NASA CR-66826

FINAL REPORT
LABORATORY CONTAMINANT SENSOR DEVELOPMENT

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ABSTRACT

The Laboratory Contaminant Sensor developed under NASA Contract NAS1-7266 was modified to increase its sensitivity; the performance of the modified instrument was evaluated with fifty five test contaminants. Many of the contaminants tested can be detected at concentrations of less than one part per million. A linear relationship exists between the mass spectrometer signal at the maximum of the desorption curve and the amount of contaminant sorbed. For contaminant-air mixtures prepared by dilution, the reproducibility of the overall process (as judged by the standard deviation) is about twenty-five percent on the average for concentrations in the range from 0.5 to 10.0 parts per million. The major source of variability is believed to be in the technique used to prepare the mixtures. The reproducibility of the analytical technique is estimated to be ten percent from earlier work. For some compounds, notably alcohols and certain sulfur compounds, quantitative analysis is limited to concentrations greater than one part per million by some apparently irreversible sorption process occurring in the system.

Identification of contaminants is contingent on recognition of their mass spectra as they desorb from the accumulator cell and are pumped out of the system. Contaminants desorb over a range of about 100°C. The mass numbers associated with a specific contaminant appear, increase in intensity, and disappear as the spectra are scanned during desorption. This thermal behavior can be helpful in identifying contaminants when they occur in mixtures. However, if there is a large number of contaminants in the sample, identification of individual contaminants depends on the ability to interpret the total spectra observed at each scan temperature in terms of the individual contaminants. In such mixtures, low voltage ionization can be used to advantage to simplify the mass spectra interpretation for identification of contaminants.

Results of this program have demonstrated the general capability of this instrument for the detection and identification of contaminants at low concentrations in atmospheric samples. The analytical technique appears to be suitable for the analysis of contaminants in spacecraft atmospheres. Application of the principles incorporated in the Laboratory Contaminant Sensor to the development of prototype flight instrumentation is the next logical extension of this program to provide on-board analysis of contaminants in spacecraft atmospheres.

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1. INTRODUCTION

Analysis of contaminants in confined atmospheres of spacecraft requires the development of instrumentation which has the capability for detection of a wide spectrum of chemical species and which meets the special constraints of flight hardware. As a first step toward achieving these objectives, a program was undertaken to develop a Laboratory Contaminant Sensor with the capability for detection of a selected group of compounds at concentrations in the part per million range in air. The results of this development program are presented in NASA CR-66606, *Final Report, Laboratory Contaminant Sensor.* A second phase effort was undertaken to investigate detection of atmospheric contaminants at concentrations of less than one part per million and to extend the number and type of contaminants tested. Results of this effort are described in this final report.

The Laboratory Contaminant Sensor consists of a mass spectrometer coupled with accumulator cells containing a sorbent material on which contaminants from the air are concentrated. Contaminants collected in the accumulator cell at room temperature are subsequently desorbed to the inlet system of the mass spectrometer by heating the cell. An initial precut removes residual air from the accumulator cell to provide pressures compatible with the mass spectrometer leak, and to increase the relative concentration of the contaminants. As the contaminants desorb, they are pumped through the inlet system, past a gold leak where a small portion of the contaminants enter the mass spectrometer for analysis and quantitative determination. By programmed temperature desorption, a partial separation of contaminants is achieved.

Three sorbent materials (each in a separate accumulator cell) are employed in the sensor to provide capability for the variety of chemical compounds of interest. These sorbents are Porapak Q, charcoal, and Molecular Sieve 5A. Most of the relatively higher molecular weight organic compounds are retained on Porapak Q. Charcoal is used to retain the lower molecular weight compounds, which are not retained on Porapak Q under the conditions used for analysis, and Molecular Sieve to retain the nitrogen oxides and certain other gases which are not retained on charcoal. The use of these three sorbents provides general capability for accumulation of a fairly wide range of chemical compounds. However, none of these sorbents proved capable of retaining carbon monoxide under the procedures used in the Laboratory Contaminant Sensor. A palladium charcoal sorbent was prepared which showed a capability for reversible adsorption of carbon monoxide from air samples; this sorbent was tested to a limited extent.

In the second phase effort described in this report, the objectives were to determine the capability of the sensor with a wider spectrum of compounds and

to increase the sensitivity of the technique to permit detection at lower concentration. Some minor modifications to the existing instrumentation were performed to achieve this latter objective.

One limitation encountered in evaluating instrumentation for detection of trace contaminants is the lack of available standards for contaminants at low concentrations. In the earlier study program analyzed contaminant-air mixtures were purchased for dilution in establishing the capabilities of the Laboratory Contaminant Sensor. In the course of evaluating the results of that study some question arose concerning the reliability of sampling pressurized cylinders so that a sample of the test gas conformed to the reported analysis. Also, the use of purchased mixtures somewhat restricted the selection of contaminants which could be tested simultaneously. For these reasons, a method of preparing gas mixtures in plastic bags was investigated for use as standards for test purposes.

Results of the second phase study effort shows that this technique has a general capability for concentrating contaminants from the air for analysis by mass spectrometry. However, programmed temperature desorption affords only a partial separation of the contaminants sorbed on a particular sorbent; and the capability for analyzing complex mixtures of organics is restricted to those mixtures for which the degree of separation during desorption is sufficient or the mass spectra are sufficiently different to permit unambiguous identification of the components. The use of low voltage ionization offers one means of simplifying the mass spectra so that some of the difficulties attendant on analyzing the complexity of fragment ion spectra are eliminated or at least significantly reduced.

In the following section of this report, the modifications to the Laboratory Contaminant Sensor are described; the method of preparing and analyzing test gas mixtures, and the results of these analyses are summarized and discussed. Test results with a second instrument are presented in Section 4 of this report.

2. EXPERIMENTAL

A description of modifications performed on the existing instrument is presented in Paragraphs 2.1.1 and 2.1.2. Modifications to the electrometer amplifier were undertaken to permit full use of the sensitivity of the mass spectrometer to monitor the desorption of contaminants. Minor modifications to the inlet system were performed to simplify operation.

The method of preparing test gas mixtures is described in Paragraph 2.2, together with the technique used with the Laboratory Contaminant Sensor for the analysis of contaminants.

2.1 MODIFICATIONS TO THE LABORATORY CONTAMINANT SENSOR

2.1.1 ELECTROMETER AMPLIFIER MODIFICATION

Determination of atmospheric contaminants at very low concentrations requires the use of the maximum sensitivity available from the detection unit, the CEC 21-614 mass spectrometer. This instrument has two sensitivity ranges available differing by a factor of 20. Use of the more sensitive range is restricted to a scan speed which is too slow to meet the ninety minute analysis time constraint. The restriction arises from the time constant of the electrometer amplifier. Modification of the feedback loop of the electrometer-amplifier was undertaken to make the more sensitive range available at reasonably fast scan speeds.

The required performance was obtained by opening up the bandwidth in the high sensitivity mode by removing the capacitor. The existing circuit is shown in Figure 2-1.

Removing the capacitor increases the bandwidth and the noise level. The major of 60Hz noise was due to the drive voltage for the solenoid relay used to change input sensitivity ranges. This device was replaced with a Teledyne relay (No. 430) which operates on dc power supplied from the emission regulator. The circuit modifications are shown in the Operation and Maintenance Manual for this instrument.

The modified amplifier was tested at different bandwidths to determine a bandwidth that would give the best compromise between noise, resolution, and scan speed for the high range. As a result of these tests, a bandwidth of 4.7 cps was chosen for the high range; higher bandwidths resulted in loss of information at scan speed three (40 seconds/octave) because of the increased noise levels. On low sensitivity, the bandwidth is 72 cps, which permits scanning at the fastest available speed (10 seconds/octave) with only 2% clipping. The response of the modified amplifier is shown in Figure 2-2. The noise level in the high sensitivity mode is approximately nine divisions on the oscillograph recorder.

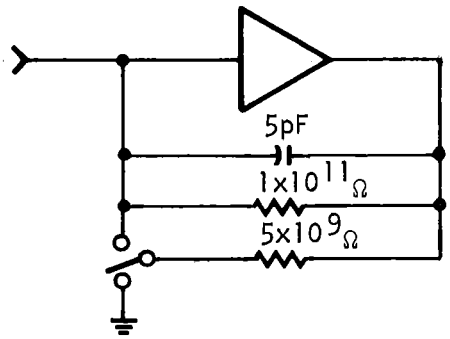


FIGURE 2-1
Amplifier Feedback Circuit

In the original instrument, a liquid nitrogen cold trap was employed in the inlet system between the metering valve and the sample vacuum pump to prevent back diffusion of the pump oil into the inlet system. This cold trap required frequent replenishment of the liquid nitrogen supply. In order to simplify the operation of the system, this cold trap was replaced by a Molecular Sieve Foreline Trap (Ultek Model 50-005).

Replacement did not affect the performance of the system in general. Satisfactory operation can be maintained by baking out the foreline trap overnight.

The inlet system was modified to permit attachment of the cells through a Cajon VCR fitting instead of the Swageloks formerly employed. The Cajon VCR's are a gasketted fitting and can be used repeatedly without difficulty. Aluminum gaskets are used for the seal between the cell and the inlet system. Individual gaskets can be used several times before replacement is necessary. Care should be exercised not to scratch the bearing surfaces on these fittings.

The temperature range of the programmed temperature controller was increased from 250°C to 300°C to permit operation of the charcoal and the Molecular Sieve accumulator cells at higher temperatures.

2.2 METHOD OF PREPARATION OF SAMPLES

Samples are prepared by diluting the compounds with air in Tedlar plastic bags. The contaminant, either in the form of the liquid, or its saturated vapor, or gas was measured with a syringe and injected through a heated Hamilton injection block into a flowing air stream which empties into the plastic bag. A schematic diagram of the apparatus is shown in Figure 2-3. The total volume of air used for dilution was determined by measuring the flow rate and the time period.

The Tedlar bags were fabricated from two-mil Tedlar sheet and heat sealed around the edges. A Swagelok quick disconnect was inserted in one wall of the bag before sealing. The bag is reinforced with a second layer of Tedlar at the point of insertion of the quick disconnect fitting. The fitting is retained in the bag with a nut machined from a one inch rod of teflon and a washer cut from teflon sheet stock. The bags were leak tested by the vendor.

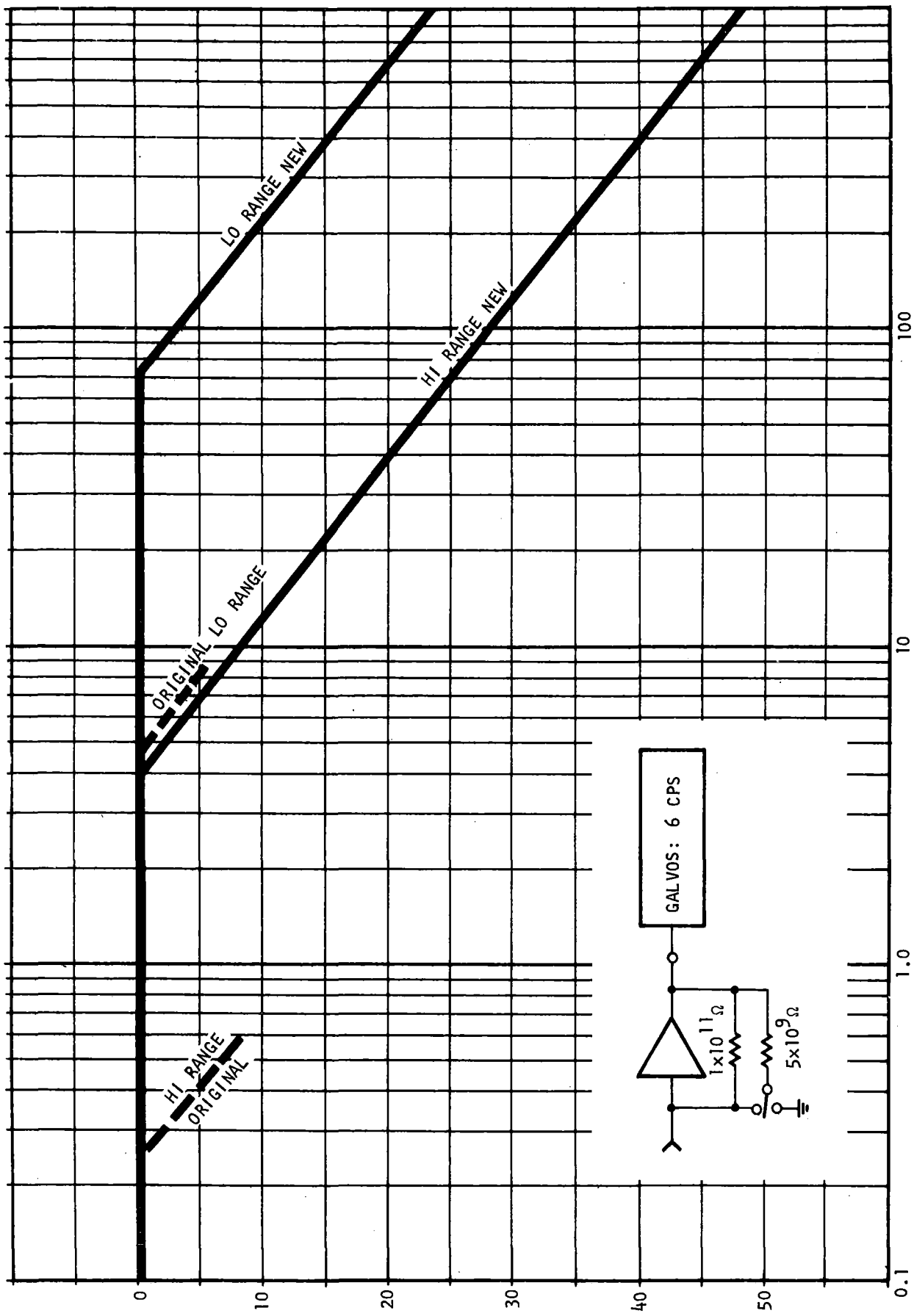


FIGURE 2-2
Modified Electrometer Amplifier Response

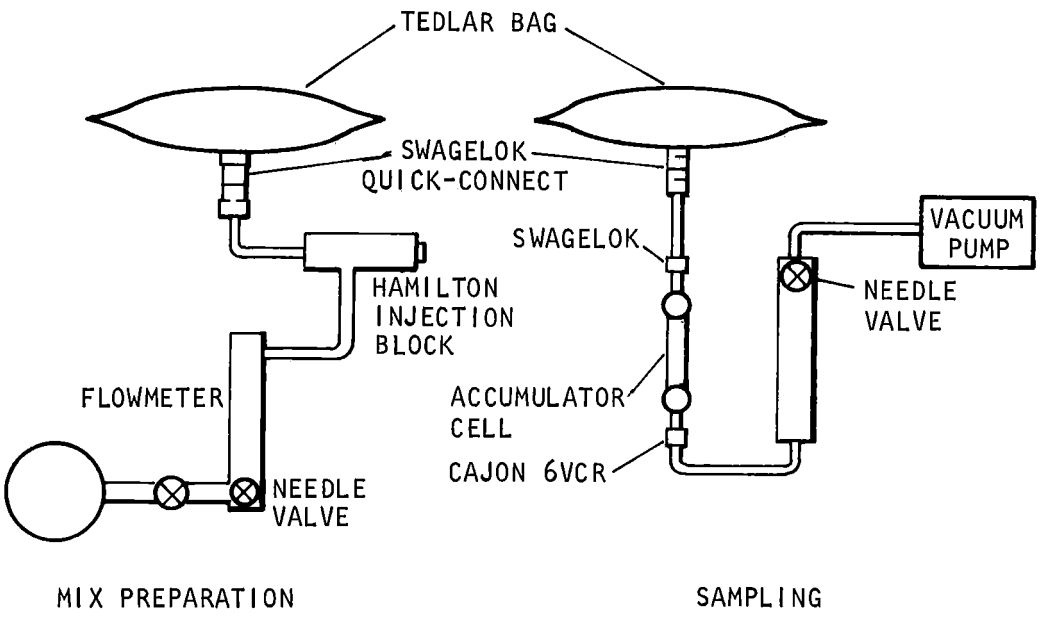


FIGURE 2-3.
Mix Preparation and Sampling Apparatus

The liquid contaminants used were obtained from Baker Chemical Corporation in the highest purity available. Gaseous contaminants were obtained from Matheson Company. The contaminants were sampled from small test tubes closed with a rubber cap. In taking saturated vapor samples, the liquid was agitated and a sample withdrawn into the syringe from near the surface of the liquid. The syringe was flushed several times with the vapor phase and the final measured volume injected into the flowing air stream, and carried into the bag in the air stream.

Liquid samples were taken directly. Gas samples were taken either by purging the syringe directly from the gas bottle or by passing the gas through a test tube and purging the syringe by slightly overpressurizing the tube and allowing the gas to flow out through the syringe.

Contaminants were injected through the rubber septum in the Hamilton injection block into a flowing air stream. Air flow was continued until the required amount of air (usually 30 liters or 10 liters) was added. Flow rates of either four or eight liters per minute were used; the total volume was calculated from the flow rate and the time period of filling. The sample was mixed by pushing on the walls of the bag. Three preparations of each sample were made; the first two were used to condition the bag, the third was sampled for analysis with the Laboratory Contaminant Sensor. Samples were discharged from the bag by pushing the gas out through two small holes cut in one corner of the bag; these holes were taped closed during the filling. Bags were purged with dry air between samples.

The technique described above was adopted because it was believed that the inner wall of the bag would adsorb contaminants and that by purging the bag twice, the final mixture would be close to the calculated composition.

Samples for analysis were taken from the bag by pumping the sample through the sorbent cell. A sampling rate of 360 cc/minute was employed. The volume of the sample was determined from the flow rate measured with a flowmeter downstream from the cell. The time period of sampling was usually 8 minutes. The flow rate was controlled from a needle valve between the flowmeter and the vacuum pump. The sampling system is shown schematically in Figure 2-3.

