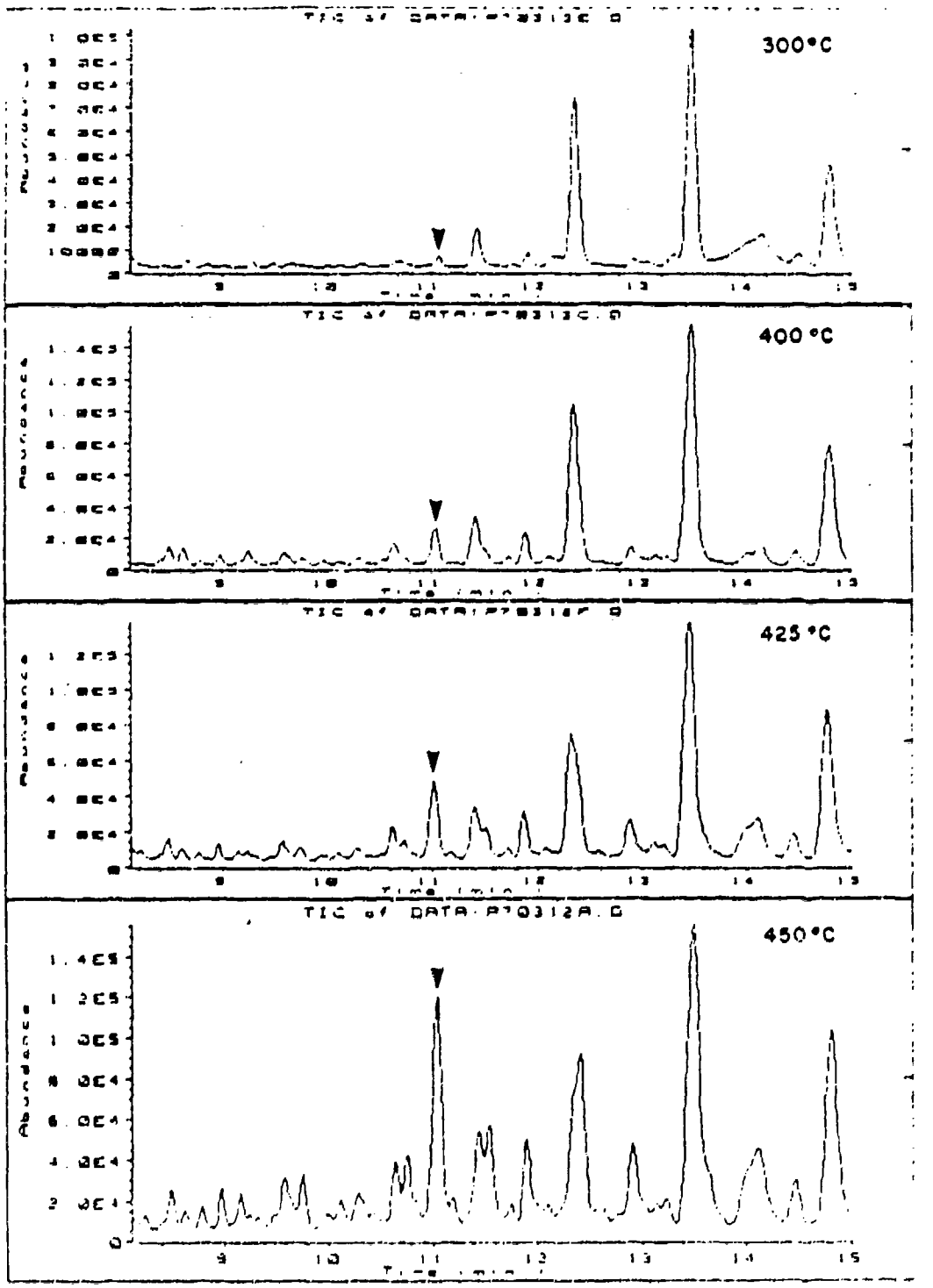


FIGURE 3 (CONTINUED)

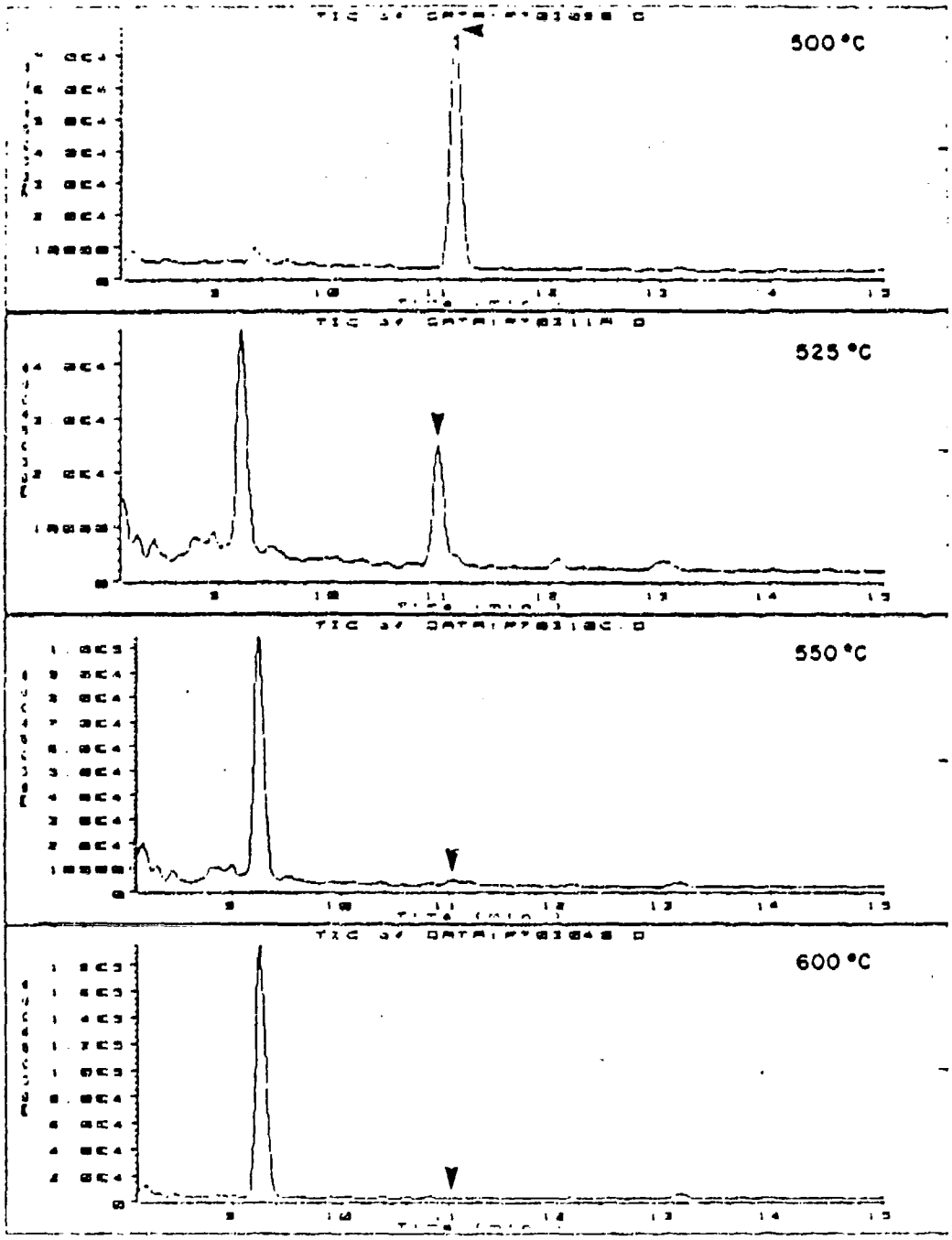
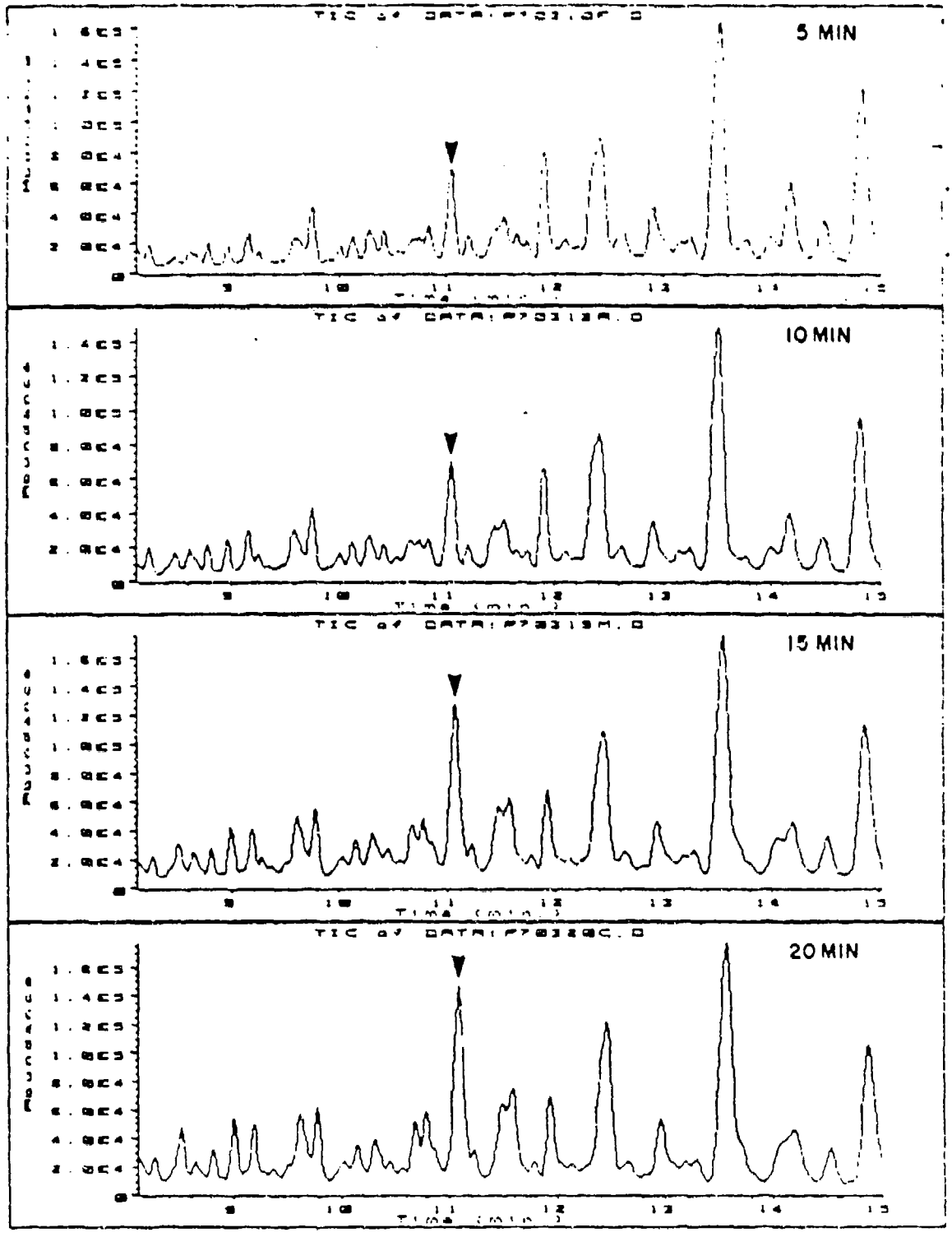
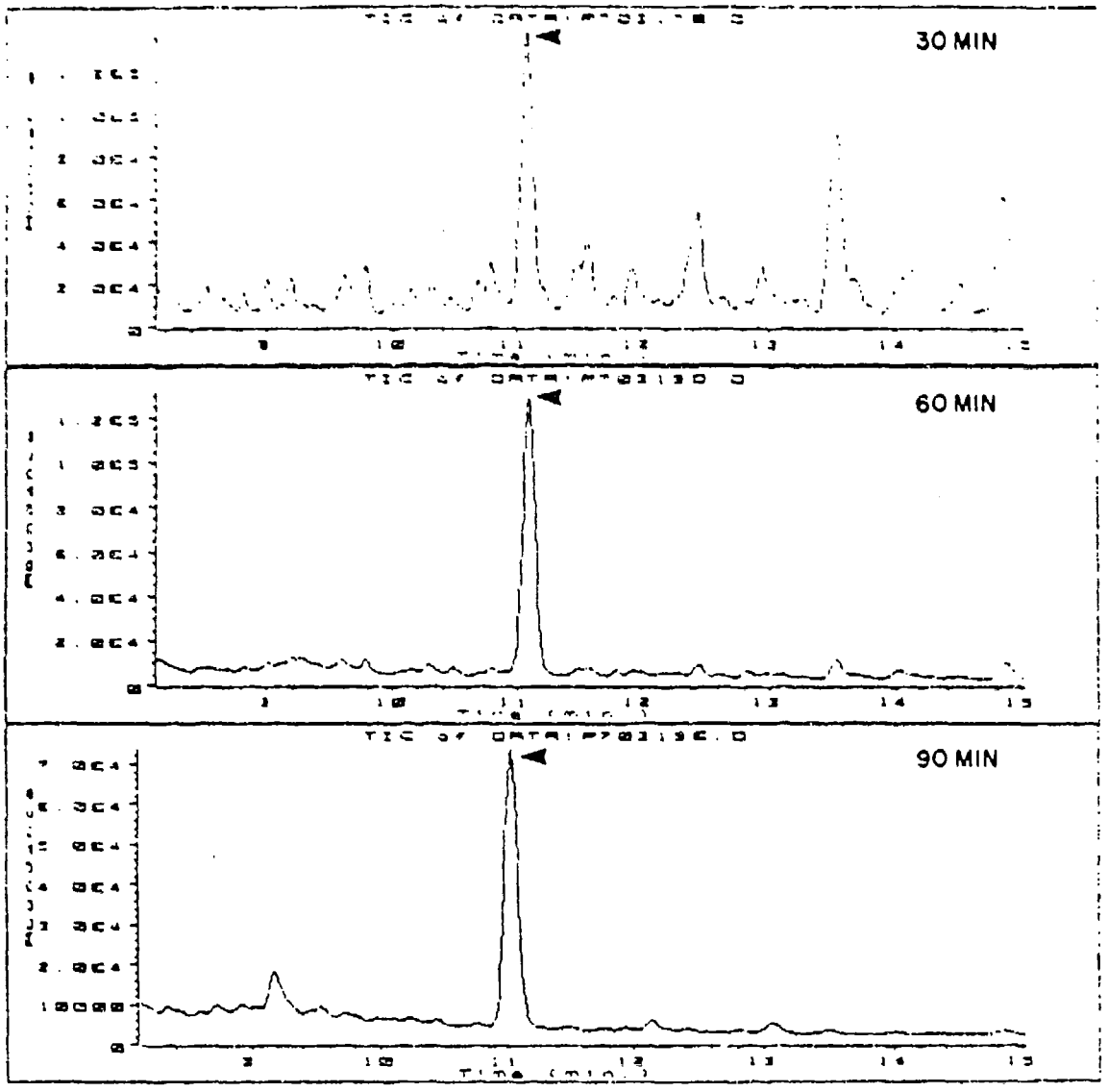


FIGURE 4
REPRESENTATIVE MSD OUTPUT
TEMPERATURE CONSTANT - TIME VARIED

2380 OIL PYROLYZED @ 450 C




30 MIN
60 MIN
90 MIN

and shows increasing amplitude with increasing temperature up to 500°C and then a rapid decline to zero at 600°C. In the temperature range between 500 and 600°C the decrease in the TMP-P peak is paralleled by an increase in a fast peak at approximately 9.5 minutes.