The sample flow rate was chosen on the basis of initial experiments which showed that low results were obtained for bag samples taken at a rate of 750 cc/minute. Samples taken at 360 cc/minute or 180 cc/minute gave results comparable to those obtained by direct sampling from a pressurized cylinder through the gas proportioner. The test samples were prepared by diluting a purchased mixture of vinyl chloride in air through the gas proportioner. The diluted mixture was run into the Tedlar bag to test the technique of sampling from the bag.

Initial experiments were performed with vinyl chloride to investigate the reproducibility of the bag dilution techniques for this gaseous compound. Results from various preparations were compared against each other, and against results obtained by gas proportioner dilution of a purchased gas mixture. Comparison of the slope of the line relating the amount of vinyl chloride (in microliters) to the mass spectrometer yielded reasonably good agreement between samples prepared in the bags and those prepared by dilution of purchased gas mixtures. However, the data points for each line are badly scattered. Calculated standard deviations for the curve are 25% for the bag samples and 15% for the gas proportioner samples. Sample concentrations were in the range from 100 ppb to 10 ppm for these tests.

Additional experiments were performed with benzene and methanol, also at low concentrations. These data were badly scattered and showed poor agreement between purchased analyzed gas mixtures and bag samples. It was initially decided, therefore, to abandon the preparation of gas mixtures in bags. However, reconsideration of the problems associated with obtaining reliably analyzed gas mixtures of relatively non-volatile compounds and sampling pressurized tanks accurately led to a decision to pursue the preparation of mixtures in bags further.

In brief, the situation was as follows. It has been reasonably well demonstrated in the first phase of the Laboratory Contaminant Sensor development program, that gas mixtures could be diluted with air and analyzed in a reproducible manner (about 10% on the average) at concentrations in the range of 10-100 ppm. However, although data indicated that sampling within this laboratory was reproducible, the calculated sensitivity values are dependent on reproducing the sample taken for analysis by the vendor. In some instances, it appeared that this process was questionable. On the other hand, preparation of individual mixture in bags yields less reproducible results but, hopefully, more truly representative of the sensitivity.

As more experience with the technique of preparing bags in samples was gained, results improved and the average error for most contaminants was about 20% for the overall process. Reviewing all the data obtained, it appears that the alcohols and certain other compounds exhibit irregularities at low concentrations which may account for the wide deviations encountered in the initial tests with methyl alcohol. These results are discussed in Section 3 of this report.

Before leaving the subject of preparation of the samples, it should be mentioned that samples taken from the bags which were tested on the charcoal cell exhibited unusually high water content. The Porapak accumulator cell does not retain water, so that the effect is not observed with this cell. The high water content appears to be associated with the bags, but how it arises is not presently understood.

2.3 ANALYSIS OF SAMPLES

Samples were analyzed in the manner described in the earlier report (NASA CR 66606). Figure 2-4 shows a schematic diagram of the system. After the accumulator cell is charged with a contaminant sample, it is valved off at both ends and attached to the inlet system of the mass spectrometer with the Cajon fitting. Air in the inlet system is pumped out through the main pump valves, B and E on Figure 2-4. When the inlet system pressure is reduced to background pressure, air is precut from the accumulator cell by opening the cell valve A for 15 seconds. This reduces the pressure in the system to a value acceptable to the gold leak of the mass spectrometer. Valves A, B and E are closed. The sample flow control valve D is opened and valve C is opened so that the flow path past the gold leak of the mass spectrometer is accessible.

The temperature programmer is started and the cell is heated to 50°C. Cell valve A is opened and as the temperature increases, the desorbing contaminants flow past the gold leak and are pumped out of the inlet system through the needle valve. A portion of the desorbed gas enters the mass spectrometer through the gold leak and the spectra of the desorbed contaminants is recorded at selected temperature intervals throughout the desorption period.

When the final desorption temperature is reached (260-270°C for charcoal and Molecular Sieve 5A, 230°C for Porapak Q), valves B and E are opened and any residual contaminants are pumped directly from the cell. The cell is pumped out for 10 to 15 minutes at this temperature and allowed to cool on the system under vacuum. It is valved off ready to accept another sample.

The cell is heated at an average rate of 6°C per minute, which is slightly less than the rate employed in the earlier program (7°C per minute). Spectra were monitored at 25°C intervals.

Mixtures containing several contaminants in air were usually tested. The desorption curves are plotted as a function of temperature. Typical desorption curves are shown in Figures 3-32 to 3-36. The highest signal observed on the oscillograph recorder due to the mass spectrum of each contaminant is used as the measure of the total contaminant in the sample. Since, in general, in testing mixtures, the peak maximum of the desorption curve of a particular

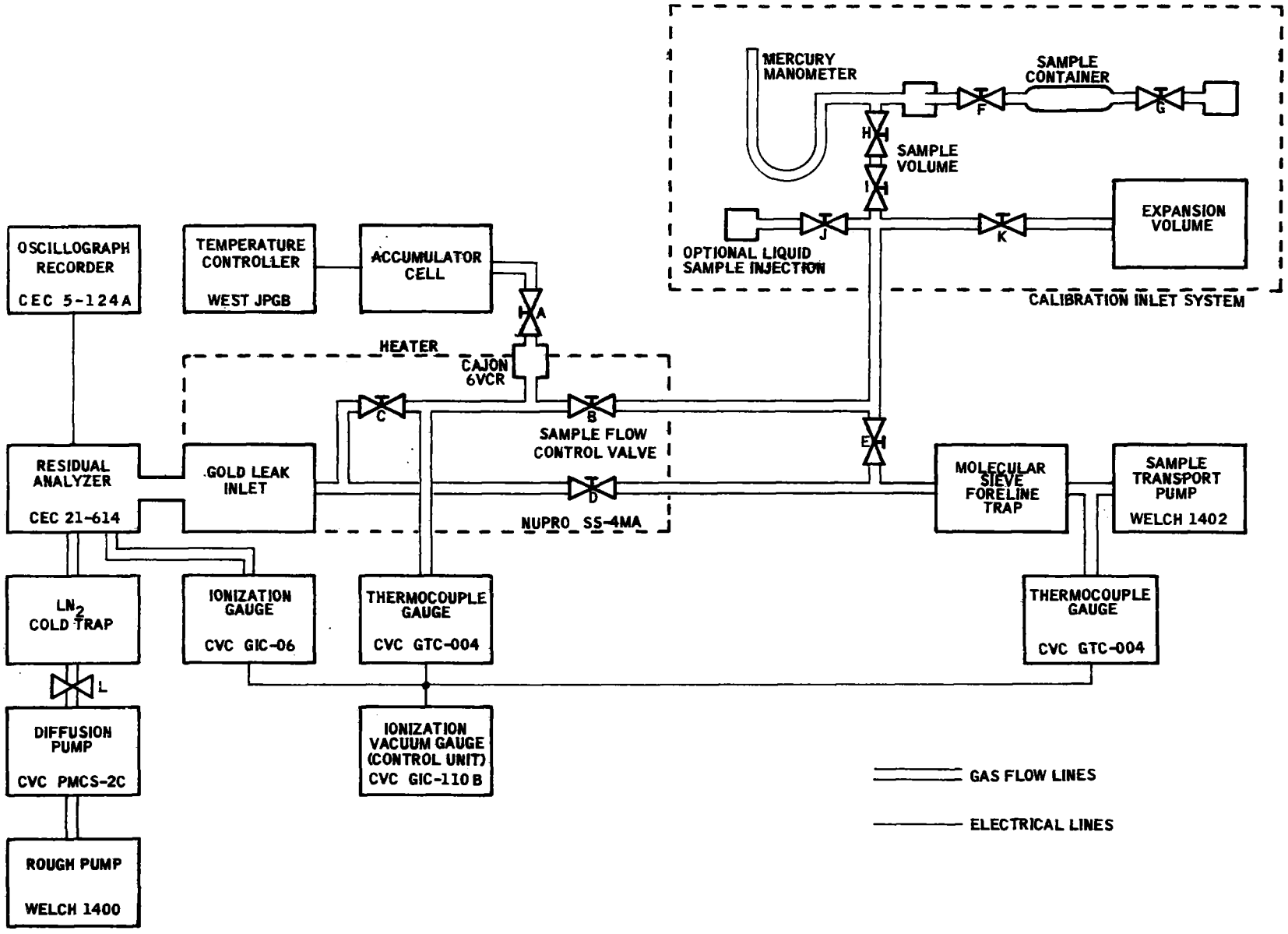


FIGURE 2-4
Laboratory Contaminant Sensor I Schematic Diagram

contaminant may not coincide with the scanning cycle time, the actual peak of the desorption curve will not be observed. The maximum error that can result from missing the desorption peak between cycles is estimated from experiments in which a single peak was monitored continuously to be about 10%.

The temperature of maximum desorption is estimated from the intersection of the ascending and descending shapes of the desorption curve. This temperature is characteristic of the contaminant and the particular sorbent. It tends to shift to higher values as the concentration of the contaminant decreases. The characteristic value is the temperature for lower concentrations.

The total amount of contaminant in the samples taken for analysis is plotted against the maximum peak observed at a mass number characteristic of the particular contaminant. Typical data are shown in Figures 3-1 to 3-29. Fifty five contaminants were tested in this study program. For about half of these, eight data points were taken at different concentrations. For the remainder, three or four data points were taken to establish the capability of the instrument for detecting these contaminants. The response of the system to each contaminant is calculated in terms of divisions per microliter calculated either from the slope of the line or from the average of individual sample values. These sensitivity values are corrected for any changes in mass spectrometer performance by normalizing the measured sensitivity to a fixed instrument response. The sensitivity of the instrument to nitrogen in air measured daily is used as the normalizing factor; during most of the experimental program this nitrogen sensitivity was in the range 700-900 divisions per micron.

The results of the test program are presented in Section 3 of this report.

2.4 MASS SPECTRAL DATA

Mass spectra of the contaminants tested in this program were recorded at 70ev and an estimated 16ev. The purpose of these calibration runs was to furnish a basis for comparing the sensitivity as measured by the desorption data with the sensitivity of the mass spectrometer itself, for the compounds. If the order of sensitivities of the compounds by direct analysis is comparable to that obtained by the accumulation technique, it provides a measure of confidence that there are not undetermined losses in the desorption technique. Further, if this correlation can be established, it should be possible to estimate the concentration of contaminants for which the system has not been calibrated from published mass spectral data.

The low voltage spectra are of interest to examine the possibility of using this technique to simplify the analysis of complex mixtures of contaminants. Ordinary mass spectra obtained with 70 volt electrons contain many fragment ion peaks which can obscure small amounts of some compounds in the presence of large amounts of others. By use of low voltage electrons for ionization, many of these fragment ion peaks are eliminated or reduced in intensity, so that parent ion peaks are more readily discernible. With low voltage electrons, however, the ionization efficiency is greatly decreased. To obtain a valid comparison between the fragmentation pattern as 70 ev and 16 ev, the spectra were run on low sensitivity for 70 ev and at high sensitivity for 16 ev. There is factor of about 25 difference between the two sensitivities.

It would be desirable to obtain low voltage spectra at lower electron energies than 16 volts because there is still an appreciable amount of fragmentation for compounds with ionization potentials in the range of 9 to 12 electron volts. The appearance potential for many fragment ions is in the range from 11 to 14 volts. Unfortunately, the design of the cycloid ion source and the low voltage modification do not permit lower energy electrons to be obtained. Actually, the value of 16 ev for the energy of the ionizing electrons is an estimate obtained from the appearance potentials of nitrogen, oxygen, argon, and helium. The measured low voltage potential between the injector and the anode is 8 volts.

The spectra of the various compounds were determined using the calibration inlet system described in the Addendum report to NASA CR-66606. A sample of the compound was introduced into the inlet system to condition the filament and the system to the particular compound. This sample was pumped out and the background in the instrument was recorded at 70 ev using low sensitivity and at 16 ev using high sensitivity. A sample at measured pressure was introduced and the spectra recorded under the same conditions as the background. The sensitivity was calculated from the signal in terms of divisions of output on the oscillograph recorder for the base peak and related to the sensitivity of nitrogen in air measured on the same day. The ratio of the signal from the base peaks at 16 ev to start at 70 ev, was calculated as a measure of the loss in sensitivity resulting from the use of low energy electrons for ionization. These results are summarized in Table 2-1. The correlation between desorption sensitivity and directly measured sensitivity is indicated by comparison between columns 2 and 5 of Table 2-1. The individual spectra are presented in Appendix B. The value of "S" at the end of each of the Appendix B tables represents the sensitivity relative to nitrogen in air. The value of "R" is the ratio of the sensitivity of the major peak at 16 ev to that of the major peak at 70 ev.

The instrument sensitivity to nitrogen in air varied about ten percent daily during the calibration experiments. A larger variation occurred on one occasion, the result of deterioration of the filament. It was necessary to replace the filament in that case. After the filament was replaced, it was noted that the sensitivity to nitrogen and oxygen at high voltage (70 ev) was comparable to earlier results, but the sensitivity at low voltage (16 ev) was decreased by a factor of three for oxygen and by a factor of ten for nitrogen. This indicates the sensitivity of low voltage spectra to conditions in the ion source, a factor which must be considered in evaluating the low voltage technique for simplifying spectral interpretations.

The mass spectra of some of these compounds requires some comment. The low voltage spectra were obtained without adjusting the repeller voltage. In this instrument, this has the effect of enhancing the apparent contribution to the spectra of the low mass ion fragments. For some of the compounds that normally have a fairly large peak at m/e 15, at low voltage, this mass fragment appears as the most intense peak in the spectra. In these cases, the low mass end of the spectra has been deleted from the tables and the ratio of the other masses adjusted accordingly. In the low voltage spectrum of nitrous oxide, the fragment ion NO^+, appearance potential 15 volts, disappears but the O^+ fragment,

with an appearance potential of 16.3 volts, increases in intensity relative to the parent mass. This is also attributed to incorrect repeller voltage. The improper adjustment results in some distortion of the ratios of the higher masses; however, it is believed that the disappearance of some peaks is representative of what may be expected to occur under true low voltage conditions.

In general, the halogenated compounds show the greatest loss of sensitivity at low voltage; this is expected, since they have some of the highest ionization potentials of all the organic compounds tested. This decrease in sensitivity will also occur for other compounds as the energy of the ionizing electrons is reduced to values near their ionization potentials.

Impurities in the spectra of some compounds are noted in the tables. The mass spectra of 1,1,1-trichloroethane indicates the presence of an impurity which has a spectrum similar to dioxane. It seems unlikely that the impurity is dioxane, but it may be some preservative to prevent the formation of phosgene. It appears in the spectra of trichloroethane observed during desorption. In the low voltage spectra this impurity stands out prominently compared to the greatly reduced intensity of the spectra of the halogenated compound and it was not possible to obtain an acceptable low voltage spectra for this compound.

TABLE 2-1

Summary of Spectral Data

Compound	Sensitivity Relative To N_2 in Air 70 ev	Relative Sensitivity at 16 ev	Ionization Potential*	Sensitivity** Measured on Desorption
Acetone	1.3		9.92	0.48
Allyl alcohol	0.58	0.064	9.67 P.I.	0.35
Benzene	1.7	0.057	9.21	1.2
Butane	1.3		10.80	***
n-Butanol	0.92	0.16	10.30	0.18
Butene-1	1.4	0.13	9.72	
Butyl acetate	2.0	0.018	10.00 P.I.	1.7
Carbon disulfide	2.1	0.05	10.13	1.1
Carbon tetrachloride	0.3		11.1	0.27
Chlorobenzene	1.0	0.037	9.42	1.1
Chloroform	0.6	0.022	11.42 P.I.	0.53
1-Chloropropane	1.1	0.083	10.7	
Cyclohexane	1.2	0.069	10.3	1.14
Diethyl ether	1.6	0.17	9.72	1.2
1,4-Dioxane	1.2	0.064	9.52	1.2
Ethyl acetate	1.9	0.014	9.97	1.8
Ethyl alcohol	0.9	0.19	10.60	
Ethylene	1.2	0.24	10.56	
Ethylene dichloride	0.69	0.05	11.12 P.I.	0.7
Ethylene oxide	0.66	0.2	11.2	
Ethyl formate	0.9	0.34		0.35
Freon-11	0.39	0.005	11.77 P.I.	0.19
n-Hexane	1.1	0.09	10.43	1.2
Isobutylene	1.6	0.18	9.35	
Methanol	0.73	0.16	10.88	0.22
Methyl acetate	2.0	0.13	10.27 P.I.	1.1
Methyl butyrate	0.93	0.033	10.07 P.I.	1.6
Methyl ethyl ketone	1.9	0.078	9.76	1.7
Methyl isopropyl ketone	2.7	0.09	9.32 P.I.	2.7

TABLE 2-1 (Continued)

Compound	Sensitivity Relative To N_2 in Air 70 ev	Relative Sensitivity at 8 ev	Ionization Potential*	Sensitivity** Measured on Desorption
Methylene chloride	0.85	0.02	11.4	
Monomethylamine	0.79	0.29	9.41	
Nitrous oxide	0.92	0.04	12.9	
Propyl mercaptan	0.7	0.10		
1-Propanol	2.0	0.089	10.42	1.5
2-Propanol	1.8	0.14	10.27	0.73
Tetrahydrofuran	1.3	0.13	9.45	1.2
Toluene	1.2	0.10	8.7 9.23	1.6
1,1,1-Trichloroethane	0.32			0.45
Trichloroethylene	0.5		9.94	0.5
Vinyl chloride	0.78	0.25	10.00 P.I.	
Vinylidene fluoride	0.43	0.18	10.30 P.I.	
o-Xylene	1.4	0.079	8.97	1.3
m-Xylene	1.6	0.076	9.02	1.8

* Ionization potentials are those reported for electron ionization unless marked P.I., which indicates potentials determined from photo-ionization. Data are from Electron Impact Phenomena, F.H. Field and J.L. Franklin, Academic Press, Inc., New York, 1957.