The spectral sequence shown in Graph 4 (temperature constant (450°C)-time varied) is somewhat different. With the exception of an increase in [illegible] peak over the time interval 5 to 60 minutes, there is no gross change in the position of peaks in the spectrum. At 60 minutes however the spectral picture is completely changed due to a loss of the slower peaks. At 90 minutes, a peak at a retention time of approximately 9.2 minutes begins to appear. In both of these studies, i.e. temperature varied and time varied, the loss of the peaks at longer retention times (>11.0 minutes) and development of the peak at 9.2-9.5 minutes indicates a loss of higher molecular weight (longer retention times) and formation of lower molecular weight (shorter retention time) products.

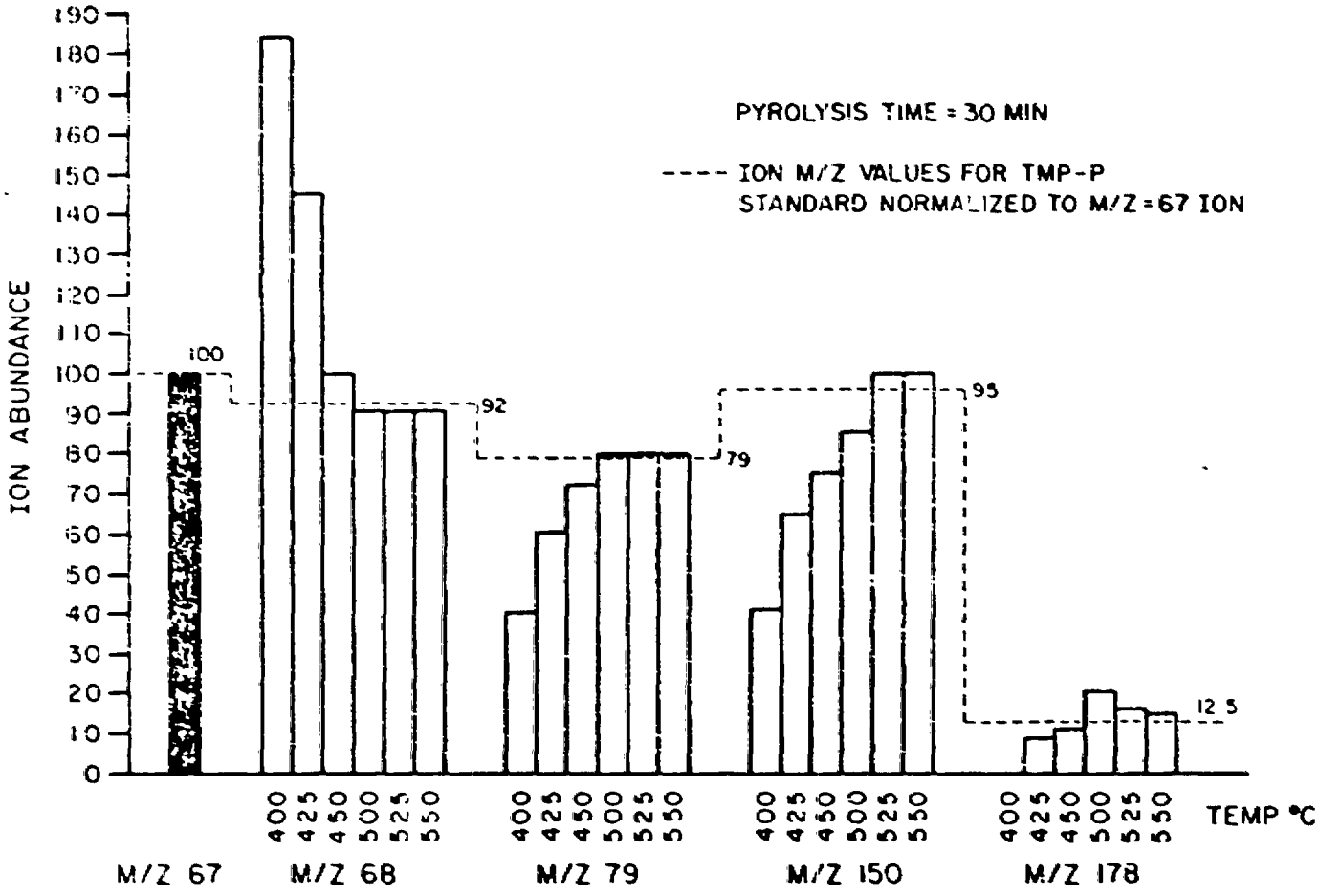
Ion Ratios

Graph 3 illustrates the ion ratios for the characteristic ions for TMP-P as temperature varies and pyrolysis time is constant (30 minutes) at each temperature. Graph 4 illustrates the effect on the characteristic ion ratios of varying pyrolysis time with temperature constant (450°C). In both situations the ion abundance has been normalized to the value of the M/Z = 67 ion (100%). The dotted line overlaid on both graphs indicates the values for the characteristic ions of the TMP-P standard.

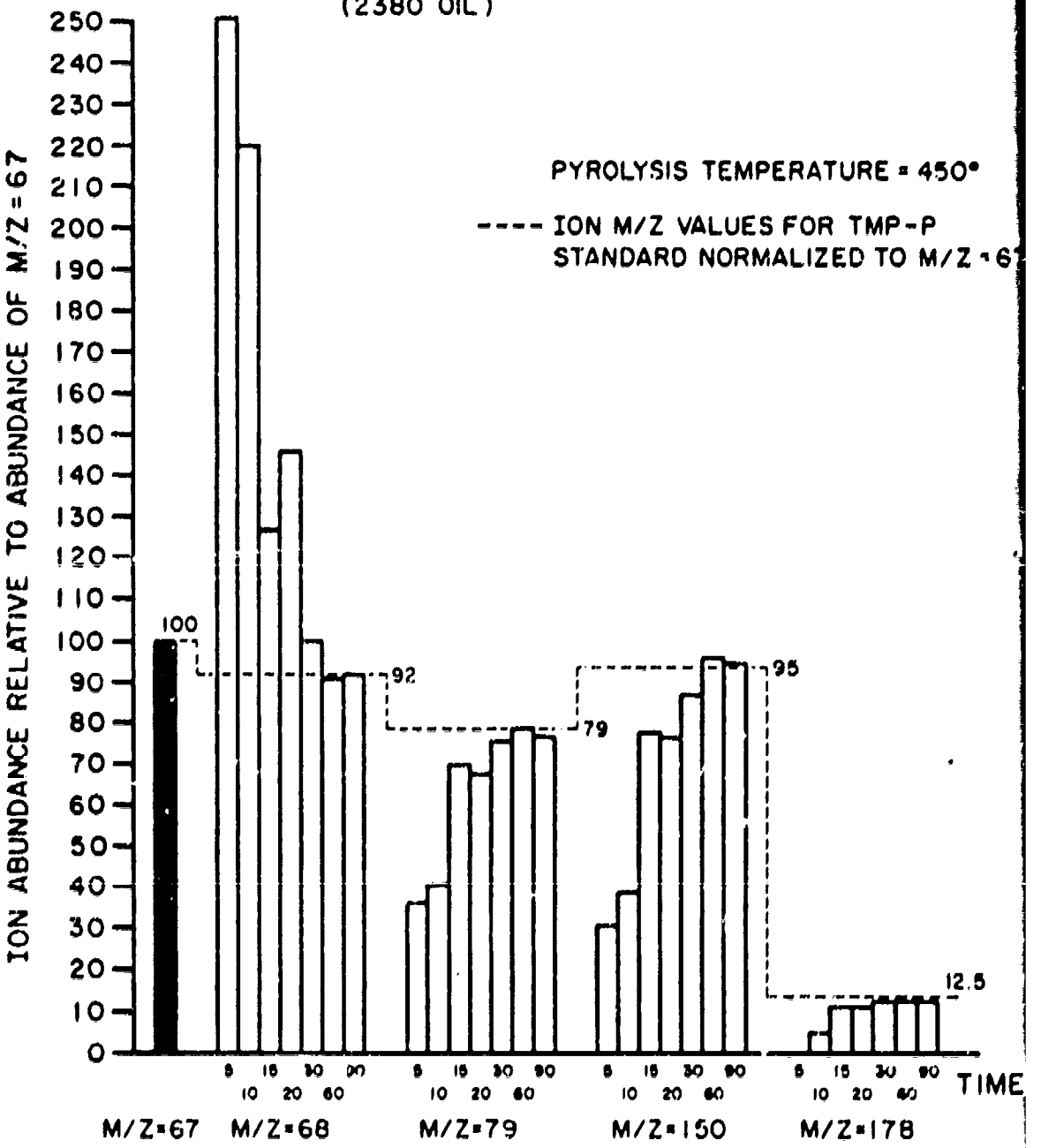
GRAPH 3, ION RATIOS

TIME CONSTANT - TEMPERATURE VARIED

2380 OIL



GRAPH 4, ION RATIOS
TEMPERATURE CONSTANT - TIME VARIED
(2380 OIL)



The relative ion abundances of the TMP-P standard were quite constant. Over a thirty day period the relative abundances of the characteristic ions for the TMP-P standard were:

| M/Z | 67 | 68 | 79 | 150 | 178 |
|---|---|---|---|---|---|
| $\bar{X}$ | 100 | 92 | 79.4 | 95 | 12.5 |
| st. dev. | 0 | 2.08 | 0.92 | 4.77 | 2.96 |

Inspection of the graphs illustrate certain similar behavior. In both the temperature-varied and time-varied studies the M/Z = 68 ion has an initial high value relative to the M/Z = 67 ion which decreases to the value of the TMP-P standard. The M/Z = 79, 150, and 178 ions have initial lower relative values than the corresponding ions in the TMP-P standard and gradually increase to the value of the TMP-P standard. For the temperature-varied study (Graph 3), the ion ratios of the sample correspond to the TMP-P standard at 500°C and for the time-varied study the standard ratio is achieved at 450°C in 30 minutes.

The ion ratios for samples pyrolyzed at 300° and 600°C for 30 minutes lacked three of the characteristic ions for TMP-P and consequently the data is not presented on Graph 4.

It is important to point out that no M/Z = 178 ion was detected at 400°C - 30 minutes in the temperature-varied study or at 450°C - 5 minute in the time-varied study. According to the criteria established for the confirmation of the presence of TMP-P, absence of the M/Z = 178 ion would preclude a positive determination. The use of ion ratios alone in the interpretation of this data can be deceptive since ion ratios give only relative values for peaks and not absolute values.

In order to provide a better visual presentation of changes in the time distribution and amplitude of the TMP-P characteristic ions, three dimensional plots for the temperature-varied study are presented in Figures 6 through 13 and for the time-varied study in Figures 14 through 19, of Appendix D. Figure 5 depicts the three dimensional plot of the TMP-P standard spectrogram and is included for comparison purposes.

Inspection of Figure 7 (400°C - 30 min) demonstrates the presence of all characteristic ions for TMP-P at the proper retention time. The amplitude of the M/Z = 178 ion is however very small. In the instrument program for establishment of peak baseline and subtraction of baseline noise for integration, these very low amplitude peaks can be processed out if the abundance is low.

Inspection of Figure 14 from the time-varied study (450°C - 5 minutes) demonstrates a rather low peak amplitude for M/Z = 79 and 150, indicating the possibility of data processing loss of the M/Z = 178 peak. This possibility becomes more obvious on inspection of Figure 15 (450°C - 10 minutes). The M/Z = 178 ion is beginning to appear with slight increase in amplitude of the other characteristic ions.

Because of the high probability that these ions were lost in instrument data processing due to their low amplitude relative to the instrument noise level, the decision was made to consider the presence of four characteristic ions to be a positive indication of TMP-P at 400°C, 30 minutes and 450°C, 5 minutes.

Screening Results - Selected Oils

The 26 selected oils, lubricants and hydraulic fluids listed in Appendix B were pyrolyzed at two temperatures, 450°C for 30 minutes and 540°C

for 20 minutes. Two replicates of each oil were pyrolyzed and analyzed at 450°C and a single sample of each oil was pyrolyzed and analyzed at 540°C.

The study at 540°C was a qualitative screening while that at 450°C was a more rigid quantitative screening. The qualitative screening detected TMP-P formation in only one oil i.e. #26, MIL-L-23699C, a synthetic aircraft engine oil, containing polyol ester. The results of the quantitative screening are presented in Table 5.

Some explanation of the data presented in Table 5 is warranted. In all of the oils screened, the characteristic ions for TMP-P were present in the ion spectrum at the proper retention time. However, there was no definitive peak at the proper retention time either in the total ion chromatogram or for the selected characteristic ions. The ions were usually distributed over the total time period of the mass spectrogram. Figure 20 illustrates this result. Such spectrograms, which show no ion peaks at the TMP-P retention time, even though the characteristic ions were present in the ion spectrum background, were given a determination that TMP-P was not present. In other spectrograms, several of the characteristic ion peaks were not present, even though the ions were determined to be present in the background. Figure 21 illustrates this condition. These oils also were also considered to be negative for TMP-P.

In Table 5, only data which showed definite peaks for the characteristic ions at the proper TMP-P retention time are recorded as positive for TMP-P.

The result of the total screening program as presented in Table 5 indicates that TMP-P is only present in one oil #26, MIL-L23699C. Even in this oil, there is no ion peak for the M/Z = 178 ion. However, considering

TABLE 5

SCREENING RESULTS

SELECTED OILS/LUBRICANTS

| OIL # | MILSPEC I.D. | REPLICATE | ION PEAK 67 | 68 | 79 | 150 | 178 | TMP-P |
|---|---|---|---|---|---|---|---|---|
| 1 | MIL-L-6086C | 1,2 | - | - | - | - | - | N.D. |
| 2 | MIL-H-176720 | 1,2 | - | + | - | - | - | N.D. |
| 3 | MIL-L-2105CAM2 | 1,2 | - | - | - | - | - | N.D. |
| 4 | MIL-H-17672CAM1 2135TH | 1,2 | - | - | - | - | - | N.D. |
| 5 | MIL-H-17672D | 1,2 | - | - | - | - | - | N.D. |
| 6 | CELLULUBE | 1 | - | + | - | - | - | N.D. |
| | | 2 | + | + | + | - | - | N.D. |
| 7 | MIL-L-2105C | 1,2 | - | - | - | - | - | N.D. |
| 8 | 2135TH | 1 | + | + | + | - | - | N.D. |
| | | 2 | - | - | - | - | - | N.D. |
| 9 | 2075TH | 1,2 | - | - | - | - | - | N.D. |
| 10 | MIL-H-17672C | 1,2 | - | - | - | - | - | N.D. |
| 11 | MIL-H-46170B | 1,2 | + | - | - | - | - | N.D. |
| 12 | MIL-L-17672 | 1,2 | - | - | - | - | - | N.D. |
| 13 | MIL-L-23699FFG-16 | 1 | - | + | - | - | - | N.D. |
| | | 2 | - | - | - | - | - | N.D. |
| 14 | MIL-F-1711B | 1,2 | - | - | - | - | - | N.D. |
| 15 | MIL-H-22072(B) | 1,2 | - | - | - | - | - | N.D. |
| 16 | MIL-L-9000G | 1,2 | - | - | - | - | - | N.D. |
| 17 | MIL-H-83282B | 1,2 | - | - | - | - | - | N.D. |
| 18 | 9250 | 1,2 | - | - | - | - | - | N.D. |
| 19 | MIL-H-19457C | 1 | + | + | + | - | - | N.D. |
| | | 1,2 | - | - | + | - | - | N.D. |
| 20 | MIL-L-17331-2190 | 1,2 | - | - | - | - | - | N.D. |
| 21 | MIL-H-17672C 2110-TH | 1,2 | - | - | - | - | - | N.D. |
| 22 | MIL-L-17331 | 1,2 | - | + | - | - | - | N.D. |
| 23 | MIL-H-5559A | 1,2 | - | - | - | - | - | N.D. |
| 24 | MIL-L-17331 | 1,2 | - | - | - | - | - | N.D. |
| 25 | MIL-H-17672 2135TH | 1,2 | + | - | - | - | - | N.D. |
| 26 | MIL-L-23699C | 1 | + | + | + | + | - | 150 ppm |
| | | 2 | + | + | + | + | - | 90 ppm |

( - ) no ion peak present
( + ) ion peak present
(N.D.) not detected

FIGURE 20

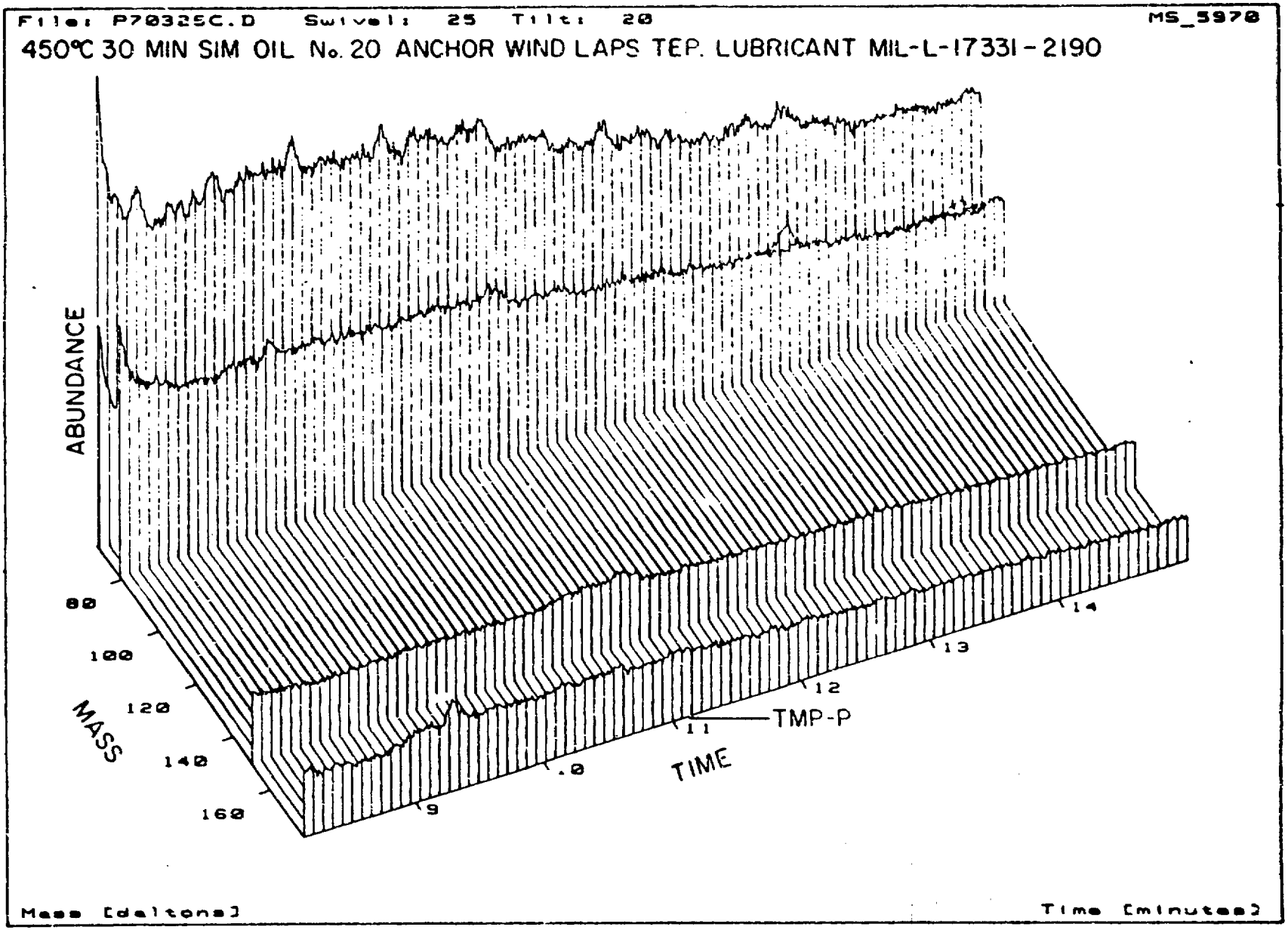
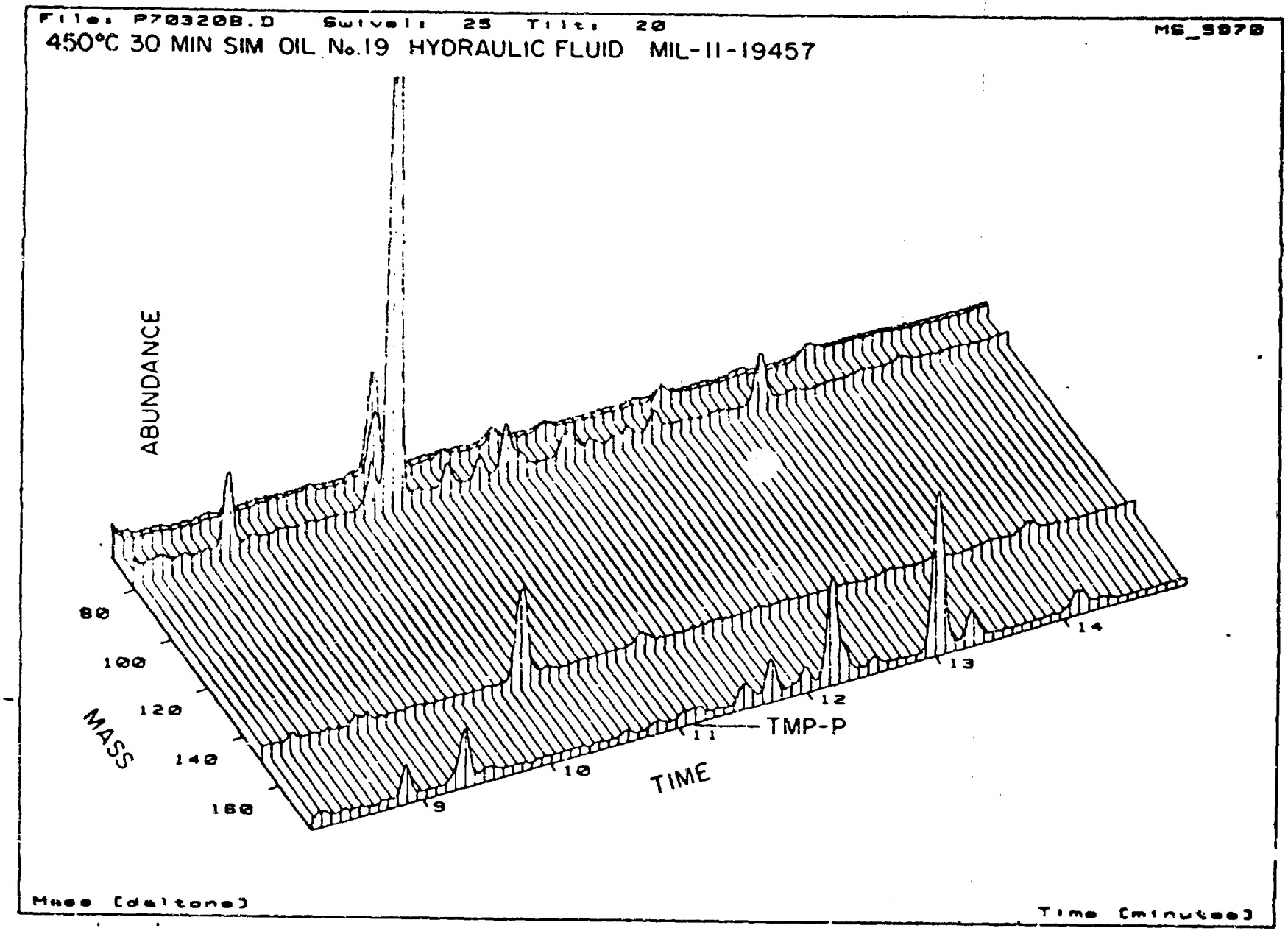

File: P7032SC.D Swivel: 25 Tilt: 20
MS_5970
450°C 30 MIN SIM OIL No. 20 ANCHOR WIND LAPS TEP. LUBRICANT MIL-L-17331-2190
ABUNDANCE
MASS
80
100
120
140
160
9
.0
11
12
13
14
TIME
TMP-P
Mass [daltons]
Time [minutes]

FIGURE 21


File: P70320B.D Swivel: 25 Tilt: 20
MS_5970
450°C 30 MIN SIM OIL No.19 HYDRAULIC FLUID MIL-II-19457
ABUNDANCE
MASS
80
100
120
140
160
TIME
9
10
11
12
13
14
TMP-P
Mass [daltons]
Time [minutes]

the low level of TMP-P calculated and the low amplitude of the peaks it is possible that the M/Z = 178 peak was unintentionally subtracted in processing the data.

## DISCUSSION

### Comparison with Other Work

The results obtained at NSMRL for this study are qualitatively and quantitatively in agreement with the data obtained by Dr. M. Birky at National Transportation Safety Board(NTSB) (Personal communication) for the pyrolyses of EXXON 2380 Turbine Oil. The results are quite similar despite the fact that the yields for TMP-P were calculated on different bases. Dr. Birky based his yield calculation on a gas chromatograph -NP detector standard curve while our calculations are based on the abundance of the M/Z = 150 ion obtained by GC/MS. Birky's summary of his results read:

> "The data show that the bicyclic compound is formed at temperatures as low as 350°C and that it is readily formed at 450°C. Furthermore, preliminary results show that the bicyclic is decomposed after its formation at 450°C when the sample is held at this temperature for three hours. The maximum concentration found in these limited experiments was 3000 ppm at 450°C during a heating period of one hour. These data suggest that decomposition is competing with the generation of TMP-P at 450°C".

Referral to Graphs 1 and 2 of this report demonstrate very similar behavior of the Exxon 2380 in our results. Specific differences between Birky's results and ours concerns the amounts of TMP-P produced and the minimal temperature for production.

Birky reported 3000 ppm at 450°C for a pyrolysis time of 60 minutes, while our results were approx 6200 ppm at 450°C for 30 minutes. Birky reported initial TMP-P production at 350°C while our results indicate a slightly higher temperature of 400°C.

These differences in results are only quantitative and can be ascribed to differences in experimental methodology, recovery methods and computational procedure. One important difference in technique is Birky's dependence on the NP detector which we found to produce different estimates of TMP-P as compared to GC/MS estimation.

The results of Birky and those of this laboratory are consistent with analysis data published in a research note on pure TMP-P by Imperial Chemical Industries(ICI). The ICI thermal decomposition curve shows a 20% loss of the original TMP-P sample at 450°C and a 93% loss at 650°C. The results of both Birky and NSMRL (Graphs 1 and 2) demonstrate this predicted rapid thermal decomposition above 450°C.

The results of NTSB and NSMRL, which both demonstrate a decrease in TMP-P at temperatures above 450°C, attributable to thermal decomposition seem to be in disagreement with the work of Kalman, et al (14). Kalman reported that TMP-P production increased as a linear function of temperature over the range 400 to 645°C using an open tube pyrolysis system.

The explanation for the differences in results is readily apparent from differences in the two experimental techniques used. NTSB and NSMRL results were based on sealed tube experiments while those of Kalman, et al. were based on an open tube system. The Kalman report reads as follows:

"During these experiments it was noted that within seconds of placing the sample boat in the heated zone of the apparatus, a

rapid increase in gas flow through the collector ensued. This flow was accompanied by splattering of sample within the tube furnace and some transport of liquid out of the heated zone. This is presumably due to volatilization of some components of oil and distillation of the bulk constituents of oil out of the heated zone of the apparatus. At approximately the same time, white solid sublimate appeared on the downstream walls of the tube furnace, out of the heated area. The solid material may contain TMP-P and certainly indicates rapid production of degradation products."

Kalman revised his experimental procedure to reduce the premature loss of the degradation products from the heated zone by eliminating gas flow through the apparatus for the first minute of heating, but nevertheless reported that distillation of liquid out of the heated zone of the pyrolysis tube continued under the revised procedures. Kalman recognized in his publication that revised procedures were needed to provide for a much longer heated path.

Since TMP-P production, as reported by Kalman, can occur rapidly (within two minutes) it is quite probably that in the dynamic (open-tube) pyrolysis method employed, that the TMP-P did not remain in the heated zone for sufficient time to have undergone significant thermal decomposition. Also the total pyrolysis time for these experiments was only five minutes. Kalman's results probably represent the initial formation of TMP-P as a function of temperature and with little or no affect of thermal decomposition, even at the higher temperatures. The results of NTSB and NSMRL (Graph 2) however, demonstrate an increasing yield of TMP-P with pyrolysis time at temperatures of 450$^{o}$C. Therefore, it is probably that Kalman's yields for the short,

five minutes pyrolysis times represent less than the maximal TMP-P production possible for the oil samples.