**Sensitivity of the major peak in the spectrum normalized to the sensitivity of methyl isopropyl ketone observed during desorption. For example, the sensitivity measured for n-Hexane is 42 divisions/microliter at m/e 86; at m/e 57, the base peak for n-Hexane, a desorption sensitivity of 332 divisions/microliter is calculated from the mass spectral data. The sensitivity relative to methyl isopropyl ketone at m/e 43 is 332/740 = X/2.7, where 740 divisions/microliter is the desorption sensitivity of the base peak (m/e 43) of methyl isopropyl ketone. In this case, X = 1.2, in good agreement with the value obtained by direct calibration with n-Hexane.

***Sensitivity values have not been entered in this column for those compounds which are not determined on Porapak Q.

3. RESULTS AND DISCUSSION

The factors that are important in evaluating the test results are the ability of the system to identify contaminants as they occur in complex mixtures in air and to determine their concentration in the atmosphere. Emphasis in this study program has been primarily directed to determining the response of the Laboratory Contaminant Sensor to contaminants which have been observed in confined atmospheres.

The sensitivities measured in this test program are summarized in Table 3-1, which lists the compounds tested in alphabetical order. The sorbent used for the determination of each compound is listed together with the temperature at which the maximum signal occurs. This temperature tends to shift to lower values as the concentration of the contaminant in the sample increases. The normalized sensitivity for each component is listed in the fourth column of Table 3-1.

The standard deviation calculated from the individual determinations is included as an indication of the reproducibility of the overall process of preparing and analyzing samples. For some contaminants, the data is too limited and the standard deviation was not calculated. In other cases, the sensitivity value was calculated from the slope of the line relating the amount of contaminant sorbed to the maximum response observed on desorption; standard deviations were not calculated in these cases. Figures 3-1 to 3-29 included at the end of this section, show the data graphically for some compounds.

Inspection of the data presented in Table 3-1 indicates that the reproducibility of the overall process of preparing and analyzing the test samples is about 20 to 25%. Considering the range of concentrations and variety of compounds tested, this is believed to be an acceptable value.

The data obtained in this second phase effort may be compared with that resulting from the first program after normalizing the original data for the instrument sensitivity. This comparison is shown in Table 3-2.

In general, the agreement between results from purchased, analyzed mixtures and from mixtures prepared in this laboratory is fairly good. Results for butene-1 are especially good, probably because of the relative inertness of this gas.

For some of the alcohols and sulfur compounds, there appears to be a nonlinear response in the low concentration range. The data for carbon disulfide and n-propanol (Figures 3-7, 3-7a, 3-24 and 3-24a) illustrate the effect. The high concentration data for carbon disulfide (4-40 ppm) extrapolate to a zero signal value at about a concentration of 1 ppm. Data for concentrations in the range up to about 1.5 ppm show a lower sensitivity. The behavior of n-propanol is similar. Other alcohols, allyl, methyl, and possibly, n-butyl, also show the effect which

TABLE 3-1
Sensitivity to Contaminants on Desorption

Contaminant	Sorbent	Temperature at Maximum on Desorption Curve (°C)	Sensitivity Divisions/µl (1000 Divisions/µl N_2 in Air)	
Acetone	Charcoal	>250	51±18	(m/e 58)
Acetaldehyde	Charcoal	180	21±6	(m/e 43)
Acetonitrile	Charcoal	200	300	(m/e 41)
Allyl alcohol	Porapak Q	140	95±32	(m/e 57)
Benzene	Porapak Q	165	335±78	(m/e 78)
Bensaldehyde	Porapak Q	>230	120	(m/e 106)
n-Butanol	Porapak Q	160	(see Fig. 3-5 of Report)	(m/e 31)
Butene-1	Charcoal	190	241±37 83±16	(m/e 41) (m/e 56)
Butyl acetate	Porapak Q	210	48±23	(m/e 73)
Butyraldehyde	Porapak Q	145	36±2	(m/e 72)
Carbon disulfide	Porapak Q	120	288 (see Fig. 3-7 of Report)	(m/e 76)
Carbon tetrachloride	Porapak Q	164	75±10	(m/e 117)
Carbon monoxide	Palladium Charcoal	180-230	90±25	(m/e 28)
Chlorobenzene	Porapak Q	210	300±19	(m/e 112)
Chloroform	Porapak Q	150	144±40	(m/e 83)
1-Chloropropane	Charcoal	230	200	(m/e 42)
Cyclohexane	Porapak Q	160	186±25	(m/e 84)
Diethyl ether	Porapak Q	125	56±17	(m/e 74)
1,4-Dioxane	Porapak Q	170	76±12	(m/e 88)
Ethyl acetate	Porapak Q	160	60±17	(m/e 61)
Ethylene dichloride	Porapak Q	160	96±15	(m/e 62)
Ethyl alcohol	Charcoal	210		
Ethyl formate	Porapak Q	120	7	(m/e 74)
Ethylene	Molecular Sieve 5A	170	80±15	(m/e 27)
Ethylene glycol	Porapak Q	155	100	(m/e 31)
Freon-11	Porapak Q	110	52±14	(m/e 101)
Furfuryl alcohol	Porapak Q	200	44	(m/e 98)
n-Hexane	Porapak Q	160	42±16	(m/e 86)
Isobutylene	Charcoal	190	75±25	(m/e 56)
Isopropyl alcohol	Porapak Q	120	200±70	(m/e 45)
Methyl alcohol	Charcoal	200	45±15	(m/e 31)
2-Methoxy ethanol	Porapak Q	145	18	(m/e 76)
Methyl acetate	Porapak Q	125	45±10	(m/e 74)
Methyl n-butyrate	Porapak Q	175	264	(m/e 74)
Methyl ethyl ketone	Porapak Q	145	66±10	(m/e 72)
Methyl isopropyl ketone	Porapak Q	165	70±7	(m/e 86)
Methylene chloride	Charcoal	185	100±14	(m/e 84)
Nitric oxide	Molecular Sieve 5A	175	136±44 (168±21 corr for blank)	(m/e 30)
Nitrous oxide	Molecular Sieve 5A	135	15±5	(m/e 30)
n-Propanol	Porapak Q	120	35±6 (see Fig. 3-24)	(m/e 59)
Propyl mercaptan	Porapak Q	150	59±5	(m/e 76)
Sulfur dioxide	Charcoal	210	24±7	(m/e 64)
Tetrahydrofuran	Porapak Q	155	80±1	(m/e 72)
Toluene	Porapak Q	205	430±60	(m/e 91)
1,1,1-Trichloroethane	Porapak Q	160	84±27	(m/e 97)
Trichloroethylene	Porapak Q	170	120±20	(m/e 130)
Vinyl chloride	Charcoal		120±30	(m/e 62)
Vinylidene fluoride	Molecular Sieve 5A	155	40±1	(m/e 64)
o-Xylene	Porapak Q	210	172±17	(m/e 106)
m-Xylene	Porapak Q	210	175±23	(m/e 106)

TABLE 3-2

Comparison of Results

Contaminant	m/e	Sensitivity (division/μℓ/ 1000 dvn/μN_2 in air)	
		NAS1-7266	NAS1-8258
Acetone	58	65.5	51±18
Acetaldehyde	43	45.5	21±6
Allyl alcohol	57	73	95±32
Benzene	78	580	335±78
Butene-1	41	254	241±37
	56	89	83±16
Carbon disulfide	76	480	288
1, 4-Dioxane	88	106	76±12
Ethyl acetate	61	32	60±17
Ethylene dichloride	62	63.5	96±15
Freon-11	101	118	52±14
Methyl alcohol	31	105	45±15
Methylene chloride	84	87.5	100±14
Nitric oxide	30	109	136±44
Nitrous oxide	30	30	15±5
Sulfur dioxide	64	128	24±7
Toluene	91	527	430±60
Vinyl chloride	62	159	120±30
M-Xylene	106	278	175±23

was noted for methanol and some other compounds in the earlier studies. For carbon disulfide, a possible explanation is that there is a fixed loss for this compound during the air precut operation, since this compound desorbs from Porapak Q at relatively low temperatures. However, the desorption temperature for methanol from charcoal is relatively high and a similar explanation will not hold. It also seems unlikely that the effect is due to irreversible absorption on the sorbent, since it is observed for alcohols on Porapak Q which is known not to retain alcohols very strongly. It may be due to the preferential adsorption of alcohols on the walls of the Tedlar bag during the preparation of the sample. The water content of samples prepared in the bags is always high. Whatever the reason for this effect, it currently limits detection of these compounds to concentrations greater than one part per million. For other compounds, the results appear to be linear down to the lowest concentrations tested within the limits of reproducibility.

The sensitivities measured with the accumulation technique follow the same order as the mass spectral sensitivities except for the alcohols and the sulfur compounds which appear low (See Table 2-1). This confirms the observation that there appears to be some loss occuring in the process for these compounds. Freon-11 and acetone also appear low in this comparison, but it is assumed that this is the result of losses in the precut operation. This correlation of sensitivities is useful in that an estimate of the sensitivity can be made from published mass spectral data for compounds for which the Contaminant Sensor has not been calibrated.

The order of desorption from Porapak Q is similar to the elution order observed for these compounds in gas chromatography. Within a given class of components, the desorption temperatures are in the same order as the boiling points. Table 3-3 shows the desorption order in the various chemical classes. Alcohols generally have lower desorption temperatures than would be expected on the basis of their boiling point in comparison to other types of compounds. However, Hollis[1] has pointed out that the solubility of a compound in the Porapak polymer is an important factor in determining its gas chromatographic retention time. The relatively low desorption temperatures and retention times of alcohols, and in particular, ethylene glycol are attributed to their low solubility in the polymer.

Compounds tested on charcoal are listed in order of desorption temperature in Table 3-4. Those compounds which are not retained on charcoal are determined on Molecular Sieve 5A. Desorption occurs over a wide temperature range for the compounds tested on Molecular Sieve -- vinylidene fluoride, ethylene, nitrous oxide, and nitric oxide.

In general, it is found that compounds which desorb at high temperatures from charcoal (e.g., acetone), desorb at low temperatures from Porapak Q. Butane and ethyl alcohol, however, desorb at too high a temperature from charcoal for detection and are lost in the air precut from Porapak Q.

Mixtures prepared with methyl mercaptan yielded a mass spectrum corresponding to dimethyl disulfide which desorbed starting at about 210°C from charcoal. Presumably oxidation of the mercaptan occurred in the cell. Di-isopropyl disulfide was observed as an impurity in propyl mercaptan. It desorbs at high temperatures from Porapak Q.

TABLE 3-3

Desorption According to Chemical Class from Porapak Q

Chemical Class	Desorption Temperature (°C)	Boiling Point (°C)	Gas Chromatograph Retention Time (Min.)*
Alcohols			
Isopropyl	120	82	3.8
n-Propyl	120	97	5.0
Allyl	120	97	
2-Methoxyethanol	145	125	
Ethylene glycol	155	198	10.5
Butyl	169	117	
Furfuryl	200	170	
Aromatics			
Benzene	165	80	14.5
Toluene	205	111	
Chlorobenzene	210	131	
Xylene	210	139-144	
Benzaldehyde	>230	179	
Esters			
Ethyl formate	120	54	
Methyl acetate	125	57	
Ethyl acetate	160	77	
Methyl butyrate	170	102	
Butyl acetate	210	126	
Halogenated Compounds			
Freon-11	110	24	
Methylene chloride	120	40	
Chloroform	150	61	
Ethylene dichloride	150	60	
1,1,1-Trichloroethane	160	74	
Carbon tetrachloride	165	77	
Chlorobenzene	210	131	
Ketones			
Acetone	110	56	3.5
Methyl ethyl ketone	150	80	
Methyl isopropyl ketone	165	95	

*Time for elution from a 6' x 3/16" column at 157°C; helium flow rate 50 cc helium.

TABLE 3-4

Desorption Order on Charcoal

Compound	Boiling Point (°C)	Desorption Temperature (°C)
Vinyl chloride	-13.9	160
Acetaldehyde	20.8	180
Butene-1	- 6.3	190
Isobutylene	- 6.6	190
Methylene chloride	40-1	190
Acetonitrile	80.06	200
Methanol	65	200
1-Chloropropane	46.6	230
Acetone		>250

Attempts to detect formic, acetic, and propionic acids were unsuccessful; this may be due to retention of these acids in the water film believed to exist on the walls of the sample bags. In the earlier test program (NAS1-7266), acetic acid was detected on Porapak Q in a mixture of acetaldehyde in air which had oxidized.

Further tests with the palladium charcoal sorbent cell for the determination of carbon monoxide were performed. Results obtained are similar to those described in the earlier program. However, attempts to detect lower concentrations (less than 10 ppm) were unsuccessful. This is attributed to the fact that at low concentrations or low total amounts of carbon monoxide sorbed, the carbon monoxide desorption peak shifts to higher temperatures and is lost in the blank value, which increases at the high temperature end of the run. This point is illustrated in Figure 3-30, which shows the m/e 28 peak for a blank (cylinder air sample), and two different concentrations of carbon monoxide. The behavior of other major peaks in the desorption spectra is shown in Figure 3-31. The lower limit for carbon monoxide by this technique thus appears to be about 10 ppm, based on the vendor's analysis of the test gas sample. This analysis was confirmed by direct analysis of the test gas mixture in our instrument, but an independent analysis by gas chromatography yielded a concentration about 2.5 times higher. If the latter analysis is correct, the lower limit for carbon monoxide detection would be about 25 ppm.

With the palladium charcoal sorbent, it has been possible to demonstrate that carbon monoxide can be extracted from air samples, and desorbed at temperatures below 250°C. However, in many respects, this sorbent is less than ideal. There are distinct disadvantages to using a carbon-based sorbent for detection of carbon monoxide. There are too many possible reactions with the normal components of air samples that can lead to the formation or destruction of carbon monoxide under the desorption conditions. The major evidence that the peak in the desorption curve for mass 28 is due to desorption of carbon monoxide is the dependence on the concentration or the amount of carbon monoxide sorbed and the fact that the carbon monoxide detector shows that carbon monoxide is sorbed and does not pass through the cell. While this is satisfactory for exploratory experiments, more convincing evidence is required for complete confidence in the analysis of carbon monoxide. Obtaining completely convincing evidence for any analytical method involves considerable experimental effort. Before undertaking such an effort, a more thorough test program with other sorbents should be considered. It appears reasonable to expect that a better sorbent - one not involving carbon - can be found for detecting carbon monoxide. It should be simpler to obtain the supporting evidence required to establish the analytical accuracy of such a sorbent than for one containing carbon.

Typical desorption curves for contaminant mixtures are shown in Figures 3-32 to Figure 3-36. These curves are illustrative of the degree of separation achieved. These mixtures were chosen for analysis because the desorption characteristics and the mass spectra of the contaminants are sufficiently different that the individual components can be readily identified and their concentration determined. The desorption curves of one rather complex mixture is illustrated in Figure 3-37. The reduction of the data taken during the analysis of this mixture is presented in Appendix A.

The main peaks in the mass spectra of the compounds which are sorbed on Porapak Q are shown in the order of increasing desorption temperature in Table 3-5. Since, at best, only a partial separation of contaminants is achieved in the desorption process, it is obvious that analyses of the mass spectral data can be a fairly tedious problem if all these compounds are present in an air sample.

There are theoretical reasons for expecting that the separation cannot be substantially improved using the present analytical technique. In the final report from the first study program, a theoretical peak shape calculated from the equation describing the desorption process was shown. This calculation showed that the desorption curves are about 50-60°C wide at half the peak maximum. Similar calculations are reported in a paper by Cvetanovic' and Amenomiya(2). Their results show that narrow peaks (10°C) are obtained only when the energy involved in the sorption process is relatively high, of the order of 80 kcal/mole. Since sorption on Porapak Q may be regarded as a solution phenomena, the activation energies are expected to be low. Calculations from gas chromatograph data yield activation energies of the order of 10 kcal/mole for sorption of aromatics on Porapak Q. The sorption processes on charcoal are expected to be different than those on Porapak but the compounds sorbed on charcoal show approximately the same peak shape on desorption, and it is concluded, therefore, that the energies of sorption are similar in magnitude to those obtained on Porapak Q.