Since the two studies, ie., dynamic flow and sealed tube, were so different, there are only a few quantitative comparisons of data which can be made. One case was the five minute pyrolysis time used by Kalman and NSMRL. Although the temperatures were somewhat different, (450°C for 5 minutes at NSMRL and 505°C for 5 minutes for Kalman), the yields are 612 and 528 ug/g for NSMRL and 674 and 369 ug/g for Kalman. These results show quite good agreement, although considering the many differences in experimental and computational technique, this agreement in results could be fortuitous.

In one sealed tube experiment Kalman reported value of 9095 ug/g of TMP-P at a temperature of 432°C for 30 minutes. This can be compared to the values of 6241 ppm for 30 minutes at 450°C reported by NSMRL and 2966 ppm for 32 minutes at 450°C by Birky. Considering the experimental and procedural differences in pyrolysis, recovery, analysis and computation, these three values can be considered to be in substantial agreement.

In summary, the three studies show good agreement and contribute substantially to qualitative and quantitative assay for the formation of TMP-P from pyrolyzed Exxon 2380 oil. None of the studies however, either individually or collectively fully describe the formation of TMP-P completely as a function of time and temperature.

Summary of Exxon 2380 Results

A review of the results obtained at three laboratories demonstrate the following information on TMP-P production from Exxon 2380 oil.

a) formation of TMP-P can occur at temperatures as low as 350° - 400°C.

b) formation of TMP-P can be very rapid with formation beginning in as little as two minutes.

c) At 30 minutes pyrolysis time, the yield of TMP-P increase as a function of temperature up to a temperature of 450°C. At 450°C, thermal decomposition of the TMP-P competes with formation and reduces the yield of TMP-P to zero at 600°C.

d) At 450°C, the yield of TMP-P increases as a function of pyrolysis time up to 60 minutes. Between 60 and 90 minutes thermal decomposition reduces the yield of TMP-P by aproximately 60%.

Navy Context of TMP-P Hazard

Results of the studies in the pyrolysis of Exxon 2380 have demonstrated that it is possible to generate high levels of TMP-P under laboratory conditions. The results indicate the possibility of a human health hazard particularly in closed spaces. The U. S. Navy requires an answer as to whether TMP-P formation poses a practical safety hazard which would endanger men on a Naval platform.

It is known that although Exxon 2380 is on the Qualified Products List (QPL) of manufacturers of MIL-L-23699, the Navy does not buy this product from Exxon because of the expense (personal communication of D. Mearns, NAVAIR). Two other manufacturers, produce synthetic ester based oils. These are Hatco Chemical Division and American Oil and Supply Co. Their oils are of unknown formulation but purchased under MIL-L-23699 standard and are likely candidates for TMP-P sources since their Product Safety Data Sheets list tricresyl phosphate as an ingredient. Our analysis indicates that only one of these oils, #26 in Table 5, showed evidence of TMP-P production on pyrolysis while the other oil, #13 which is also polyol ester based, showed no evidence of TMP-P production under the conditions studied.

It should be pointed out that the formulation of additives in these oils and lubricants are proprietary and were not available for this study. This had the effect of reducing any bias in the interpretation of results. In effect, it became a "blind" study in which "the results speak for themselves".

CONCLUSIONS

1. It is possible to generate large quantities of TMP-P from Exxon 2380 oil under laboratory conditions.
2. Of the 26 oils which were analyzed and which were actually found in the U.S. Navy inventory, only one, MIL-L-23699C, demonstrated evidence of formation of TMP-P. It appeared to produce only 1/30 the TMP-P of Exxon 2380.

Recommendations

1. Research should be initiated for overall toxicity of combined, combustion byproducts rather than for any individual combustion product present.
2. All polyol ester based synthetic oils in the U.S. Navy inventory should be tested for toxic byproduct production.
3. The Exxon 2380 formulation for MIL-L-23699 should not be included in the U.S. Navy inventory because of it's high potential for producing TMP-P on pyrolysis.

APPENDIX A

Mechanism of Action

The toxic 4-alkyl bicyclophosphate esters produce convulsive seizures and death in mice within a few minutes (1). The definitive mechanisms by which bicyclophosphate esters affect the nervous system are not known exactly, but the general convulsive properties indicate that it acts as an antagonist to the gamma amino butyric acid (GABA) neurotransmitter substance at nerve endings.

This inference has been derived from certain similarities to the toxic effects produced by organophosphorus (OP) compounds. Organophosphorus compounds have diverse effects on both the central and peripheral nervous systems. The most extensively studied effects of OP compounds, which include insecticides and nerve gases, is the inhibition of acetylcholine (ACh). When nerve impulses are transmitted through the nervous system, a neurotransmitter substance is secreted at the point where two nerve cells must meet. This neurotransmitter substance such as ACh facilitates the passage of the nerve impulse across the gap between the two nerve cells. After passage of the nerve impulse, the acetylcholine is hydroyzed by an enzyme, acetylcholinesterase (AChE). Hydrolysis of ACh by AChE prevents the continuous, uncontrolled passage of nerve impulses which would produce convulsive symptoms. The intoxication syndrome of acute OP poisoning in mammals includes muscular twitching, weakness and convulsions. Death is usually caused by respiratory paralysis.

Even after a single exposure, many OP compounds can produce a delayed polyneuropathy which may occur as an axonal degeneration occurring concurrently in the peripheral nervous system as well as in selected tracts of the central nervous system. Spencer and Shaumberg (24) have labeled the neuropathy "central-peripheral distal axonopathy". Johnson (13) has reported that initiation of this effect does not involve the inhibition of acetylcholinesterase but rather the inhibition of another esteratic enzyme, "neurotoxic esterase". The resulting paralysis is caused by distal degeneration of long, large diameter nerve fibers (axones) in peripheral nerves and in the spinal cord, rather than by muscle fiber necrosis.

The toxic signs produced by 4-alkyl bicyclic phosphorus esters in mice and rats do not completely resemble the characteristic manifestations of poisoning by anticholinesterase agents such as chemical warfare agents. With bicyclo-phosphate esters there is no indication of excessive parasympathetic stimulation, twitching of the muscles, paralysis, or clonic convulsions. Bellet and Casida (1) have found that even when the concentration of the isopropyl-bicyclophosphate was high enough to produce death within 5 minutes, the brain AChE activity was not inhibited. They also reported that barbiturates may be useful in combating acute convulsions produced by the bicyclic phosphorus esters.

Bellett and Casida also pointed out the structural similarity of bicyclic phosphate esters to cyclic phosphate adenosine 3', 5'-monophosphate (cyclic AMP), Cyclic AMP is a normal biochemical constituent of cells and acts to

implement hormonal stimuli reaching the exterior of the cell into functions taking place in the interior of the cell, primarily by activation of cellular enzyme systems. They speculated that such structural similarity might be relevant to the action of bicyclophosphate esters. In a later study of structure-toxicity relationships, Casida (7) proposed that changes observed in cyclic AMP levels in animals challenged with bicyclophosphate ester only reflected the convulsive state of the animal rather than an interaction of bicyclophosphate ester and cyclic AMP metabolism and function.

Mattsson et al. (20) reported that bicyclophosphate ester compounds elevate cyclic guanosine 3', 5'-monophosphate (cyclic GMP) levels in rat cerebellum and a similar finding was reported by Coult et al. (8) in the mouse. Cyclic GMP is thought to have a cellular activation function somewhat similar to that of cyclic AMP, although it acts on different hormones than cyclic AMP.

The significance of such reported changes in cyclic AMP and cyclic GMP after bicyclophosphate ester challenge with the possible involvement of excitatory and inhibitory transmitters is unknown. It has been suggested that some drug induced changes in cyclic GMP levels might only reflect altered locomotor activity (17).

Other investigators (21) have reported no significant changes in cyclic AMP concentrations. Coult and Howells (8) and Blenkinsop et al. (2) studied the possible role of cyclic AMP and cyclic GMP in the mechanism of action of bicyclic organophosphate on the concentrations of the nucleotides in mouse

cerebellum at various times after the intracerebroventricular application of a range of doses of convulsant. They concluded that time after treatment and time into convulsions are critical when studying cyclic nucleotide changes. Ozoe et al. (22) have reported the binding of toxic bicyclic phosphates to rat brain synaptic membrane fractions. Mager (18) reported on the structure-toxicity relationships of bicyclic phosphate esters and showed that as the number of carbon atoms attached to the bridgehead carbon atom increases, the toxicity of the caged phosphate ester also increases.

Hill et al (12) has proposed that bicyclophosphate esters produce their neurological effect through interaction with another neurotransmitter, gamma amino butyric acid (GABA). GABA is a neurotransmitter which acts on inhibitory nerves. Antagonism between the bicyclophosphate ester and GABA would prevent the normal inhibitory nerve impulses which serve to regulate and control excitatory nerve effects.

Hill found that that potency of bicyclophosphate esters as GABA antagonists depends solely on the alkyl group in the molecule. Increasing the size of this group from ethyl to isopropyl produced a substantial increase in potency both as a convulsant and as a GABA antagonist but a further increase in size to pentyl produced a dramatic decrease in potency.

Although the neurological effects are not clearly delineated, it is known that at both convulsive and subconvulsive doses, the bicyclophosphates increase the cyclic GMP level in rat cerebellum possibly due to a primary action on the inhibitory GABA mechanism. The convulsant properties of the

bicyclophosphates are generally attributed to antagonism of the actions of synaptically released GABA (3,4,5,6,9,16). Highly potent convulsants require a symmetrical cage, high electron density at the 1 position and a suitable hydrophobic branched alkyl group (7,11). These requirements are also applicable to their high potency as GABA antagonists.

Bicyclophosphates are resistant to metabolism by microsomal esterases and oxygenases (7). However, it is likely that they are rapidly metabolized by other mechanisms or excreted based on their brief action in animals (1, 7, 15), their lack of cumulative effects (7,15), and their similar toxicity in a large variety of mammals and birds (15).

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APPENDIX B

| NUMBER | LOCATION | TYPE | DESCRIPTION |
|---|---|---|---|
| 1 | USS Inchon* | LPH12 | MIL-L-6086C<br>9150-00-240-2235<br>LUBE-OIL/GEAR GRADE |
| 2 | PNSYD** Lumber Yard | | MIL-H-176720<br>9150-00-582-5480<br>HYD FLUID<br>IMPERIAL OIL CO. |
| 3 | PNSYD** Lumber Yard | | MIL-L-2105 CAM2<br>9150-01-035-5394<br>LUBE OIL GEAR<br>IMP. OIL CO. |
| 4 | USS Inchon* | LPH12 | MIL-H-17672C AM1 2135TH<br>9150-00-985-7237<br>AFT STEERING |
| 5 | PNSYD** Lumber Yard | | MIL-H-17672D<br>9150-00-584-2566<br>PHIPPS PRODUCTS<br>HYD FLUID |
| 6 | USS Inchon* | LPH12 | CELLULUBE |
| 7 | USS Inchon* | LPH12 | MIL-L-2105C<br>9150-01-035-5393<br>Lube Oil Gear<br>IMPERIAL OIL CO. |
| 8 | USS Conygham*** | DDG-17 | 2135TH<br>9150-00-985-7237<br>AFT -STORAGE |
| 9 | PNSYD** Lumber Yard | | 2075TH<br>9150-00-985-7233<br>HIPPS PROP CORP Hyd. Fl.<br>BOSTON |

* USS Inchon is a Helicopter Aircraft Carrier
** Philadelphia Naval Shipyard
*** USS Conygham is a Guided Missile Destroyer
**** USS Clifton Sprague is a Fast Frigate
***** USS Fulton is a Submarine Tender

| NUMBER | LOCATION | TYPE | DESCRIPTION |
|---|---|---|---|
| 10 | PNSYD** Lumber Yard | | MIL-H-17672C<br>9150-00-985-7233<br>2075TH<br>HYD #1 |
| 11 | USS Inchon* | LPH12 | MIL-H-46170B<br>9150-01-131-3324<br>TYPE II<br>Preservative Fluid<br>BRAY OIL |
| 12 | USS Conygham*** | DDG-17 | 2075TH<br>NO- NSN<br>MIL-L-17672 |
| 13 | USS Clifton Sprague**** | FFG-16 | MIL-L-23699 FFG-16<br>9150-00-985-7099 QT<br>MAIN GAS TURBINE LUBE OIL |
| 14 | PNSYD** Lumber Yard | | MIL-F-17111B<br>9150-00-261-8318<br>HYD FLUID<br>ROYAL PRODUCTS CO. |
| 15 | PNSYD** Lumber Yard | | MIL-H-22072(B)<br>(AS)AM1<br>9150-01-080-5962<br>HYD FLUID CATAPULT<br>EF HOUGHTON CO. |
| 16 | PNSYD** Lumber Yard | | MIL-L-9000G<br>9150-00-181-8097<br>LUBE OIL, SHIPBOARD<br>BATTEN FIELD |
| 17 | USS Inchon* | LPH12 | MIL-H-83282B<br>9150-00-149-7432<br>AMERICAN OIL CO.<br>PNEUM TOOL HYDRAULIC JACK |
| 18 | USS Conygham*** | DDG17 | 9250<br>9150-00-181-8229 |

* USS Inchon is a Helicopter Aircraft Carrier
** Philadelphia Naval Shipyard
*** USS Conygham is a Guided Missile Destroyer
**** USS Clifton Sprague is a Fast Frigate
***** USS Fulton is a Submarine Tender

| NUMBER | LOCATION | TYPE | DESCRIPTION |
|---|---|---|---|
| 19 | USS Inchon* | LPH12 | MIL-H-19457<br>9150-01-113-2045<br>STAUFER CHEM. CO. |
| 20 | USS Conygham*** | DDG17 | MIL-L-17331 -2190<br>9150-00-235-9061<br>Anchor Wind Laps TEP |
| 21 | USS FULTON***** | AS11 | MIL-H-17672C 2110-TH<br>9150-00-985-7234<br>IMPERIAL OIL CO. BATCH 610 |
| 22 | USS FULTON***** | AS11 | MIL-L-17331<br>9150-00-235-9061<br>2190TH |
| 23 | PNSYD** Lumber Yard | | MIL-H-5559A<br>9150-00-243-1087<br>ARRESTING GEAR<br>OCTAGON PRODUCTS |
| 24 | USS Conygham*** | DDG17 | 2190TH<br>NO - NSN<br>MIL-L-17331<br>After Capstan 2190 TEP |
| 25 | USS FULTON***** | AS11 | MIL-H-17672 2135-TH<br>9150-00-985-1237<br>IMPERIAL OIL CO. BATCH 010 |
| 26 | PNSYD** Lumber Yard | | MIL-L-23699C<br>9150-00-985-7099<br>Lube Oil Acft Turboshaft<br>Eng. Synthetic<br>DL A600-82-C-088<br>Hatch Qual 03A |

* USS Inchon is a Helicopter Aircraft Carrier
** Philadelphia Naval Shipyard
*** USS Conygham is a Guided Missile Destroyer
**** USS Clifton Sprague is a Fast Frigate
***** USS Fulton is a Submarine Tender

## APPENDIX C

1. Calculate gm. TMP-P in Standard injected into GC/MS

$$\text{TMP-P conc. in standards } \frac{\text{ug}}{\text{ml}} \times \frac{10^{-3}\ \text{ml}}{\text{ul}} \times \text{injection volume (ul)}$$

$$= \text{ug TMP-P in injected standard}$$

$$\text{ug TMP-P} \quad \frac{10^{-6}}{\text{ug}} = \text{gm TMP-P in injected standard}$$

2. Calculate (g) TMP-P in Injected Pyrolysate

$$\frac{\text{ion abundance in pyrolysate}}{\text{ion abundance in standard}} \times \text{gm. TMP-P in injected standard}$$

$$= \text{gm. TMP-P in pyrolysate}$$

3. Calculate yield of TMP-P in Pyrolysate

$$\frac{(\text{gm TMP-P in injected pyrolysate})(\text{total volume of pyrolysate rinse (ul)})}{\text{volume of pyrolysate rinse injected (ul)}}$$

$$= \text{Total TMP-P in pyrolysate rinse (gm)}$$

4. Calculate recovery of TMP-P (ug TMP-P/gm oil)

$$\frac{\text{gm. TMP-P in Pyrolysate}}{\text{gm oil pyrolyzed}} \times \frac{10^{6}\ \text{ug}}{\text{gm}}$$

$$= \frac{\text{ug TMP-P in pyrolysate}}{\text{gm oil}} = \text{ppm TMP-P}$$

## APPENDIX D

### THREE DIMENSIONAL PLOTS FOR QUANTITATIVE STUDIES

FIGURE 5

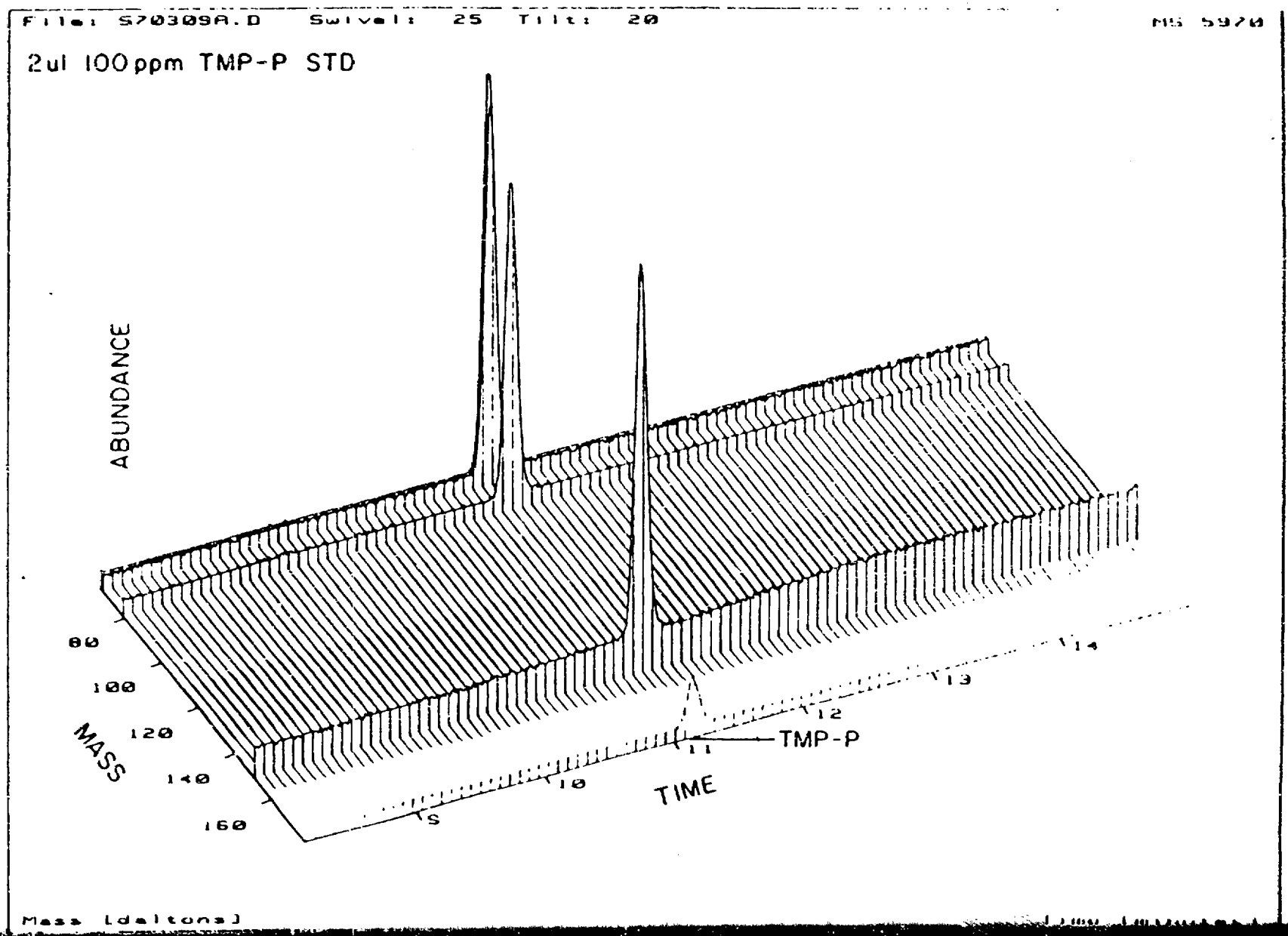

File: S70309A.D Swivel: 25 Tilt: 20
MS 5970
2ul 100ppm TMP-P STD
ABUNDANCE
MASS
80
100
120
140
160
TIME
8
10
11
12
13
14
TMP-P
Mass (daltons)

FIGURE 7

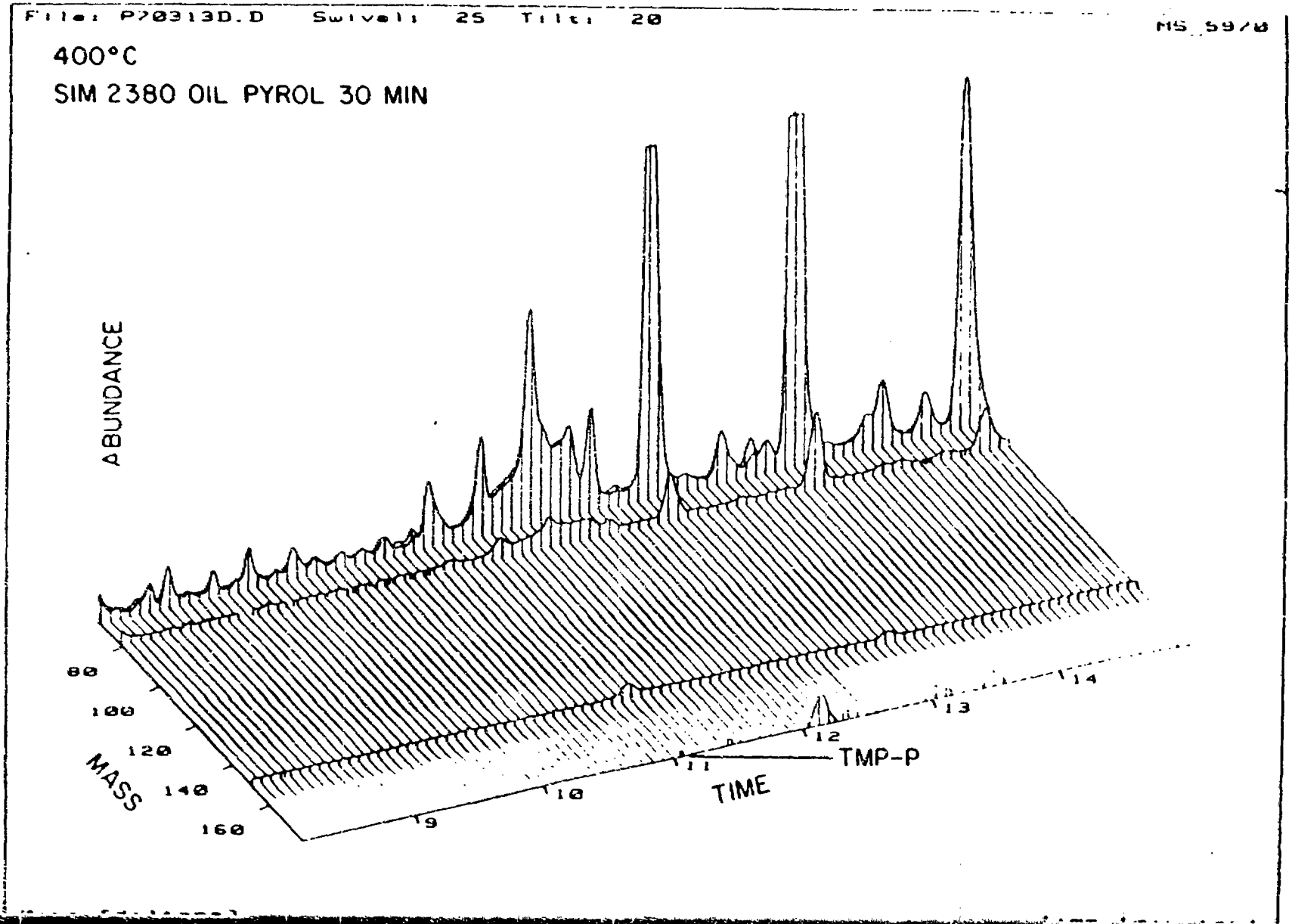

File: P70313D.D Swivel: 25 Tilt: 20
MS 5970
400°C
SIM 2380 OIL PYROL 30 MIN
ABUNDANCE
MASS
80
100
120
140
160
9
10
11
12
13
14
TIME
TMP-P

FIGURE 8

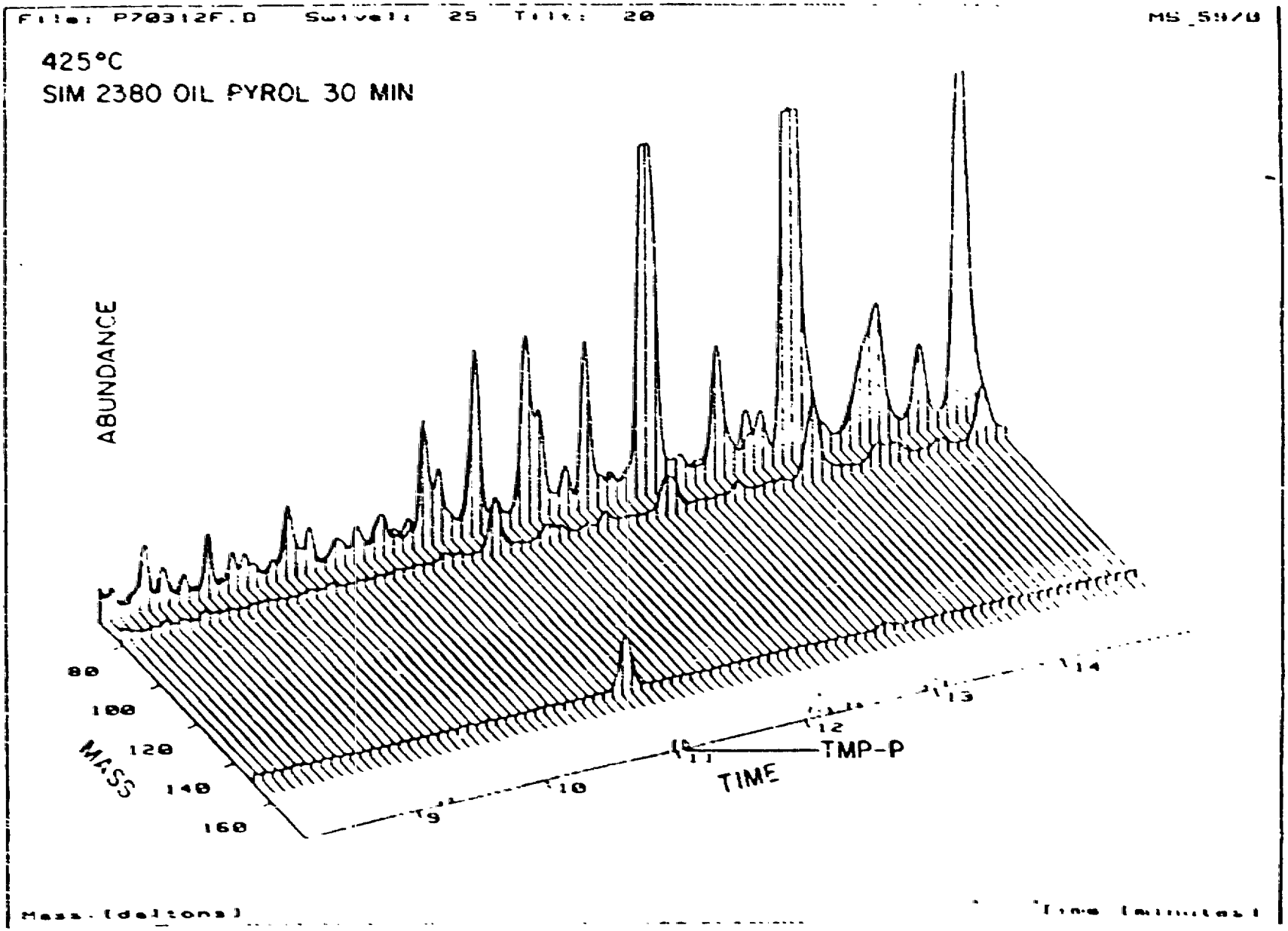

File: P70312F.D Swivel: 25 Tilt: 20
MS 5970
425°C
SIM 2380 OIL PYROL 30 MIN
ABUNDANCE
80
100
120
140
160
MASS
9
10
11
12
13
14
TIME
TMP-P
Mass (daltons)
Time (minutes)