TABLE 3-5

Mass Spectra of Contaminants on Porapak Q

	°C Temp.	m/e 24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42
Acetone	110		1.2	5.4	8.1	3.2	4.8								1.6	1.7	3.1		1.8	6.8
Freon-11	110								20.9				24.2		6.4				1.7	1.0
Methylene chloride	120												6.6	1.5	1.9				7.8	4.3
2-Propanol	120			1.7	15.4	2.2	8.7		6.6							1.3	4.5		6.4	3.0
Allyl alcohol	120		3.2	16.8	40.7	30.6	56.6	27.9	62.2	3.3					4.0	5.5	32.7	9.9	6.7	2.0
1-Propanol	120			2.5	11.8	5.8	11.7	1.7	100.0	2.2	1.0						2.3		4.6	7.6
Ethyl formate	120		1.0	10.0	40.7	100.0	57.5	4.2	98.5	1.6										1.2
Carbon disulfide	120									9.5					12.9	1.0				
Diethyl ether	125			4.1	21.3	11.7	49.1	1.8	100.0	2.1									3.0	
Methyl acetate	125		3.5	6.6					3.5	1.0										8.9
Methyl ethyl ketone	135			4.1	13.0	2.8	23.3													4.2
Butyraldehyde*	145		2.1	3.4	100.0	26.6	95.6	2.2	6.3						5.1	8.0	35.4	4.4	62.2	15.6
2-Methoxyethanol*	145				8.3		36.1		25.7											
Chloroform	150												14.6	2.3	4.0				1.0	
Propyl mercaptan	150			4.6	49.2	9.8	7.4			2.3	2.4	1.7	7.0		2.1	3.2	20.2	4.3	57.6	52.8
Ethyl acetate	150-160			2.2	9.9	4.0	20.6		1.1											5.0
Ethylene dichloride	150-160		4.8	20.2	100.0	7.3							3.4	1.8	1.2					
Cyclohexane	155-165			3.0	24.6	12.0	11.8									1.7	21.6	4.7	60.6	31.0
Ethylene glycol	155				5.1	6.8	14.3		100.0	10.4	32.0									2.8
Tetrahydrofuran	155			3.0	20.7	5.3	12.7		3.3							1.9	13.4	8.7	41.8	100.0
1-Butanol	160			5.1	51.5	22.7	31.8	2.0	100.0	2.5	8.4				1.1	2.0	13.9	3.3	65.6	34.1
n-Hexane	160			3.0	39.5	9.5	59.8	1.2								1.3	17.9	2.7	73.7	42.3
1, 1, 1-Trichloroethane	165	2.0	12.9	43.9	30.7	16.1	5.8	2.7	2.4				14.8	5.1	5.2	1.8				
Carbon tetrachloride	165												38.1	1.3	9.9				2.0	1.4
Benzene	165			2.7	2.8										3.9	6.8	18.5			
Methyl isopropyl ketone	165			1.5	12.1	4.6	1.6										5.1		12.4	4.7
Trichloroethylene	165-170	4.7	21.6										12.8	1.9	4.0					
1, 4-Dioxane	165-170			5.9	11.5	100.0	29.4	13.0	15.6											1.1
Methyl n-butyrate	175			3.5	35.4	9.3	12.7	1.0	4.9		1.4					1.6	12.2	1.7	28.1	16.2
Furfuryl alcohol*	200				48.0	8.0	59.5	4.9		28.6			2.0	3.0	20.6	32.0	96.8	12.0	97.8	77.3
Toluene	205			1.4	4.5										1.9	3.8	18.7	1.9	2.1	
Chlorobenzene	200-210			2.0	3.0									1.1	6.0	18.8	3.2			
Butyl acetate	210			1.2	9.1	6.5	10.9	5.5									3.2		14.8	4.1
0-Xylene	210			1.5	12.6										1.0	2.8	18.0	1.6	2.9	
m-Xylene	210			1.2	11.1										1.0	2.7	17.4	1.7	2.6	
Benzaldehyde	230						9.3													

*Spectra from literature

TABLE 3-5 (Continued)

	°C Temp.	m/e 43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61
Acetone	110	100.0	2.5														30.5	1.3		
Freon-11	110					14.8		4.0												
Methylene chloride	120					13.6	7.6	100.0	2.9	29.8										
2-Propanol	120	15.2	3.4	100.0	2.0													3.3		
Allyl alcohol	120	4.6										1.3		4.5		100.0	27.1	1.0		
1-Propanol	120	1.7		1.0														7.9	5.1	
Ethyl formate	120	6.9	1.4	26.3	1.4	7.6									2.0			1.0		
Carbon disulfide	120		12.3																	
Diethyl ether	125																			
Methyl acetate	125	100.0	2.4															5.3		
Methyl ethyl ketone	135	100.0	2.4													5.7				
Butyraldehyde*	145	80.8	87.7	4.3					1.4			1.4	1.4	2.3		18.8			1.4	
2-Methoxyethanol*	145	9.5		100.0	3.8	5.6														
Chloroform	150					34.5	17.1	11.5	4.7											
Propyl mercaptan	150	100.0	3.8	17.9	18.2	66.1	7.5	2.9								1.3	2.8	2.4		7.0
Ethyl acetate	150-160	100.0	2.5	14.4																12.0
Ethylene dichloride	150-160					1.8	2.2	11.7											2.1	9.3
Cyclohexane	155-165	15.4							1.4	2.1		3.3	5.0	33.0	100.0	4.1				
Ethylene glycol	155	7.6																		
Tetrahydrofuran	155	17.7	3.6																	
1-Butanol	160	63.8	5.7	5.9								1.0		11.4	85.3	5.9				
n-Hexane	160	80.6	2.4							1.0		1.6		9.2	56.0	100.0	3.9			
1,1,1-Trichloroethane	165		2.8	1.8		5.9		2.4								1.3	2.9	1.7	9.0	72.8
Carbon tetrachloride	165					40.9		11.4									7.7	7.4	2.4	
Benzene	165							1.8	15.3	18.1	21.2									
Methyl isopropyl ketone	165	100.0	2.4	1.1									1.0							
Trichloroethylene	165-170	1.1				11.4	3.2	3.6	1.2									5.8	41.4	2.6
1,4-Dioxane	165-170	9.1	2.2	2.6												5.8	22.9			
Methyl n-butyrate	175	100.0	4.4	3.5										7.1		1.0		22.7		
Furfuryl alcohol*	200	21.5	12.8					5.3	3.1	23.1	17.8	65.9	6.4	3.4	2.1	1.9	1.2	1.3		
Toluene	205	2.6	1.0	9.3	5.9				4.8	9.3	2.0	1.0								1.4
Chlorobenzene	200-210							3.2	20.8	24.8	2.1				9.1	2.7				1.3
Butyl acetate	210	100.0	2.5											5.8	31.9	3.1	1.4			10.3
O-Xylene	210	1.9							5.8	19.7	8.4	3.4								
m-Xylene	210								5.1	18.4	9.6	3.3								
Benzaldehyde	230								27.1	44.3	10.8									

*Spectra from literature

TABLE 3-5 (Continued)

	°C Temp.	m/e 62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81
Acetone	110																				
Freon-11	110					18.5		5.0													
Methylene chloride	120																				
2-Propanol	120																				
Allyl alcohol	120																				
1-Propanol	120																				
Ethyl formate	120												1.1	6.9							
Carbon disulfide	120															100.0	2.3	8.9			
Diethyl ether	125																				
Methyl acetate	125													15.6							
Methyl ethyl ketone	135											14.3									
Butyraldehyde*	145										4.5	44.8	2.6								
2-Methoxyethanol*	145															6.0					
Chloroform	150																				
Propyl mercaptan	150					3.6			1.0			1.7	1.6	1.0	53.8	2.2	2.3				
Ethyl acetate	150-160									5.7			2.7								
Ethylene dichloride	150-160	50.2	16.5	16.5	3.6																
Cyclohexane	155-165						2.1	1.5		1.0											
Ethylene glycol	155	2.6																			
Tetrahydrofuran	155										22.3	24.1	1.0								
1-Butanol	160											1.1	1.3								
n-Hexane	160								3.5		4.4										
1,1,1-Trichloroethane	165	6.8	23.9																		
Carbon tetrachloride	165																				
Benzene	165												1.2	3.6	1.4	3.2	16.8	100.0	6.6		
Methyl isopropyl ketone	165										3.1										
Trichloroethylene	165-170	11.3			4.1	3.8	1.1														
1,4-Dioxane	165-170																				
Methyl n-butyrate	175										49.4	2.0		60.3	1.9						
Furfuryl alcohol*	200					1.9	1.8	4.0	33.8	34.4	3.8								1.5	1.4	65.7
Toluene	205	3.1	7.9	1.7	13.2	1.2											1.0				
Chlorobenzene	200-210	1.2	1.0										2.8	5.5	5.8	4.1	60.4	4.0			
Butyl acetate	210										1.0		11.0								
O-Xylene	210	2.0	5.5	1.1	7.2	1.0								2.0	1.0	1.0	13.9	5.1	6.0		
m-Xylene	210	1.9	5.2	1.1	7.1									1.1	1.0		13.2	5.3	5.5		
Benzaldehyde	230													8.8			100.0	18.0			

*Spectra from literature

TABLE 3-5 (Continued)

	°C Temp.	m/e 82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101
Acetone	110																				
Freon-11	110	4.5		2.9																	100.0
Methylene chloride	120		1.2	49.0	1.3	30.4		4.4													
2-Propanol	120																				
Allyl alcohol	120																				
1-Propanol	120																				
Ethyl formate	120																				
Carbon disulfide	120																				
Diethyl ether	125																				
Methyl acetate	125																				
Methyl ethyl ketone	135																				
Butyraldehyde*	145																				
2-Methoxyethanol*	145																				
Chloroform	150	3.0	100.0	3.0	62.3		10.5														
Propyl mercaptan	150																				
Ethyl acetate	150-160							2.6													
Ethylene dichloride	150-160																	7.9		4.8	
Cyclohexane	155-165		3.3	58.9	3.5																
Ethylene glycol	155																				
Tetrahydrofuran	155																				
1-Butanol	160																				
n-Hexane	160			1.2		12.3															
1, 1, 1-Trichloroethane	165	2.2	1.4					3.3							2.6		100.0	1.6	64.5		9.1
Carbon tetrachloride	165	30.3		16.8		2.8															
Benzene	165																				
Methyl isopropyl ketone	165					9.4															
Trichloroethylene	165-170	1.6	1.3	1.0										5.0	100.0	4.0	63.5	1.2	8.9		
1, 4-Dioxane	165-170						1.5	24.2													
Methyl n-butyrate	175						12.6														
Furfuryl alcohol*	200	13.5													7.9	3.3	55.1	100.0	5.8		
Toluene	205								3.2	1.3	100.0	69.6	4.9								
Chlorobenzene	200-210				1.1	1.1															
Butyl acetate	210																				
O-Xylene	210																				
m-Xylene	210																				
Benzaldehyde	230																				

*Spectra from literature

TABLE 3-5 (Continued)

	°C Temp.	m/e 103	104	105	106	107	112	113	114	117	118	119	120	121	123	130	132	134	136
Acetone	110																		
Freon-11	110	62.4		9.2															
Methylene chloride	120																		
2-Propanol	120																		
Allyl alcohol	120																		
1-Propanol	120																		
Ethyl formate	120																		
Carbon disulfide	120																		
Diethyl ether	125																		
Methyl acetate	125																		
Methyl ethyl ketone	135																		
Butyraldehyde*	145																		
2-Methoxyethanol*	145																		
Chloroform	150										1.3		1.3						
Propyl mercaptan	150																		
Ethyl acetate	150-160																		
Ethylene dichloride	150-160																		
Cyclohexane	155-165																		
Ethylene glycol	155																		
Tetrahydrofuran	155																		
1-Butanol	160																		
n-Hexane	160																		
1, 1, 1-Trichloroethane	165									22.9		21.7		6.0					
Carbon tetrachloride	165									100.0		100.0		33.8	2.3				
Benzene	165																		
Methyl isopropyl ketone	165															89.4	86.8	27.1	2.5
Trichloroethylene	165-170																		
1, 4-Dioxane	165-170																		
Methyl n-butyrate	175																		
Furfuryl alcohol*	200																		
Toluene	205																		
Chlorobenzene	200-210						100.0	1.1	29.9										
Butyl acetate	210																		
O-Xylene	210	4.3	1.3	21.4	50.6	2.4													
m-Xylene	210	3.9	1.0	18.7	35.3	2.2													
Benzaldehyde	230			91.5	95.0														

*Spectra from literature

Intuitively, one would expect that compounds which are sorbed with very high heats of sorption would have high temperatures for desorption, but ideally to obtain narrow desorption peaks, it would be desirable to have contaminants which desorb at about 100°C with an energy of 80 kcal/mole. Such desorption characteristics could only be expected for rather selective sorption processes, and considering the broad range of types of compounds which are of interest in this program, it does not appear feasible to investigate such selective sorbents for each type of compound. There are, of course, other techniques which could be studied as a means of obtaining better separation of components during the desorption processes, if this is required.

One alternative, which appears attractive is to use low voltage ionization as a means of simplifying the mass spectral patterns. Some measure of the simplification which can be obtained is shown in Table 3-6. This table shows the mass spectra obtained at approximately 16 ev with the cycloidal focusing instrument. The reduction in the number of fragment ions is apparent on inspection. Of the 31 compounds on this table for which mass spectral data are available, 17 can be determined from single mass number measurements. In contrast with the high voltage data, only 9 of the compounds can be associated with a single mass number. A comparison for the components tested on charcoal is shown in Table 3-7.

These spectra do not represent the optimum which can be achieved by the low voltage technique. The limitations of the instrument do not permit spectra to be obtained at lower ionization energies. However, if the energy of the ionizing electrons is reduced to values nearer the ionization potential, even greater simplification could be achieved.

The major disadvantage to low voltage ionization is the loss of sensitivity due to the decreased ionization efficiency. At the low energy employed in obtaining the spectra presented in this report, the sensitivity is decreased on the average by a factor of ten. Those compounds which have the highest ionization potentials show the greatest loss of sensitivity, and it can be expected that if still lower electron energies are used, the sensitivity may decrease by two orders of magnitude, for some compounds. This loss in sensitivity can be partially overcome by changing the design of the system, and increasing the sample size so that higher pressures are obtained in the ion source during the desorption process. In the present system, at the lower contaminant concentrations, pressures in the ion source are estimated to be in the range of 10^{-6} torr. The source pressure can be increased to 10^{-4} torr without seriously degrading the performance of the instrument at low voltage so that the loss of efficiency can be, to some extent, overcome.

The optimum operating conditions for analysis of contaminants on-board a spacecraft must, to a certain extent, be determined by the actual contamination problem encountered. At present, it is assumed that there may be a general, very low background level concentration of many contaminants in the spacecraft at all times. Contaminants of interest for analysis are those which exceed this background level by one or two orders of magnitude, perhaps in the range of 0.5 to 1.0 ppm concentration. It is expected that (depending on environmental factors) this will occur for only a few contaminants at any particular

TABLE 3-6
Low Voltage Spectra

	°C Temp.	m/e 26	27	28	29	30	31	32	33	35	36	38	39	40	41	42	43	44	45	46
Acetone	110		1.0	2.7	3.8											1.0	100.0	3.0	1.0	
Freon-11	110																			
Methylene chloride	120																			
2-Propanol	120		6.2		2.6												4.2	4.4	100.0	2.2
Allyl alcohol	120	1.2	5.3	46.1	63.6	90.1	24.6	4.5					2.6	12.7	2.4	1.3	3.3			
1-Propanol	120			2.0	2.6		100.0	2.0								9.1				
Ethyl formate	120		4.0	100.0	17.5	1.9	46.6												6.0	
Carbon disulfide	120							1.6												
Diethyl ether	125		0.9	2.5	22.1		100.0								2.3				6.4	
Methyl acetate	125			2.3	1.2		4.5	1.5								2.0	100.0	2.2		
Methyl ethyl ketone	135		3.5	1.2	48.2											1.0	100.0	2.9		
Butyraldehyde	145																			
2-Methoxyethanol	145																			
Chloroform	150										4.7	1.8			1.3					
Propyl mercaptan*	150		29.0	5.0	5.0			1.0		3.0			1.0	6.0	34.0	66.0	100.0	3.3	1.0	12.4
Ethyl acetate	155		2.0	17.6	60.2	1.0										2.3	100.0	2.7	51.0	1.1
Ethylene dichloride	155		100.0																	
Cyclohexane	160		1.7	8.5	2.7										10.5	41.0	20.3			
Ethylene glycol	155																			
Tetrahydrofuran	155		6.4	2.0	2.6		3.4							1.3	7.5	100.0	11.7	1.8		
1-Butanol	160		12.7	16.6	11.3	1.0	100.0	1.6	16.0					1.1	27.3	26.3	40.5	4.5	1.8	
n-Hexane	160		3.5	3.0	43.6										20.2	66.5	77.0	1.9		
1, 1, 1-Trichloroethane	165																			
Carbon tetrachloride	165																			
Benzene	165																			
Methyl isopropyl ketone	165		5.0	5.7	1.0										2.0	2.0	100.0	2.8	1.0	
Trichloroethylene	170		1.1								2.2					3.6	1.8	1.3		
1, 4-Dioxane	170			100.0	16.1	22.5	28.1										1.0	4.4	3.3	
Methyl n-butyrate	175		7.7	6.8	10.0		5.9	4.6	5.7						1.7	7.8	90.7	2.4		
Furfuryl alcohol	200																			
Toluene	205																			
Chlorobenzene	205																			
Butyl acetate	210			5.5	4.4		14.2	1.2	2.4						7.1	3.3	85.1	1.9		
o-Xylene	210																			
m-Xylene	210																			
Benzaldehyde	230																			

*Spectra from literature

TABLE 3-6 (Continued)

	°C Temp.	m/e 47	48	49	50	51	54	55	56	57	58	59	60	61	62	63	64	66	68	69
Acetone	110										80.0	2.5								
Freon-11	110																			
Methylene chloride	120		2.3	100.0	1.1	28.1														
2-Propanol	120											1.4								
Allyl alcohol	120									100.0	50.6	0.3								
1-Propanol	120											4.1	3.5							
Ethyl formate	120	2.4																		
Carbon disulfide	120																			
Diethyl ether	125											22.9								
Methyl acetate	125											2.3								
Methyl ethyl ketone	135									12.7										
Butyraldehyde	145																			
2-Methoxyethanol	145																			
Chloroform	150																			
Propyl mercaptan*	150	43.4	6.3	1.7										4.9				2.2		
Ethyl acetate	155												1.5	34.0						
Ethylene dichloride	155			3.5											16.8	3.8	4.3			
Cyclohexane	160						2.3	13.9	100.0	4.0									1.5	18.6
Ethylene glycol	155																			
Tetrahydrofuran	155																			
1-Butanol	160							4.2	82.5	4.1										
n-Hexane	160							1.3	71.5	100.0	4.3									2.3
1,1,1-Trichloroethane	165																			
Carbon tetrachloride	165																			
Benzene	165																			
Methyl isopropyl ketone	165																			
Trichloroethylene	170																			
1,4-Dioxane	170									2.2	21.4									
Methyl n-butyrate	175											2.9								
Furfuryl alcohol	200																			
Toluene	205																			
Chlorobenzene	205																			
Butyl acetate	210							3.2	100.0	4.7	2.2			21.3						
o-Xylene	210																			
m-Xylene	210																			
Benzaldehyde	230																			

*Spectra from literature

TABLE 3-6 (Continued)

	°C Temp.	m/e 70	71	72	73	74	75	76	77	78	79	83	84	85	86	87	88	89	91
Acetone	110																		
Freon-11	110			11.3															
Methylene chloride	120												11.5		7.0		1.6		
2-Propanol	120																		
Allyl alcohol	120																		
1-Propanol	120																		
Ethyl formate	120					1.5													
Carbon disulfide	120							100.0	2.4	8.5									
Diethyl ether	125				1.1	17.3													
Methyl acetate	125					11.3	1.0												
Methyl ethyl ketone	135			32.6	1.3														
Butyraldehyde	145																		
2-Methoxyethanol	145																		
Chloroform	150											100.0		65.9		9.4			
Propyl mercaptan*	150					1.3	1.0	75.0	2.8	3.2									
Ethyl acetate	155	14.2			4.1												4.3		
Ethylene dichloride	155																		
Cyclohexane	160	0.9										0.9	70.0	3.7					
Ethylene glycol	155																		
Tetrahydrofuran	155		15.3	32.1	1.2														
1-Butanol	160			0.8															
n-Hexane	160		3.7												8.6				
1, 1, 1-Trichloroethane	165																		
Carbon tetrachloride	165																		
Benzene	165									100.0	6.1								
Methyl isopropyl ketone	165			7.2											13.2				
Trichloroethylene	170																		
1, 4-Dioxane	170																33.3	0.9	
Methyl n-butyrate	175		46.7	1.5		100.0	3.5									4.4			
Furfuryl alcohol	200																		
Toluene	205																		
Chlorobenzene	205									1.5									
Butyl acetate	210		0.9		6.7											1.0			
o-Xylene	210																		2.3
m-Xylene	210																		
Benzaldehyde	230																		

*Spectra from literature

TABLE 3-6 (Continued)

	°C Temp.	m/e 92	93	95	97	101	102	103	105	106	107	112	114	118	120	130	132	134	136
Acetone	110																		
Freon-11	110					100.0		50.0	11.2										
Methylene chloride	120																		
2-Propanol	120																		
Allyl alcohol	120																		
1-Propanol	120																		
Ethyl formate	120																		
Carbon disulfide	120																		
Diethyl ether	125																		
Methyl acetate	125																		
Methyl ethyl ketone	135																		
Butyraldehyde	145																		
2-Methoxyethanol	145																		
Chloroform	150													1.6	1.6				
Propyl mercaptan*	150																		
Ethyl acetate	155																		
Ethylene dichloride	155																		
Cyclohexane	160																		
Ethylene glycol	155																		
Tetrahydrofuran	155																		
1-Butanol	160																		
n-Hexane	160																		
1, 1, 1-Trichloroethane	165																		
Carbon tetrachloride	165																		
Benzene	165																		
Methyl isopropyl ketone	165																		
Trichloroethylene	170			4.9	3.0											100.0	91.6	27.9	2.1
1, 4-Dioxane	170																		
Methyl n-butyrate	175						2.0												
Furfuryl alcohol	200																		
Toluene	205	100.0	5.5																
Chlorobenzene	205											100.0	28.2						
Butyl acetate	210																		
o-Xylene	210									100.0	3.9								
m-Xylene	210	2.8								100.0	3.5								
Benzaldehyde	230																		

*Spectra from literature

TABLE 3-7

Comparison of Compounds Tested on Charcoal

70 eV

	°C	m/e 24	25	26	27	28	29	30	31	32	33	35	36
Vinyl chloride		2.3	11.1	29.4	100.0	1.8						2.9	
Acetaldehyde*	180	1.0	3.2	6.3	3.5	3.6	100.0	1.1					
Butene-1	190		1.2	9.2	26.5	30.4	13.8						
Isobutylene	190			4.4	18.2	22.8	11.7						
Methylene chloride	190											6.6	1.5
Acetonitrile**	202			0.2	0.1	0.3	0.1						
Methanol	200					6.5	45.7	6.0	100.0	70.2	1.0		
Chloropropane	230			6.7	55.2	29.6	52.9	1.2					1.4
Acetone	250		1.2	5.4	8.1	3.2	4.8						

*Old Data

**Spectra from literature

16 eV

		m/e 26	27	28	29	30	31	32	33	39	40	41
Vinyl chloride		8.1	100.0	2.2								
Acetaldehyde	180				56.5							
Butene-1	190		2.5	50.4	7.5					3.0	4.7	98.5
Isobutylene	190			26.0	4.5					2.0	4.3	57.8
Methylene chloride	190											
Acetonitrile	202											
Methanol	200				1.2	1.7	65.6	100.0	1.1			
Chloropropane	230		23.5	20.4	65.8	1.2						6.1
Acetone	250			1.5	2.1							

TABLE 3-7 (Continued)

70 eV

	°C	m/e 37	38	39	40	41	42	43	44	45	47	48	49
Vinyl chloride		1.0									2.5	1.1	
Acetaldehyde*	180					3.6	9.2	30.5	56.6	1.3			
Butene-1	190	1.9	3.5	31.4	5.7	100.0	3.4						1.1
Isobutylene	190	2.7	5.2	38.2	9.1	100.0	3.0						1.3
Methylene chloride	190	1.9				7.8	4.3				13.6	7.6	100.0
Acetonitrile**	202			18.0	54.0	100.0							
Methanol	200												
Chloropropane	230	3.4	4.1	13.6	3.0	27.0	100.0	37.7	1.6				4.3
Acetone	250	1.6	1.7	3.1		1.8	6.8	100.0	2.5				

*Old Data
**Spectra from literature

16 eV

		m/e 42	43	44	45	49	50	51	54	55	56	57	58
Vinyl chloride													
Acetaldehyde	180		17.3	63.4	1.3								
Butene-1	190	3.0							1.7	6.8	100.0	4.2	
Isobutylene	190	1.9								4.2	100.0	4.2	
Methylene chloride	190					100	1.1	28.0					
Acetonitrile	202												
Methanol	200												
Chloropropane	230	100.0	32.7	1.1									44.6
Acetone	250		55.8	1.7									

TAble 3-7 (Continued)

70 eV

	°C	m/e 50	51	53	54	55	56	57	58	59	60	61
Vinyl chloride										1.3	4.4	7.5
Acetaldehyde*	180											
Butene-1	190	4.4	3.5	5.0	1.8	17.4	36.5	1.5				
Isobutylene	190	4.6	3.3	4.7	1.5	16.5	41.4	1.6				
Methylene chloride	190	2.9	39.8									
Acetonitrile**	202											
Methanol	200											
Chloropropane	230		1.4									
Acetone	250								30.5	1.3		

*Old Data
**Spectra from literature

16 eV

		m/e 59	62	63	64	78	84	86	88
Vinyl chloride			60.0	1.0	18.1				
Acetaldehyde	180								
Butene-1	190								
Isobutylene	190								
Methylene chloride	190						11.5	7.0	1.6
Acetonitrile	202								
Methanol	200								
Chloropropane	230					1.2			
Acetone	250	1.4							

TABLE 3-7 (Continued)

70 eV

	°C	m/e 62	63	64	65	78	83	84	85	86	88
Vinyl chloride		94.7	3.9	29.4							
Acetaldehyde*	180										
Butene-1	190										
Isobutylene	190										
Methylene chloride	190						1.2	49.0	1.3	30.4	4.4
Acetonitrile**	202										
Methanol	200										
Chloropropane	230		7.2		2.2	4.8					
Acetone	250										

*Old Data
**Spectra from literature

16 eV

Vinyl chloride	
Acetaldehyde	180
Butene-1	190
Isobutylene	190
Methylene chloride	190
Acetonitrile	202
Methanol	200
Chloropropane	230
Acetone	250

time. If this situation is actually encountered, analysis under normal (70 volt) conditions should prove satisfactory. However, if it appears that many contaminants will be present simultaneously in a concentration range that represents a hazardous condition, use of simplification afforded by low voltage ionization will be required.

In summary, this analytical technique appears to be well suited for application to the analysis of contaminants in spacecraft atmospheres. The basic principles involved are simple, and the instrumentation required probably represents the minimum necessary for identification and quantitative determination of the anticipated variety of contaminants. The system has the capability for detecting unanticipated contaminants and can provide an estimate of this concentration. Development of a flight prototype mass spectrometer suitable for this application is already well under way. Design of a flight prototype contaminant sensor is the logical extension of this study program.

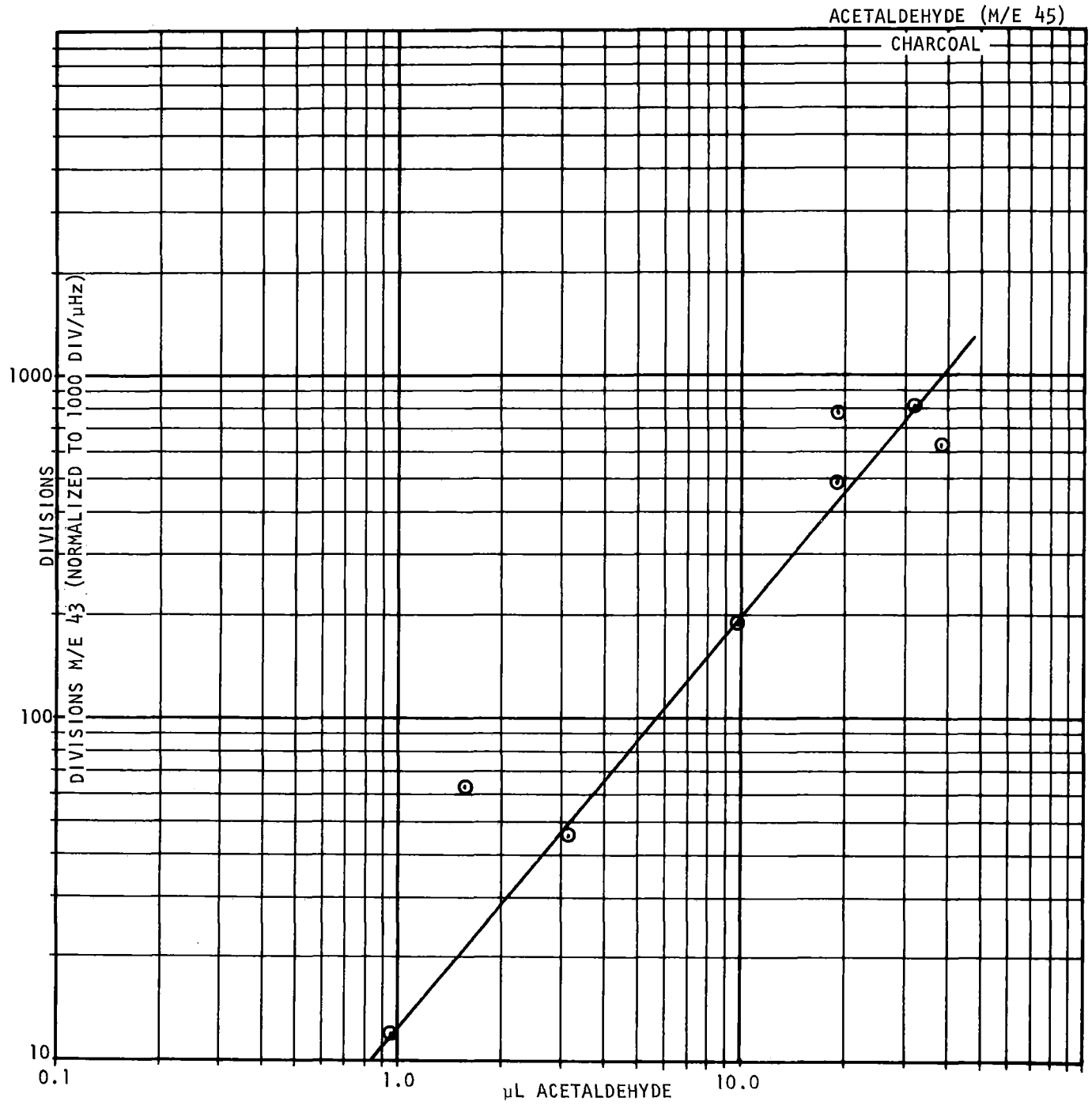

ACETALDEHYDE (M/E 45)
CHARCOAL
DIVISIONS
DIVISIONS M/E 43 (NORMALIZED TO 1000 DIV/μHz)
1000
100
10
0.1
1.0
10.0
μL ACETALDEHYDE

FIGURE 3-1

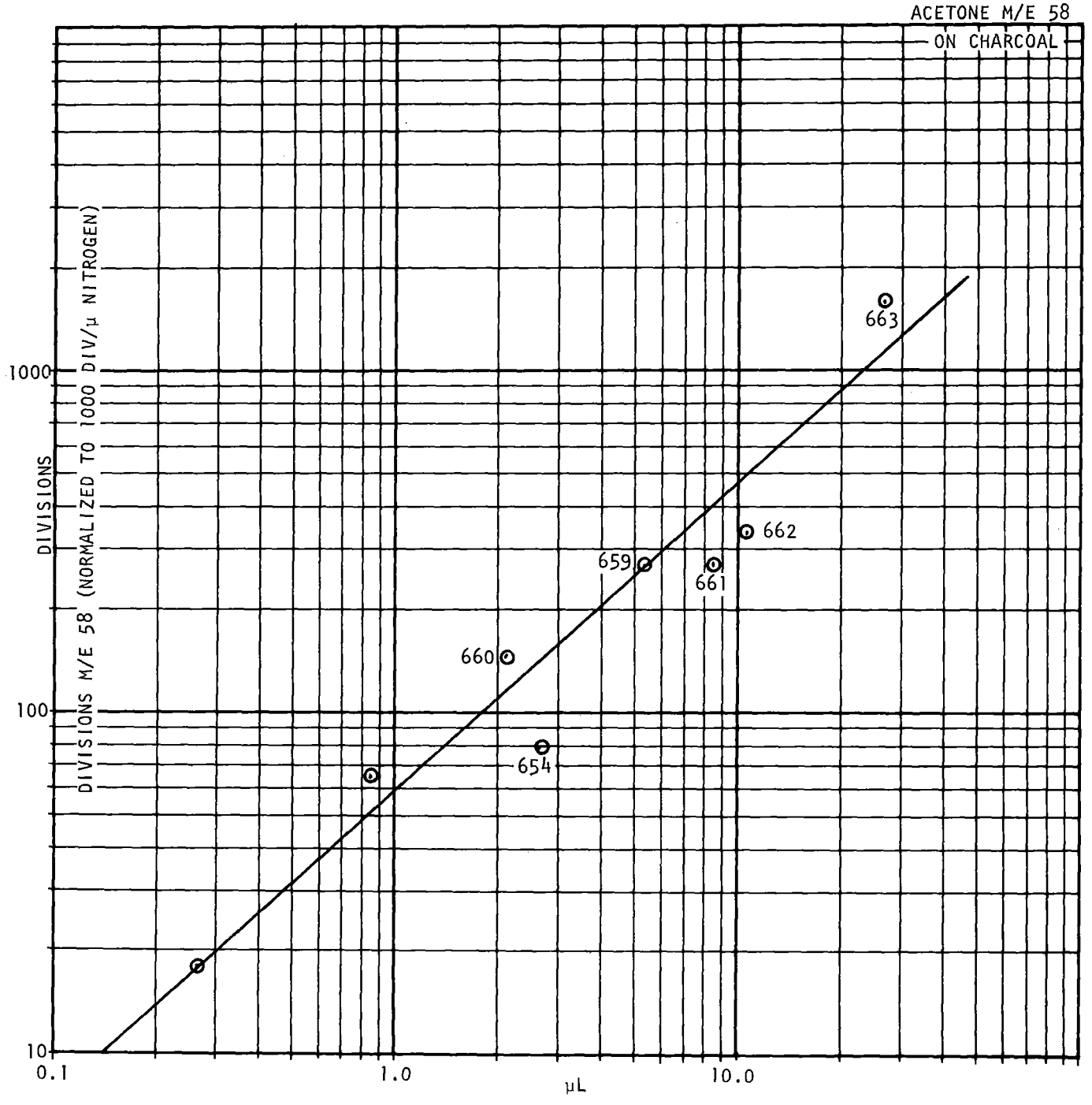

ACETONE M/E 58
ON CHARCOAL
DIVISIONS M/E 58 (NORMALIZED TO 1000 DIV/μ NITROGEN)
DIVISIONS
1000
100
10
0.1
1.0
10.0
μL
663
662
659
661
660
654

FIGURE 3-2

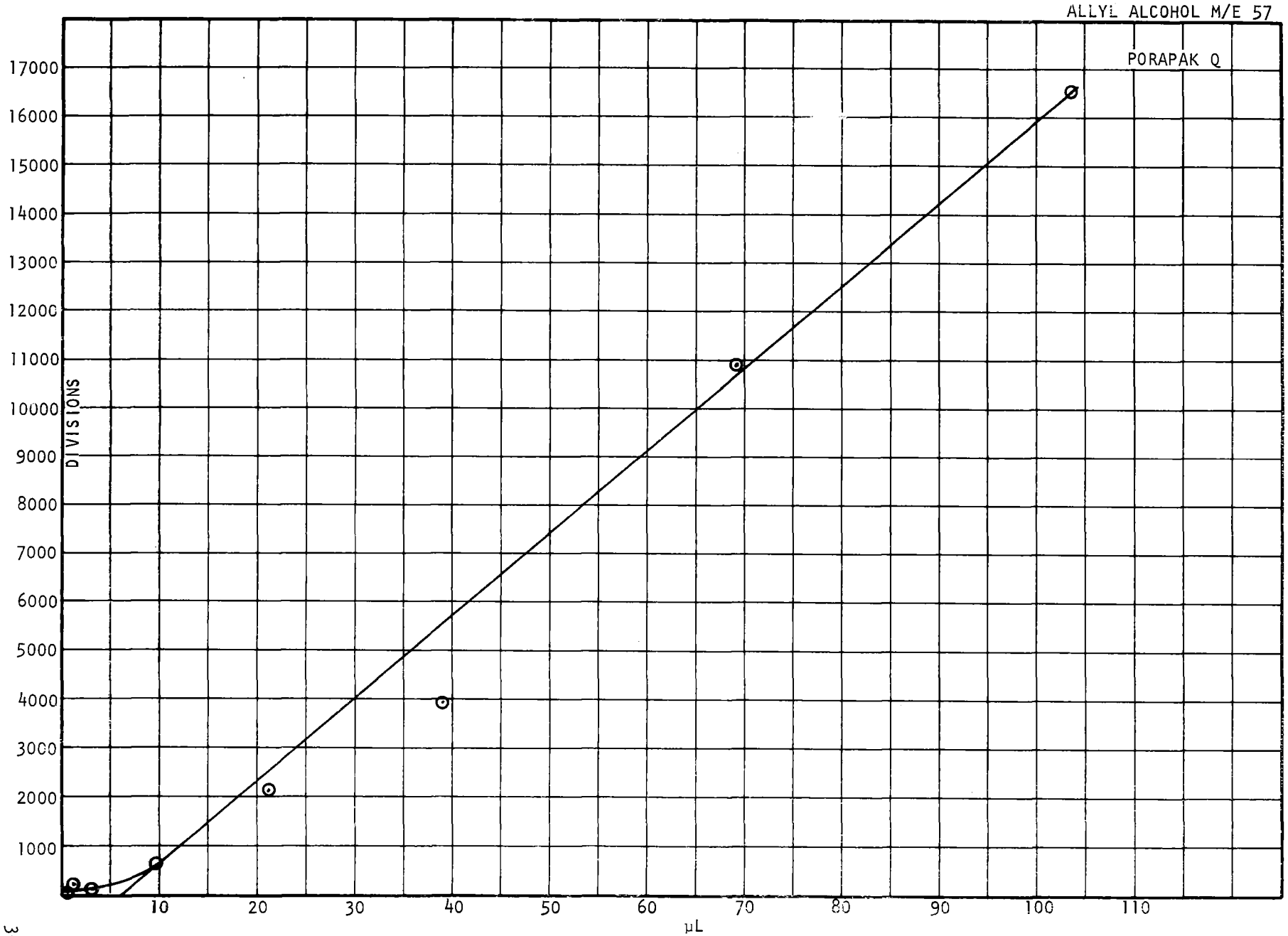

ALLYL ALCOHOL M/E 57
PORAPAK Q
DISINTEGRATIONS
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
10
20
30
40
50
60
70
80
90
100
110
µL