FIGURE 9

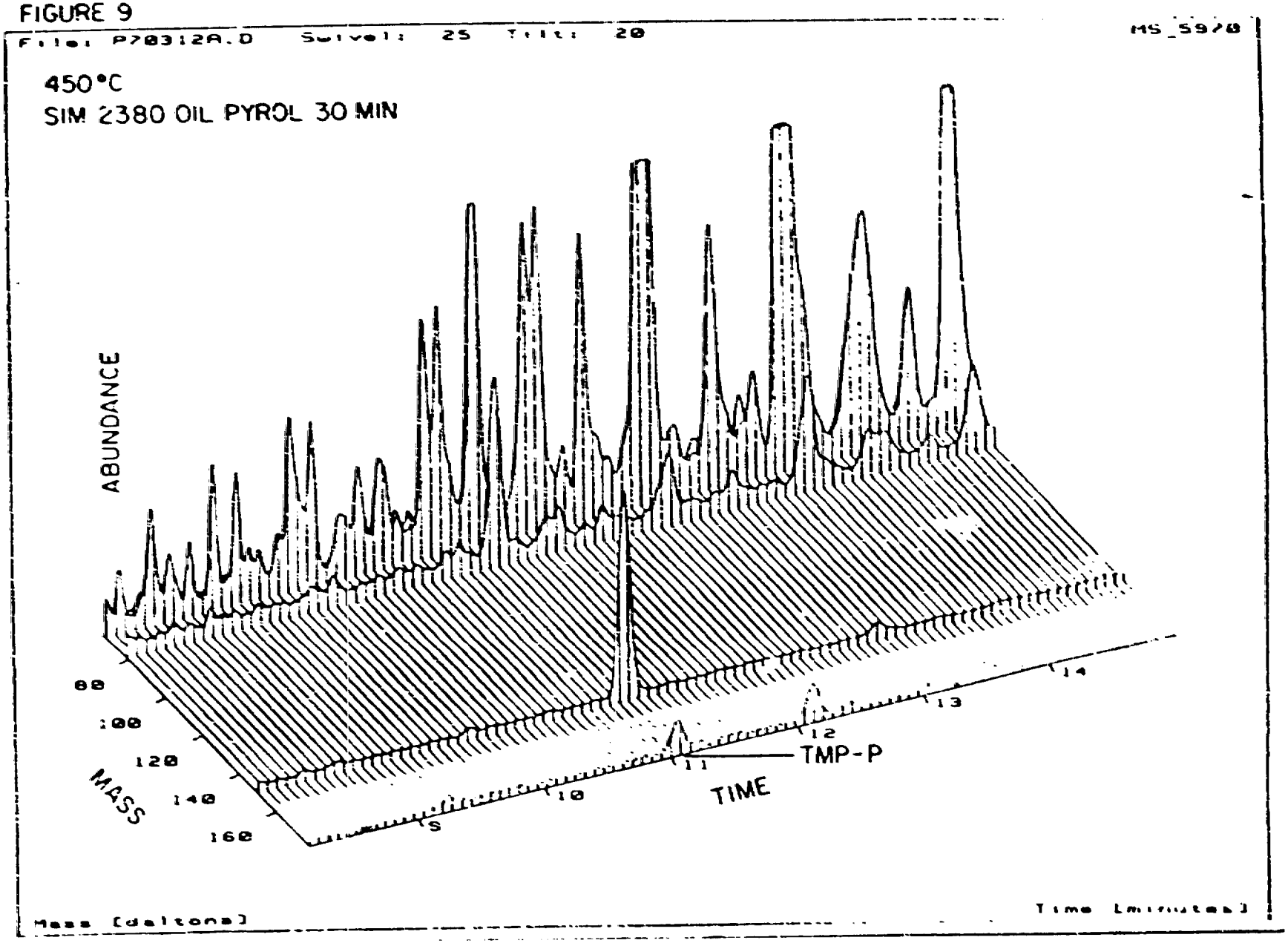

File: P70312A.D Swivel: 25 Tilt: 20
MS_5970
450°C
SIM 2380 OIL PYROL 30 MIN
ABUNDANCE
MASS
80
100
120
140
160
TIME
5
10
11
12
13
14
TMP-P
Mass [daltons]
Time [minutes]

FIGURE 10

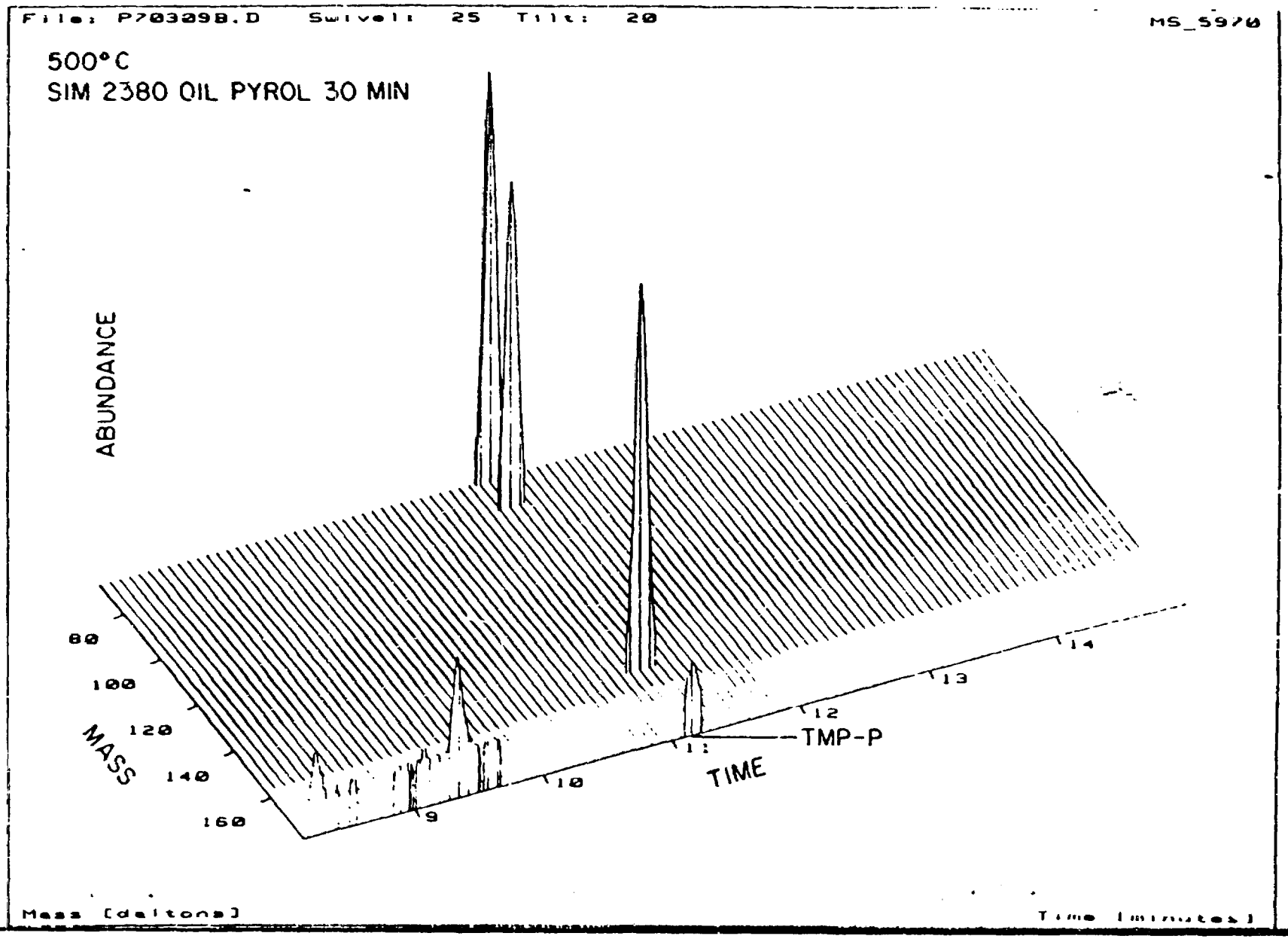
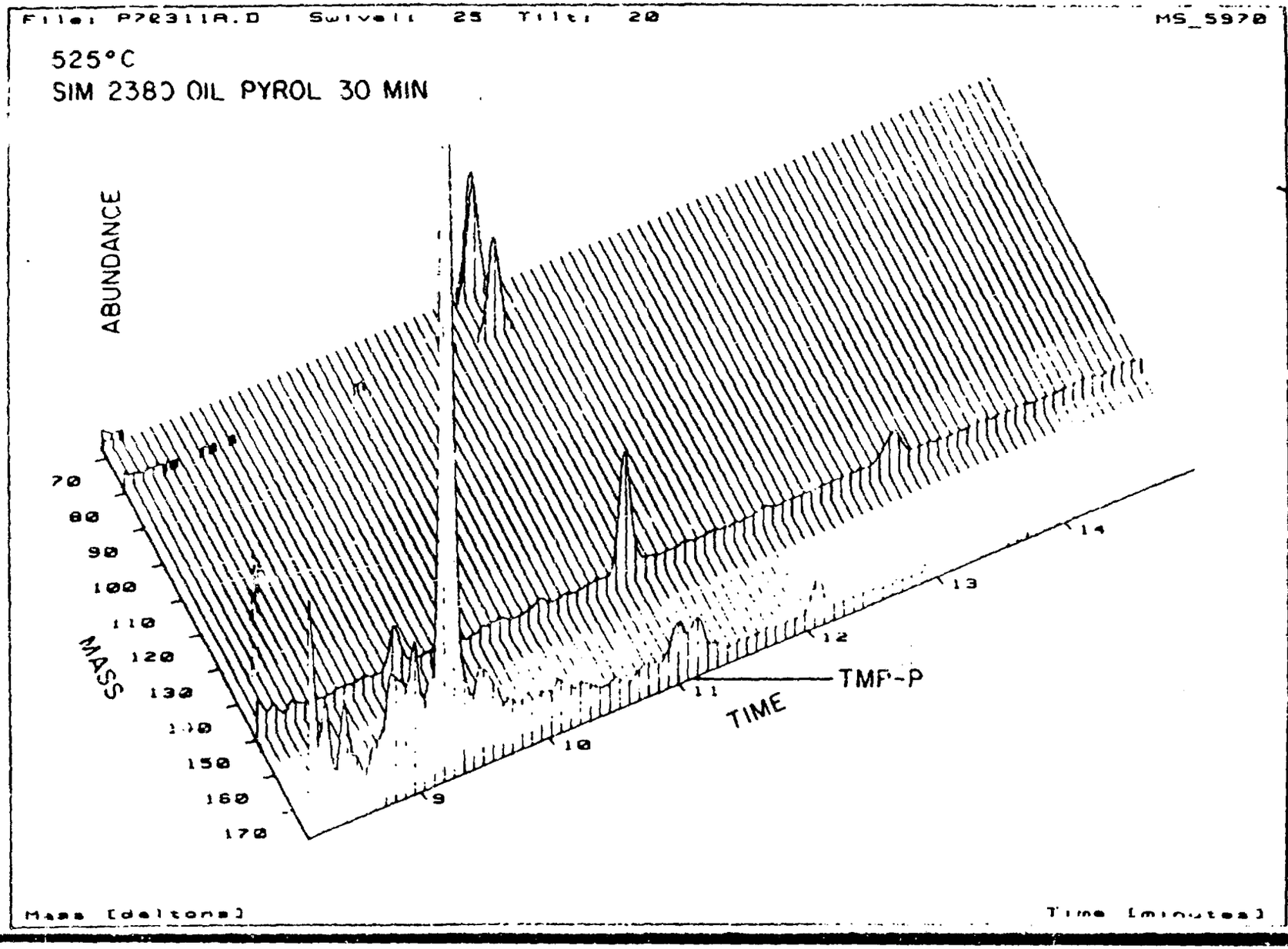

File: P703098.D Swivel: 25 Tilt: 20
MS_5970
500°C
SIM 2380 OIL PYROL 30 MIN
ABUNDANCE
MASS
80
100
120
140
160
9
10
11
12
13
14
TIME
TMP-P
Mass [daltons]
Time [minutes]

FIGURE 11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MS_5970
525°C
SIM 2380 OIL PYROL 30 MIN
ABUNDANCE
MASS
70
80
90
100
110
120
130
140
150
160
170
9
10
11
12
13
14
TIME
TMF-P
Mass [daltons]
Time [minutes]

FIGURE 12

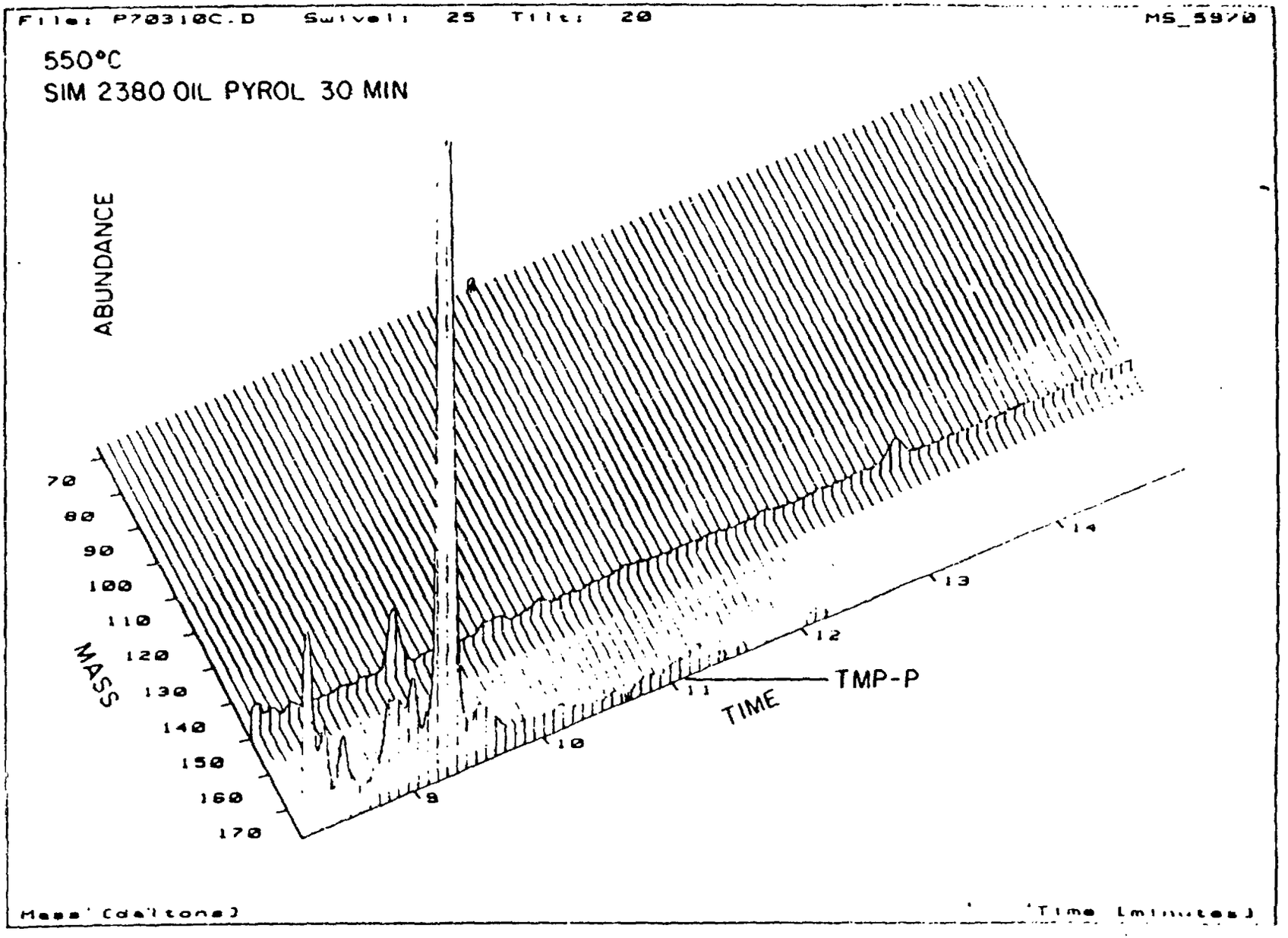

File: P70310C.D Swivel: 25 Tilt: 20
MS_5970
550°C
SIM 2380 OIL PYROL 30 MIN
ABUNDANCE
MASS
70
80
90
100
110
120
130
140
150
160
170
8
9
10
11
12
13
14
TIME
TMP-P
Mass (daltons)
Time (minutes)