FIGURE 3-3

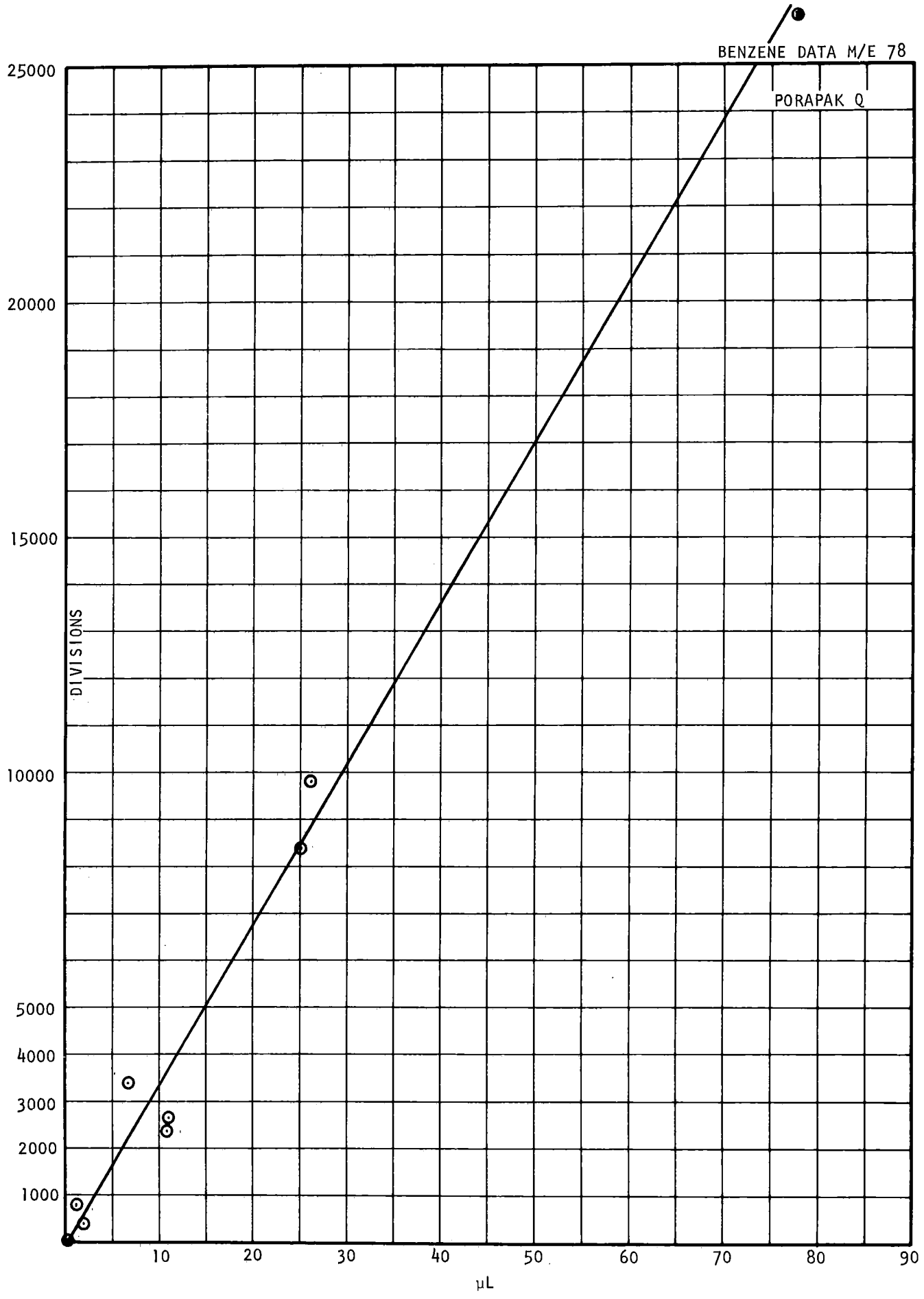

BENZENE DATA M/E 78
PORAPAK Q
25000
20000
15000
10000
5000
4000
3000
2000
1000
DIVISIONS
10
20
30
40
50
60
70
80
90
µL

FIGURE 3-4

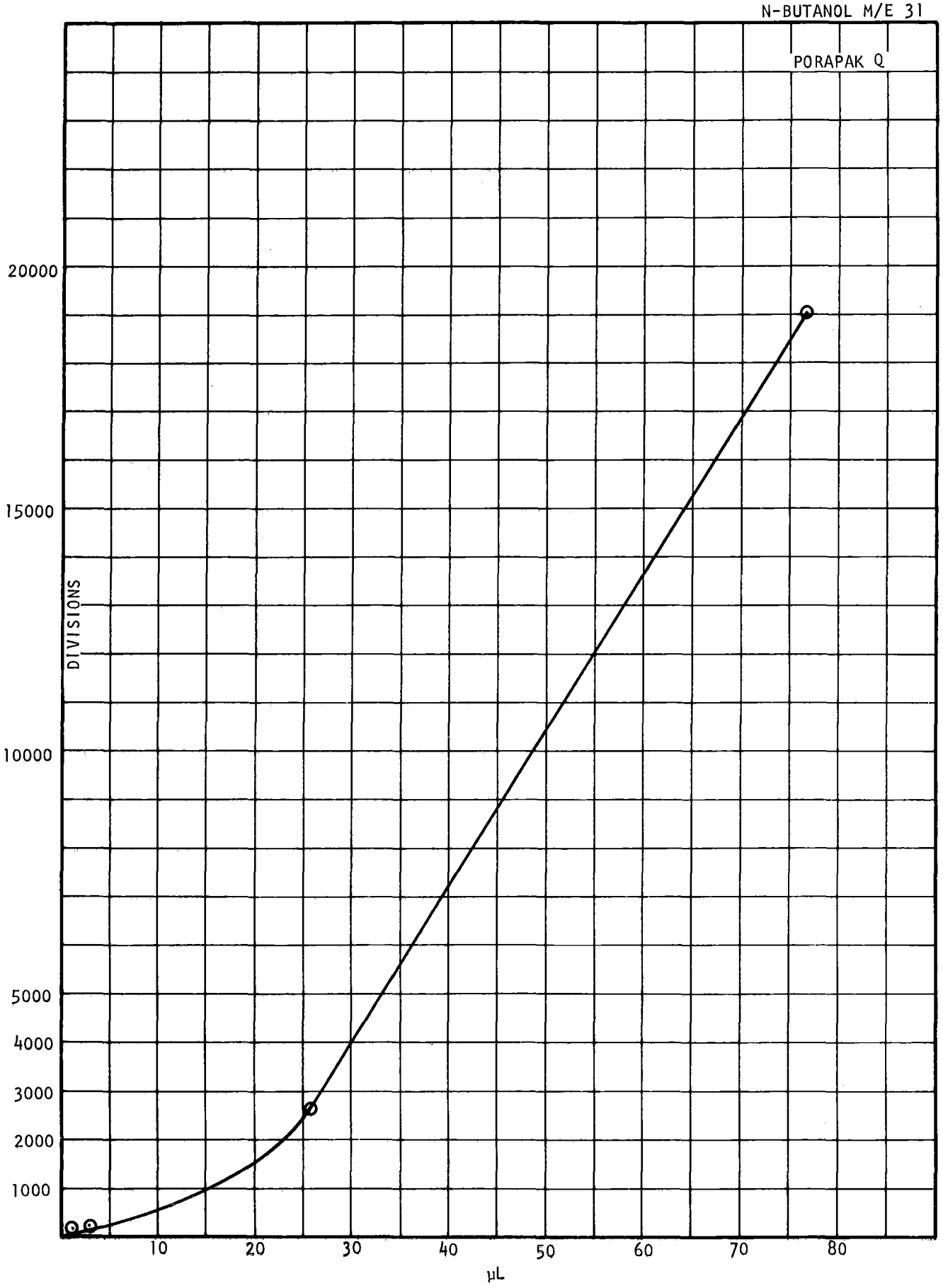

N-BUTANOL M/E 31
PORAPAK Q
20000
15000
10000
5000
4000
3000
2000
1000
DIVISIONS
10
20
30
40
50
60
70
80
µL

FIGURE 3-5

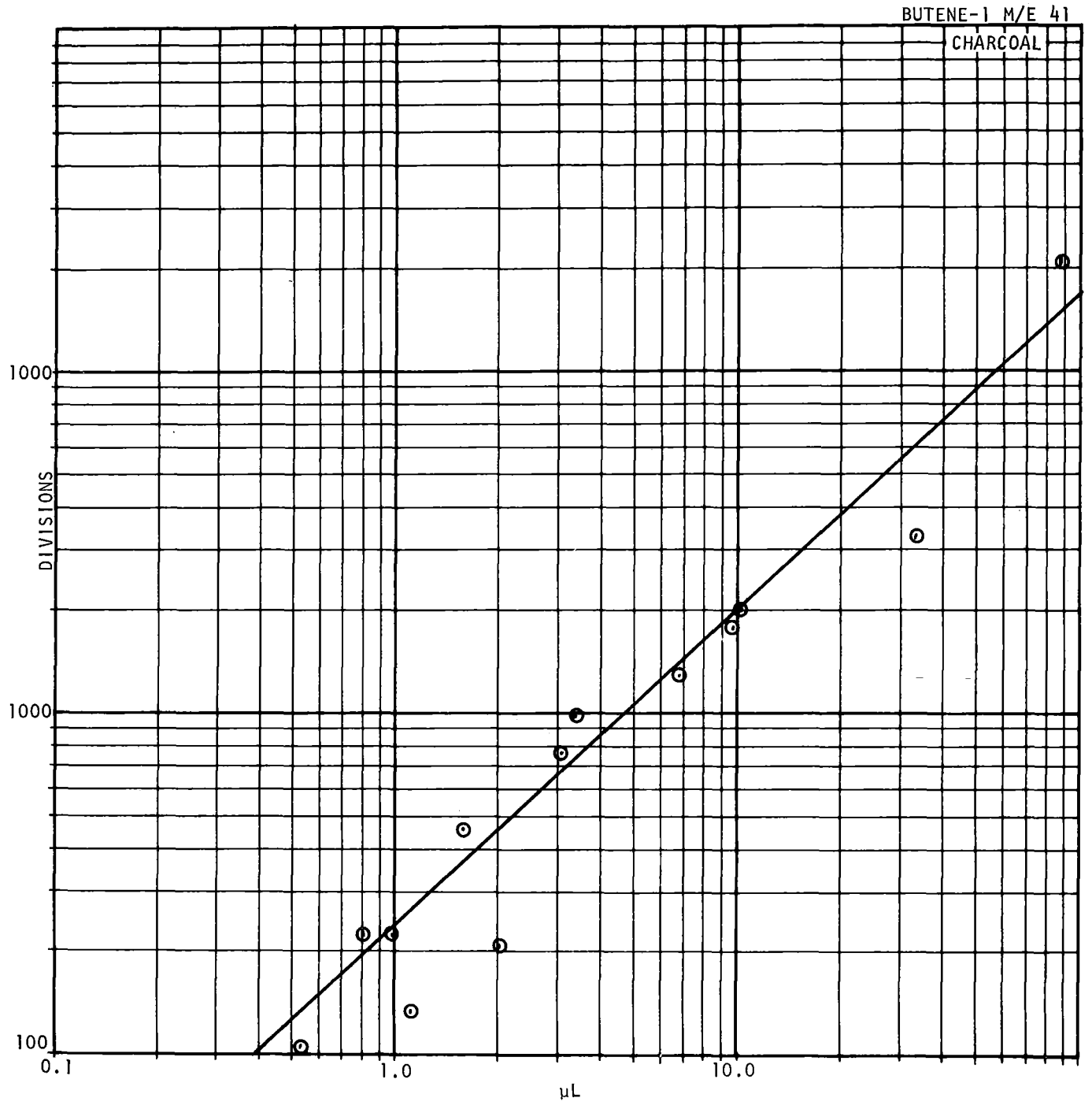


FIGURE 3-6

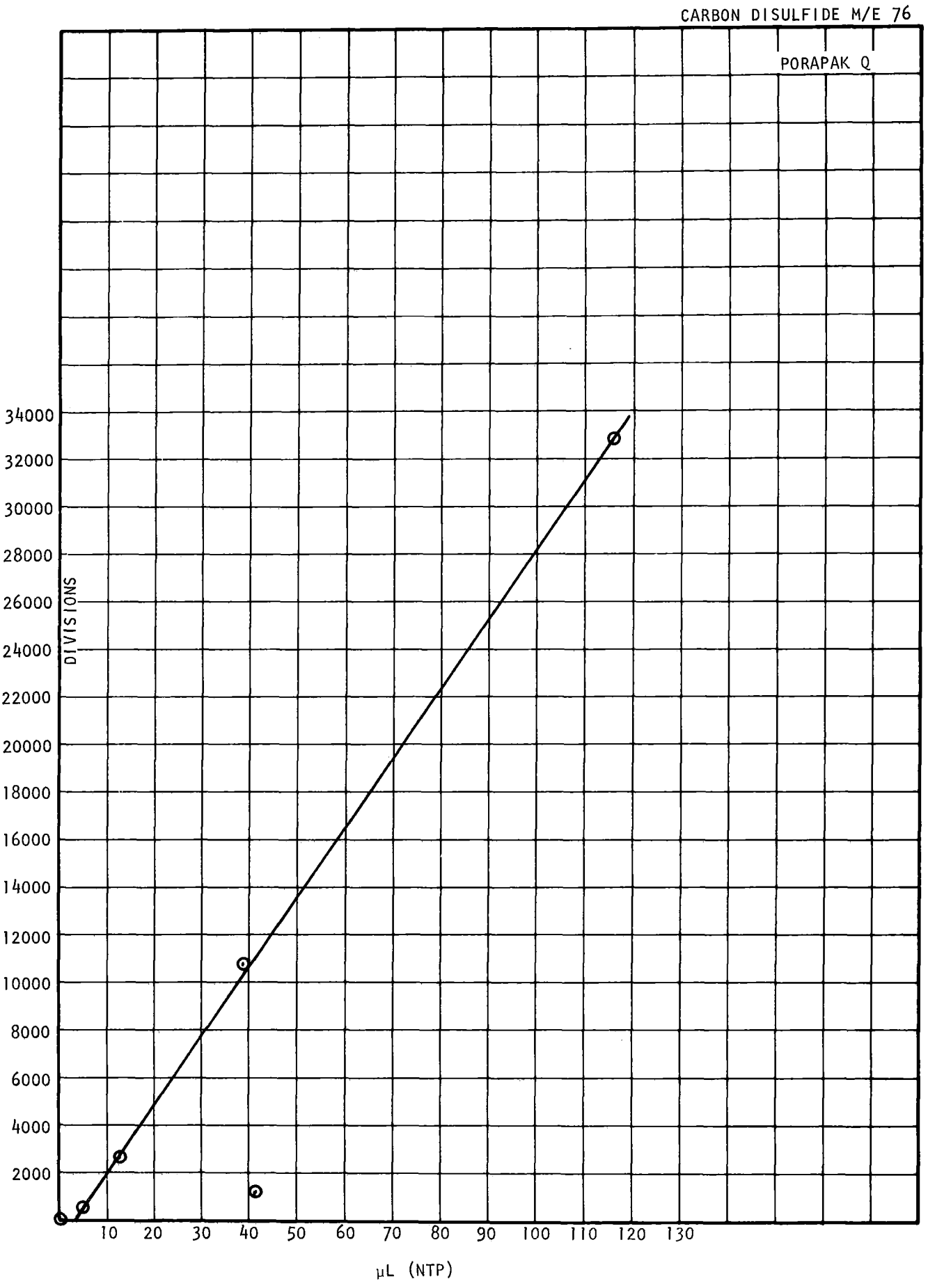

CARBON DISULFIDE M/E 76
PORAPAK Q
DIVISIONS
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
10
20
30
40
50
60
70
80
90
100
110
120
130
µL (NTP)

FIGURE 3-7

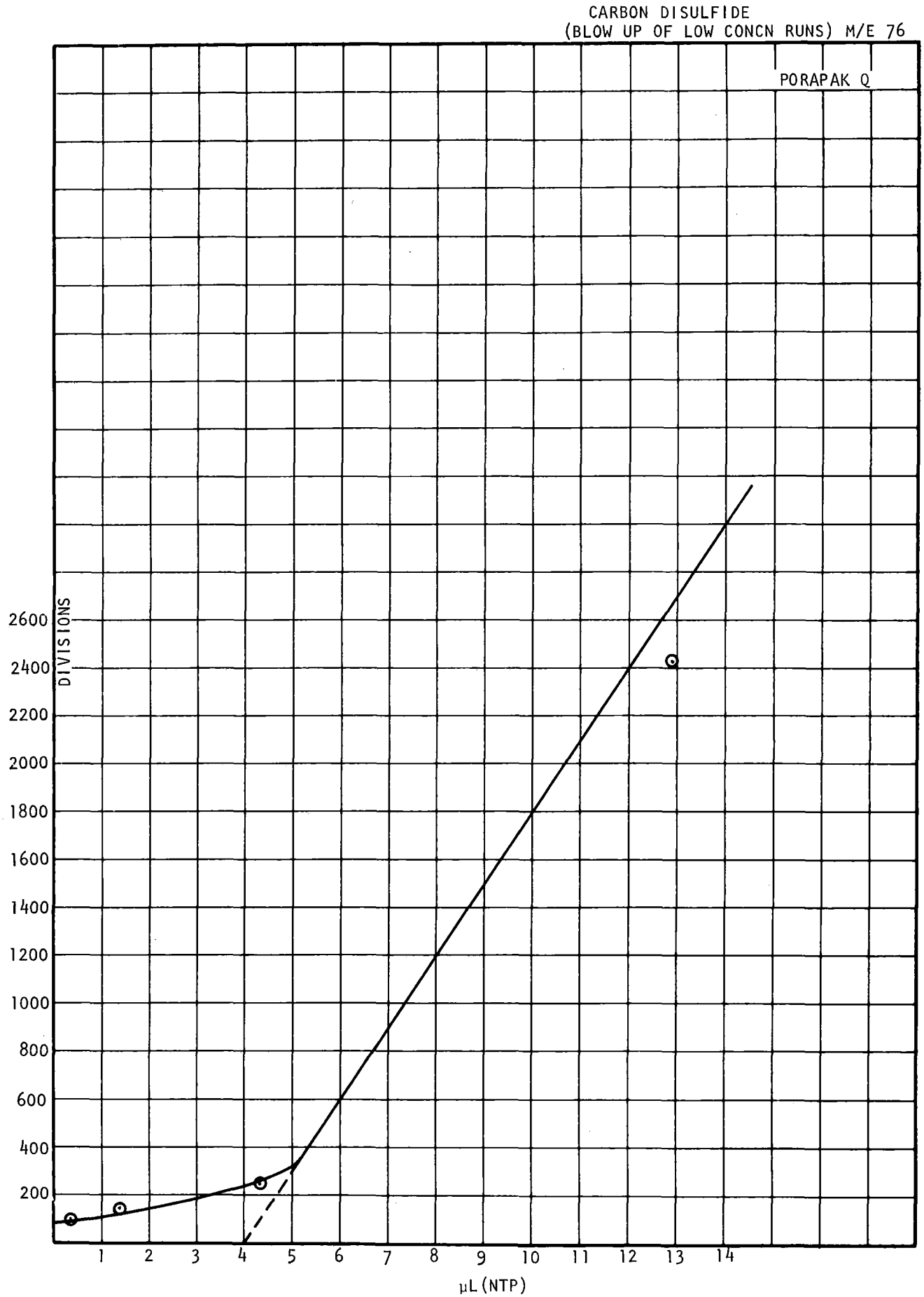

CARBON DISULFIDE
(BLOW UP OF LOW CONCN RUNS) M/E 76
PORAPAK Q
DIVISIONS
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
1
2
3
4
5
6
7
8
9
10
11
12
13
14
µL (NTP)

FIGURE 3-7A

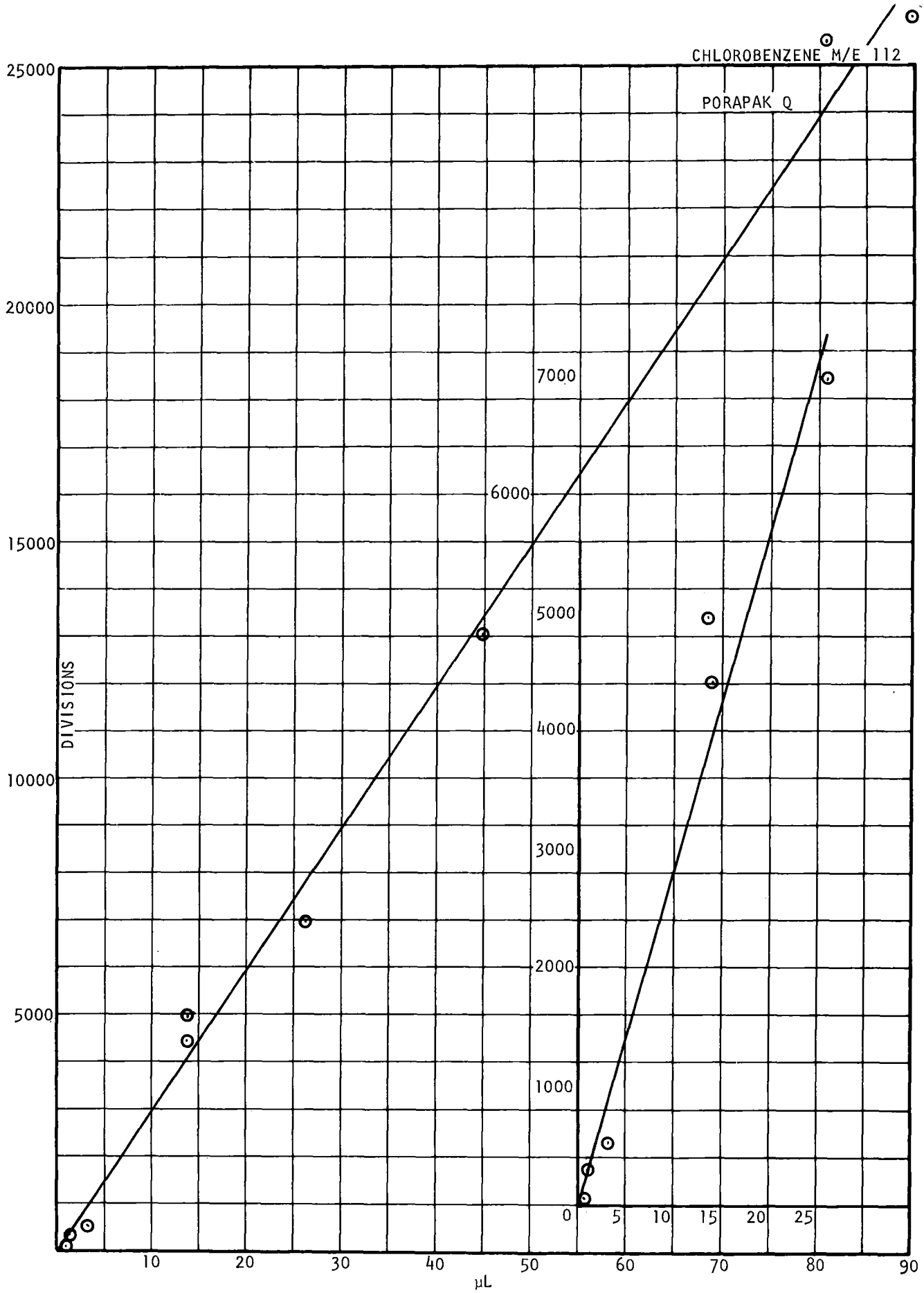

CHLOROBENZENE M/E 112
PORAPAK Q
DIVISIONS
25000
20000
15000
10000
5000
7000
6000
5000
4000
3000
2000
1000
0
5
10
15
20
25
10
20
30
40
50
60
70
80
90
µL

FIGURE 3-8

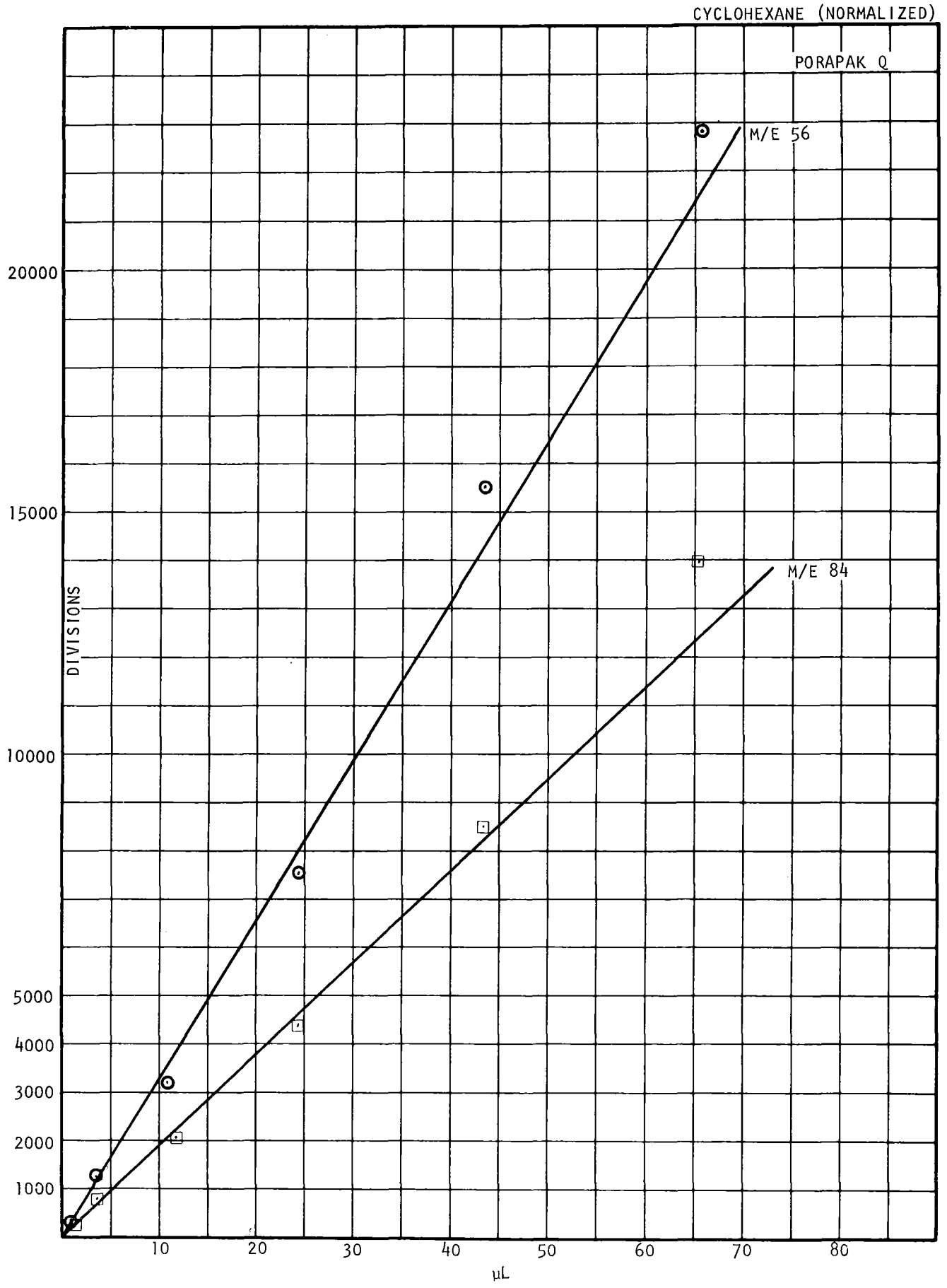

CYCLOHEXANE (NORMALIZED)
PORAPAK Q
M/E 56
M/E 84
DIVISIONS
20000
15000
10000
5000
4000
3000
2000
1000
10
20
30
40
50
60
70
80
µL