FIGURE 13

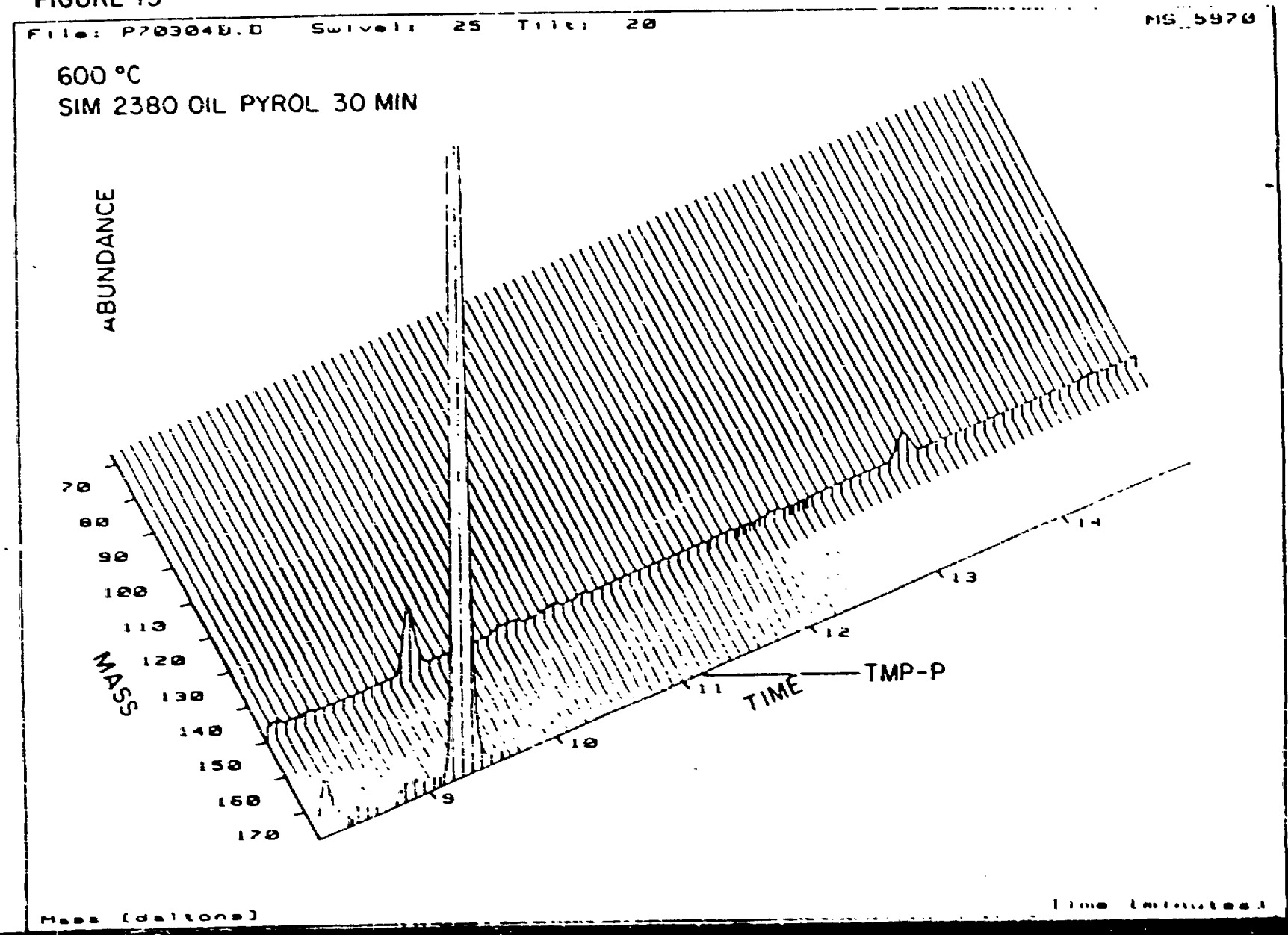
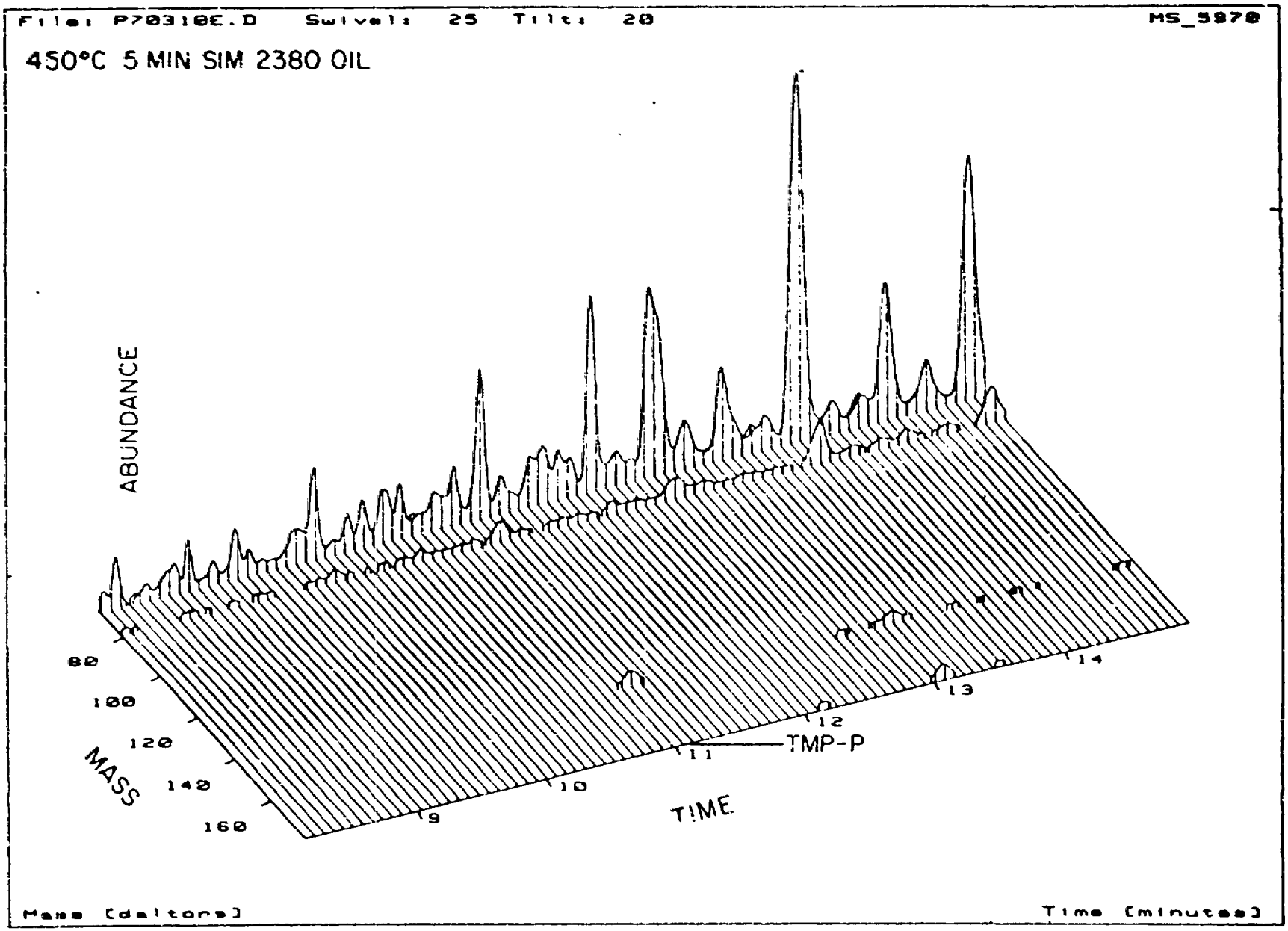

File: P70304B.D Swivel: 25 Tilt: 20
MS 5970
600 °C
SIM 2380 OIL PYROL 30 MIN
ABUNDANCE
MASS
70
80
90
100
110
120
130
140
150
160
170
9
10
11
12
13
14
TIME
TMP-P
Mass (daltons)
Time (minutes)

FIGURE 14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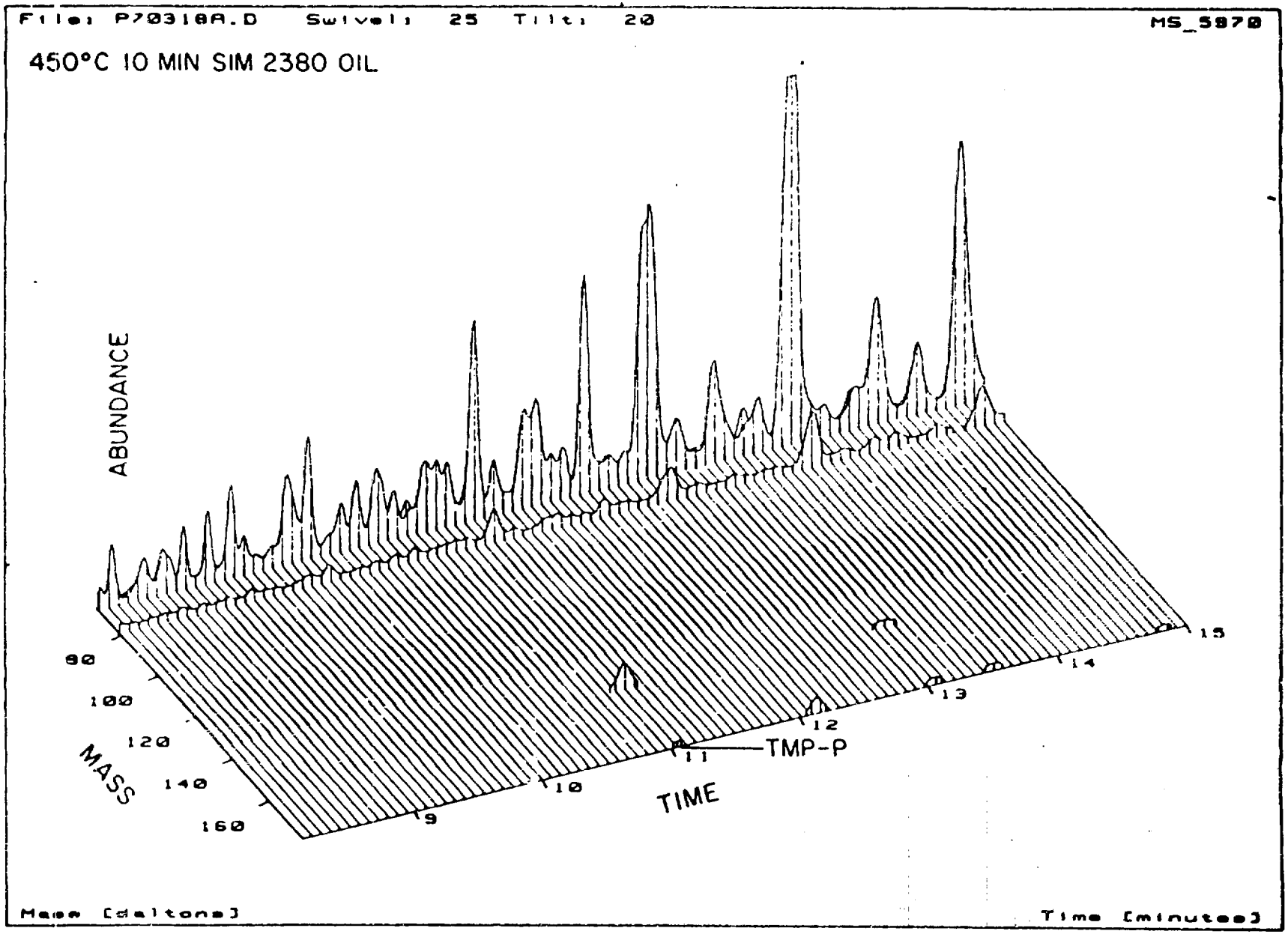
MS_5970
450°C 5 MIN SIM 2380 OIL
ABUNDANCE
MASS
80
100
120
140
160
9
10
11
12
13
14
TIME
TMP-P
Mass [daltons]
Time [minutes]

FIGURE 15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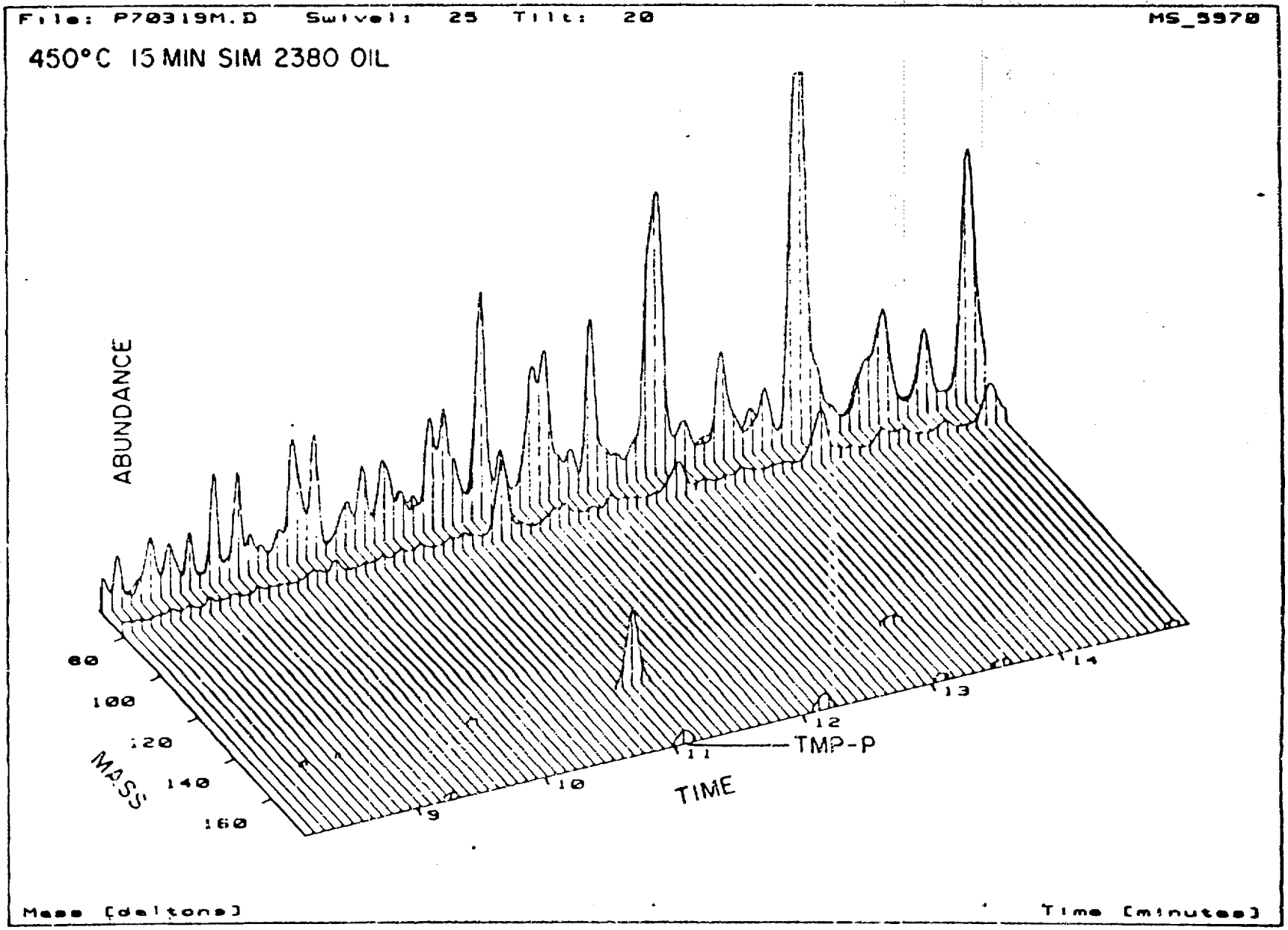
ABUNDANCE
MASS
90
100
120
140
160
TIME
9
10
11
12
13
14
15
TMP-P
Mass [daltons]
Time [minutes]

FIGURE 16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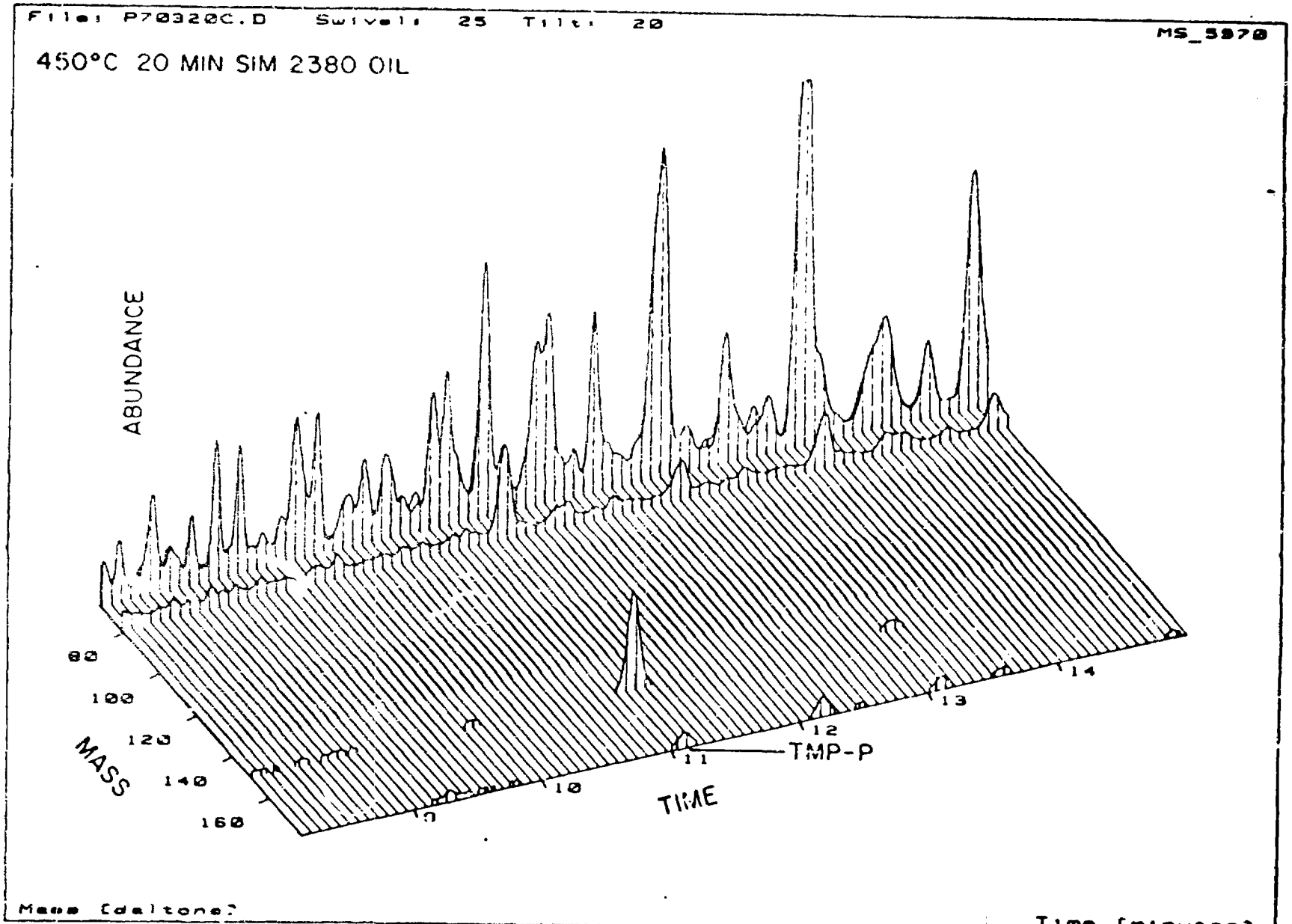
MS_5970
450°C 15 MIN SIM 2380 OIL
ABUNDANCE
MASS
60
100
120
140
160
9
10
11
12
13
14
TIME
TMP-P
Mass [daltons]
Time [minutes]

FIGURE 17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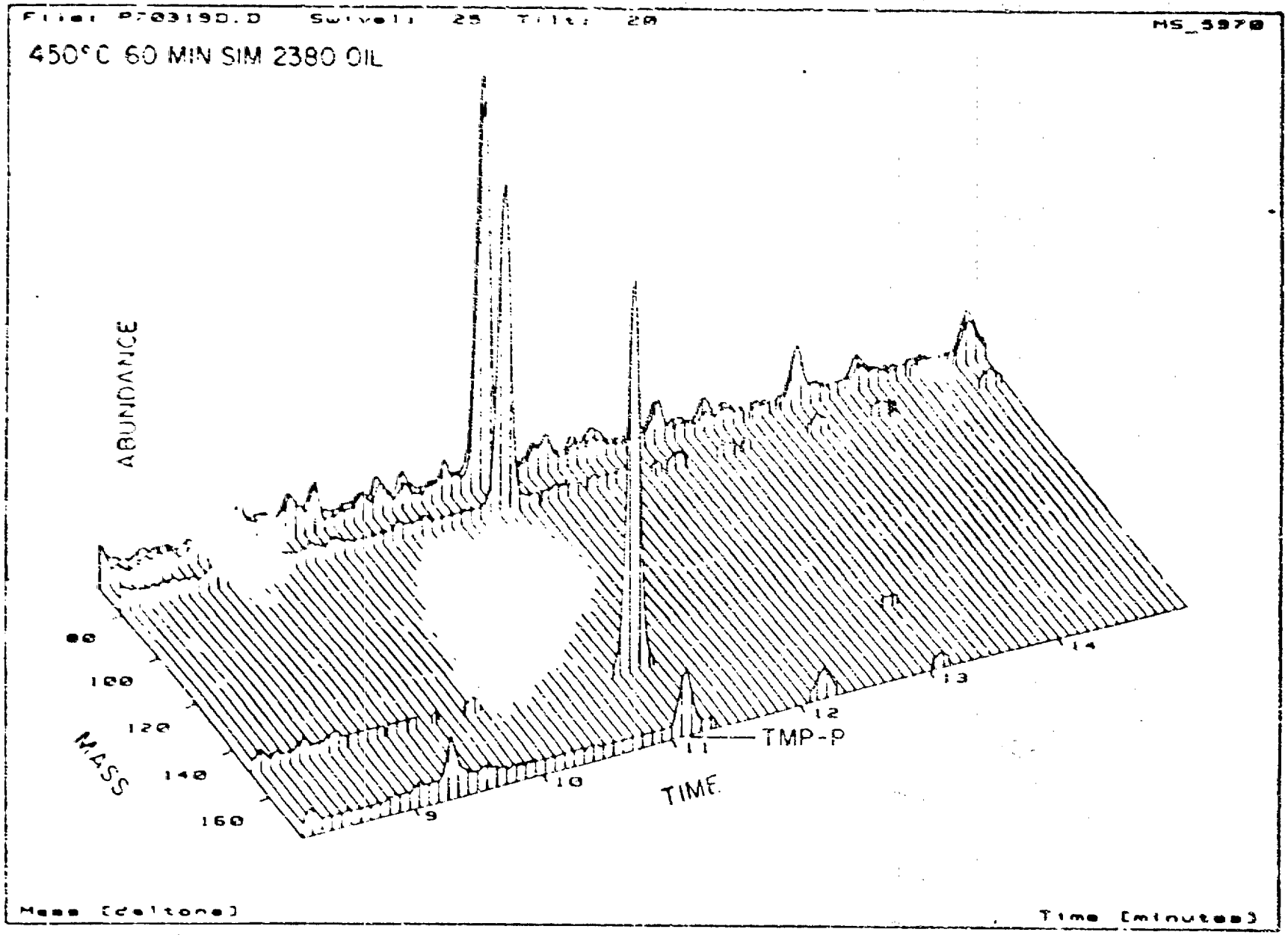
MS_5970
450°C 20 MIN SIM 2380 OIL
ABUNDANCE
MASS
80
100
120
140
160
TIME
10
11
12
13
14
TMP-P
Mass (daltons)
Time (minutes)

FIGURE 18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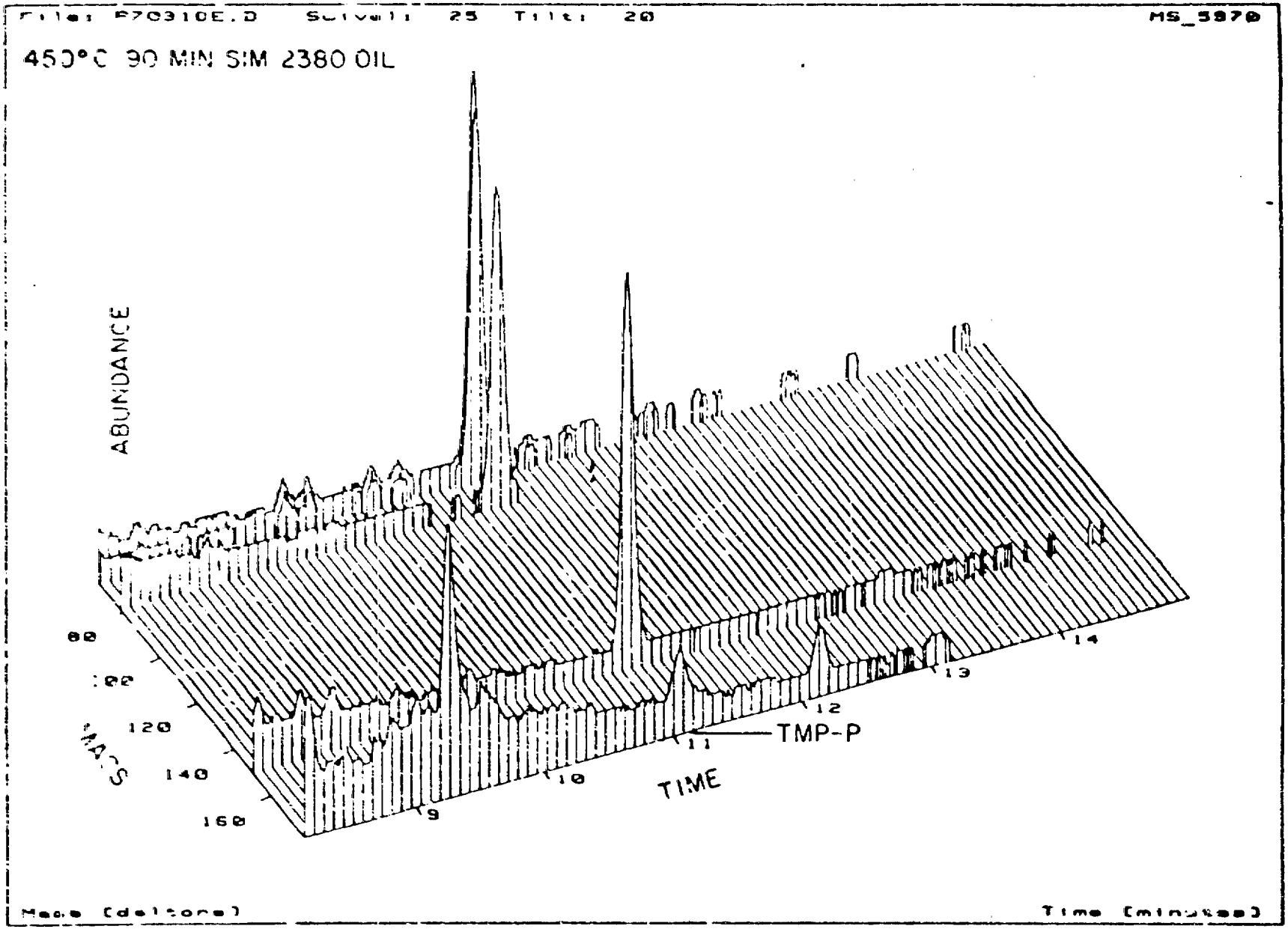
MS_5970
450°C 60 MIN SIM 2380 OIL
ABUNDANCE
MASS
80
100
120
140
160
9
10
11
12
13
14
TMP-P
TIME
Mass (daltons)
Time (minutes)

FIGURE 13


File: P70310E.D Scivell: 25 Tilt: 20
MS_5970
450°C 90 MIN SIM 2380 OIL
ABUNDANCE
80
100
120
140
160
MASS
9
10
11
12
13
14
TIME
TMP-P
Mass (deltons)
Time (minutes)

APPENDIX E
SUPPLEMENTARY BIBLIOGRAPHY ON TMP-P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