FIGURE 3-9

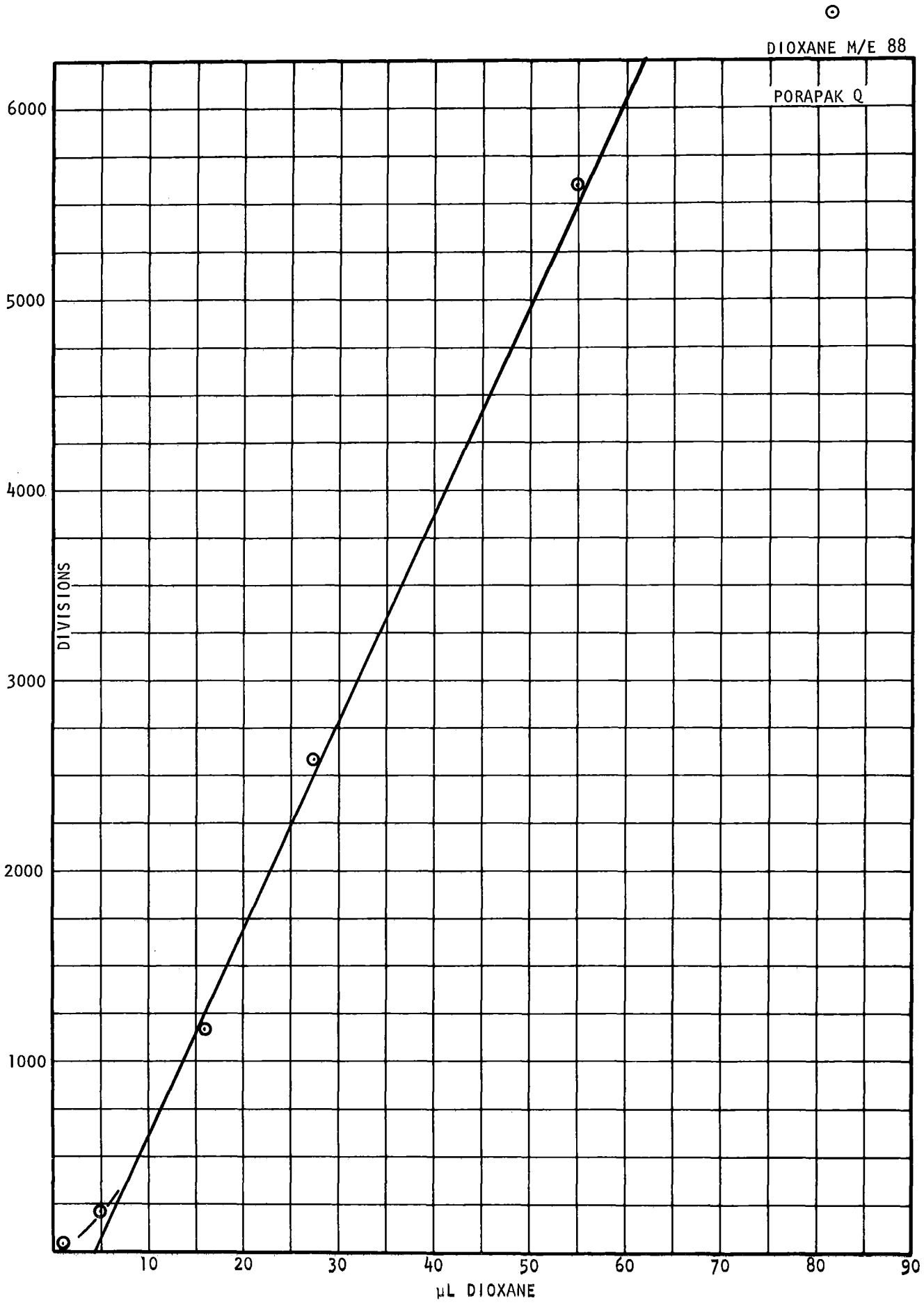

DIOXANE M/E 88
POROPAK Q
6000
5000
4000
3000
2000
1000
DIVISIONS
10
20
30
40
50
60
70
80
90
µL DIOXANE

FIGURE 3-10

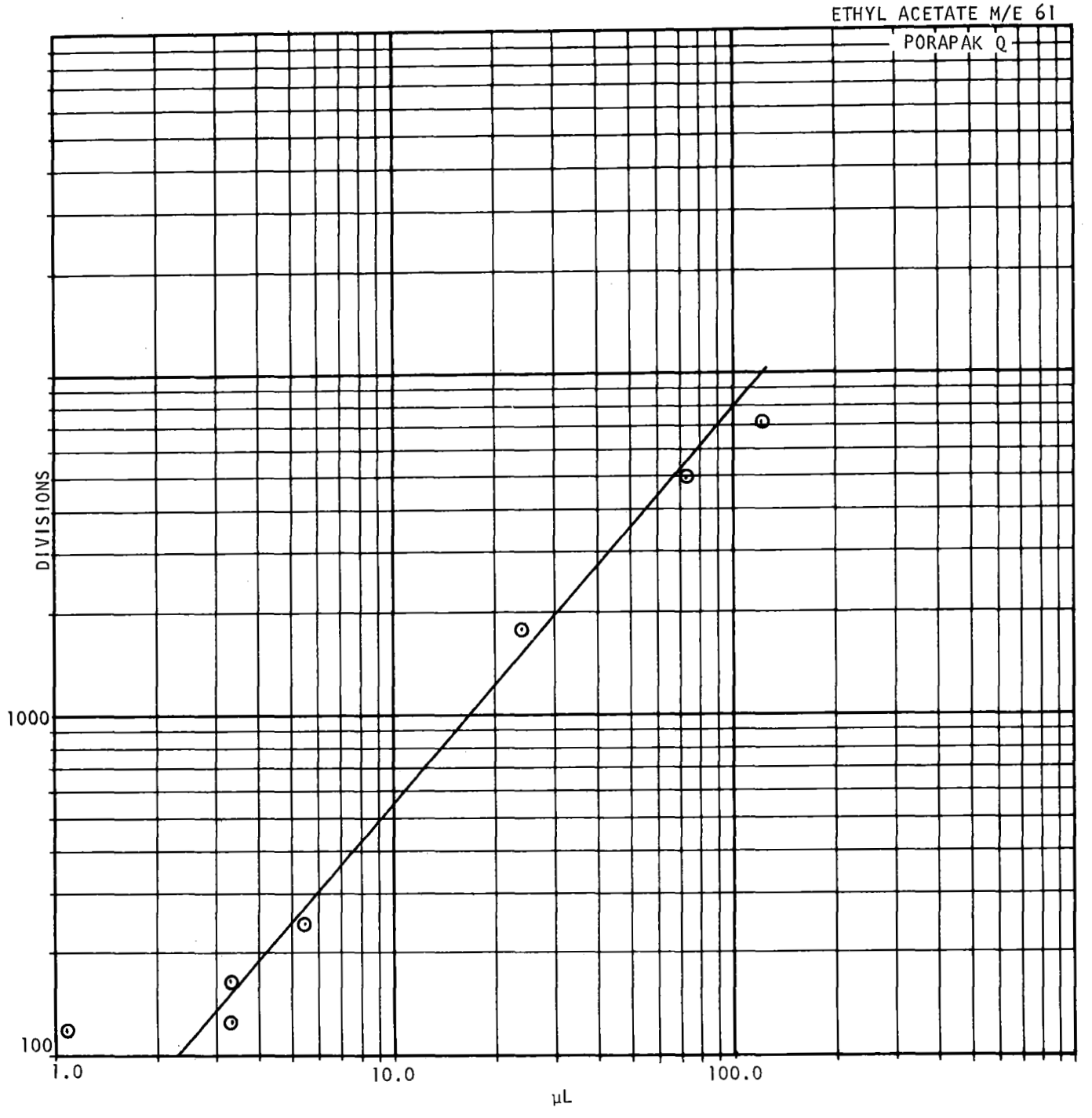

ETHYL ACETATE M/E 61
PORAPAK Q
DIVISIONS
1000
100
1.0
10.0
100.0
µL

FIGURE 3-11

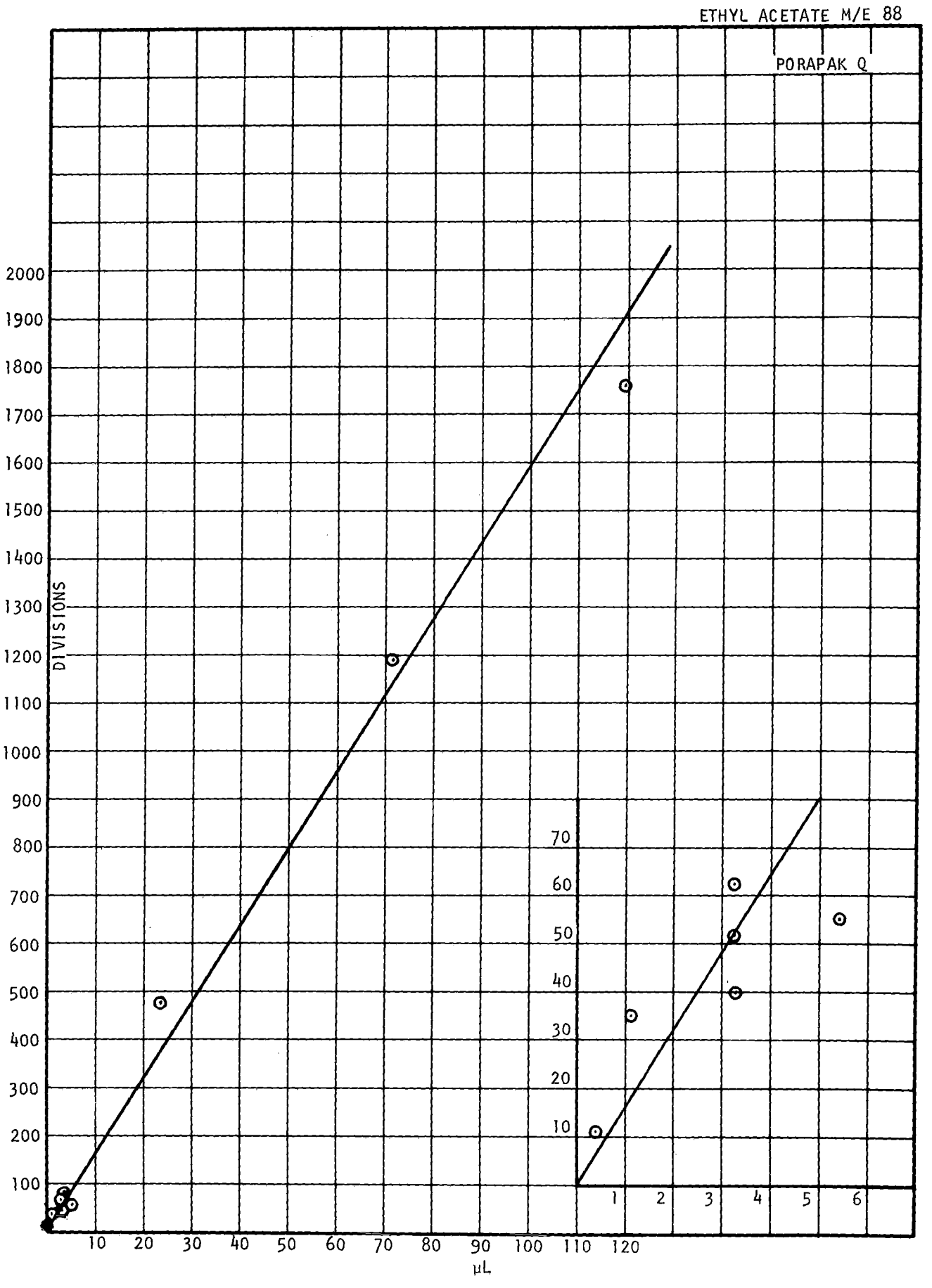

ETHYL ACETATE M/E 88
POROPAK Q
DIVISIONS
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
10 20 30 40 50 60 70 80 90 100 110 120
µL
70
60
50
40
30
20
10
1 2 3 4 5 6

FIGURE 3-11A

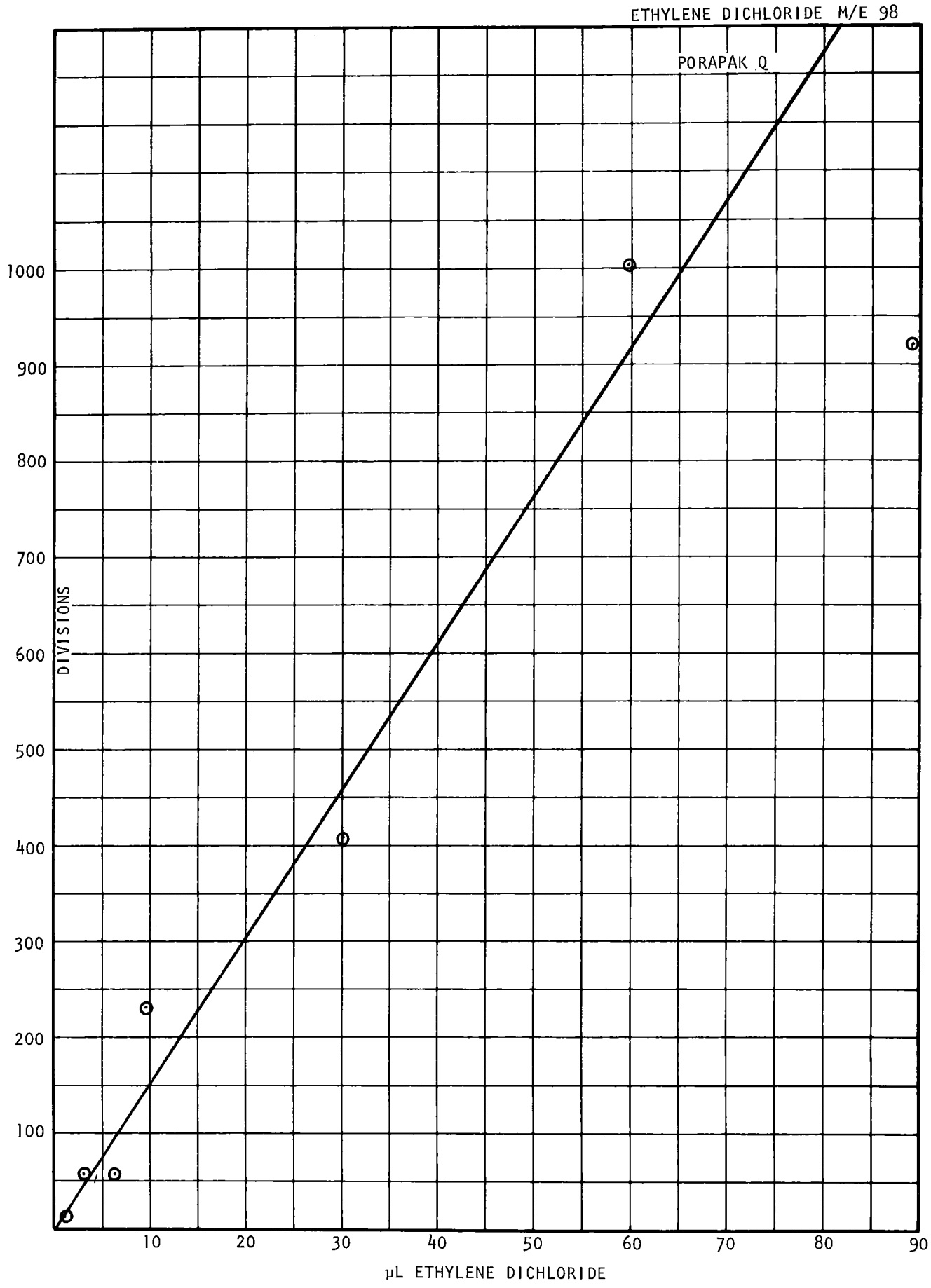

ETHYLENE DICHLORIDE M/E 98
PORAPAK Q
DIVISIONS
1000
900
800
700
600
500
400
300
200
100
10
20
30
40
50
60
70
80
90
µL ETHYLENE DICHLORIDE

FIGURE 3-12

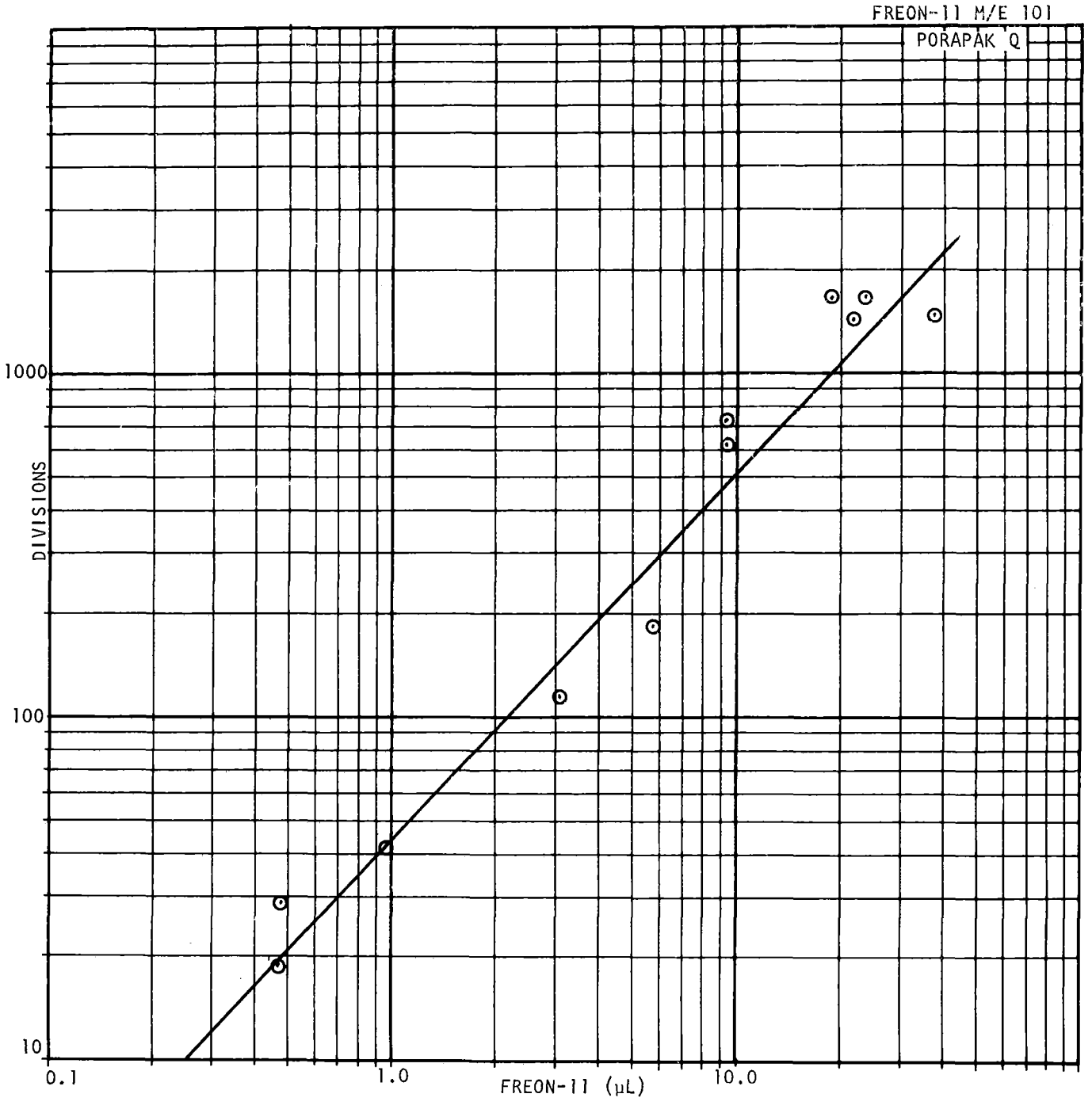

FREON-11 M/E 101
PORAPAK Q
1000
100
10
DIVISIONS
0.1
1.0
10.0
FREON-11 (µL)

FIGURE 3-13

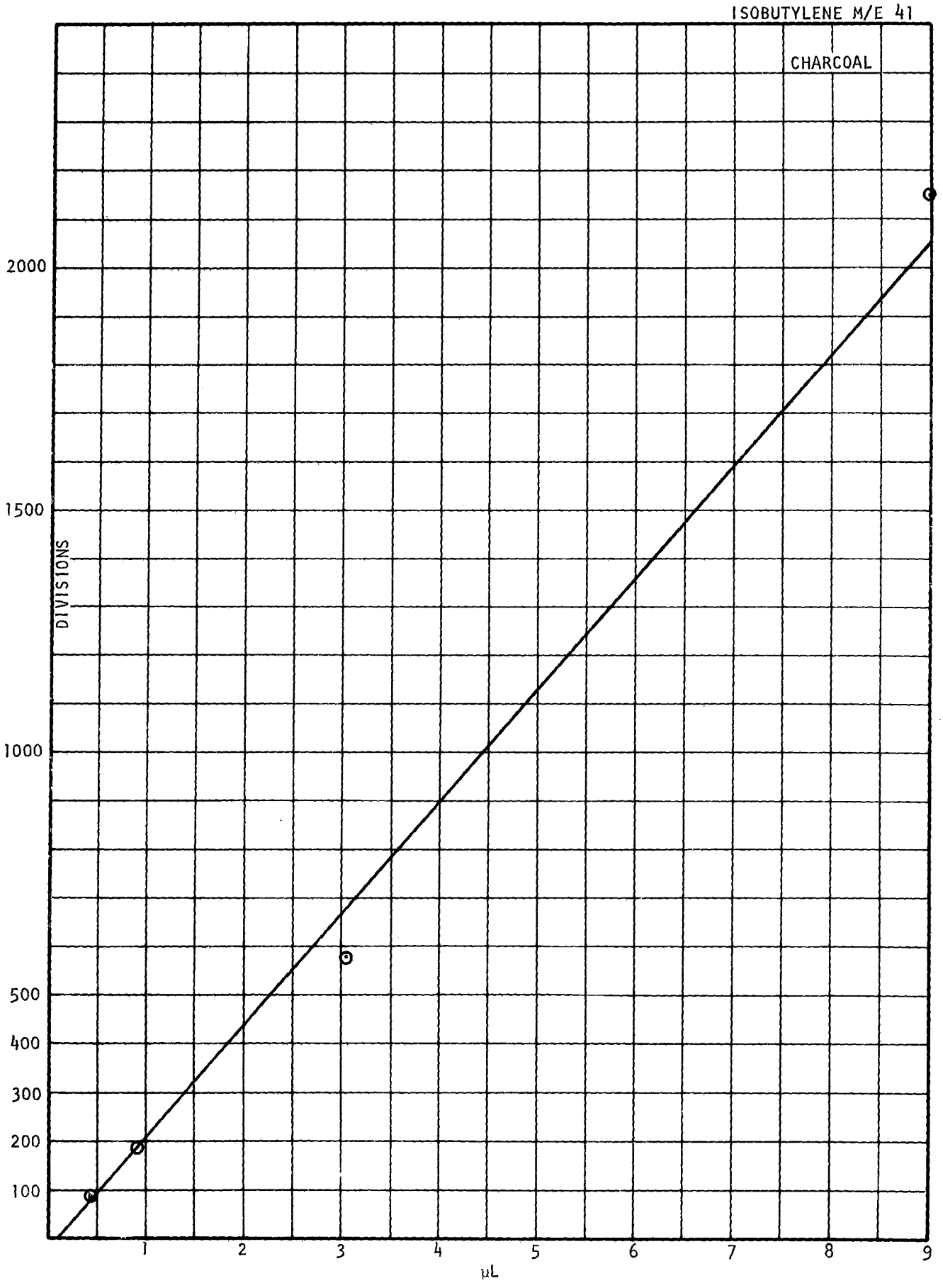

ISOBUTYLENE M/E 41
CHARCOAL
DIVISIONS
2000
1500
1000
500
400
300
200
100
1
2
3
4
5
6
7
8
9
µL

FIGURE 3-14

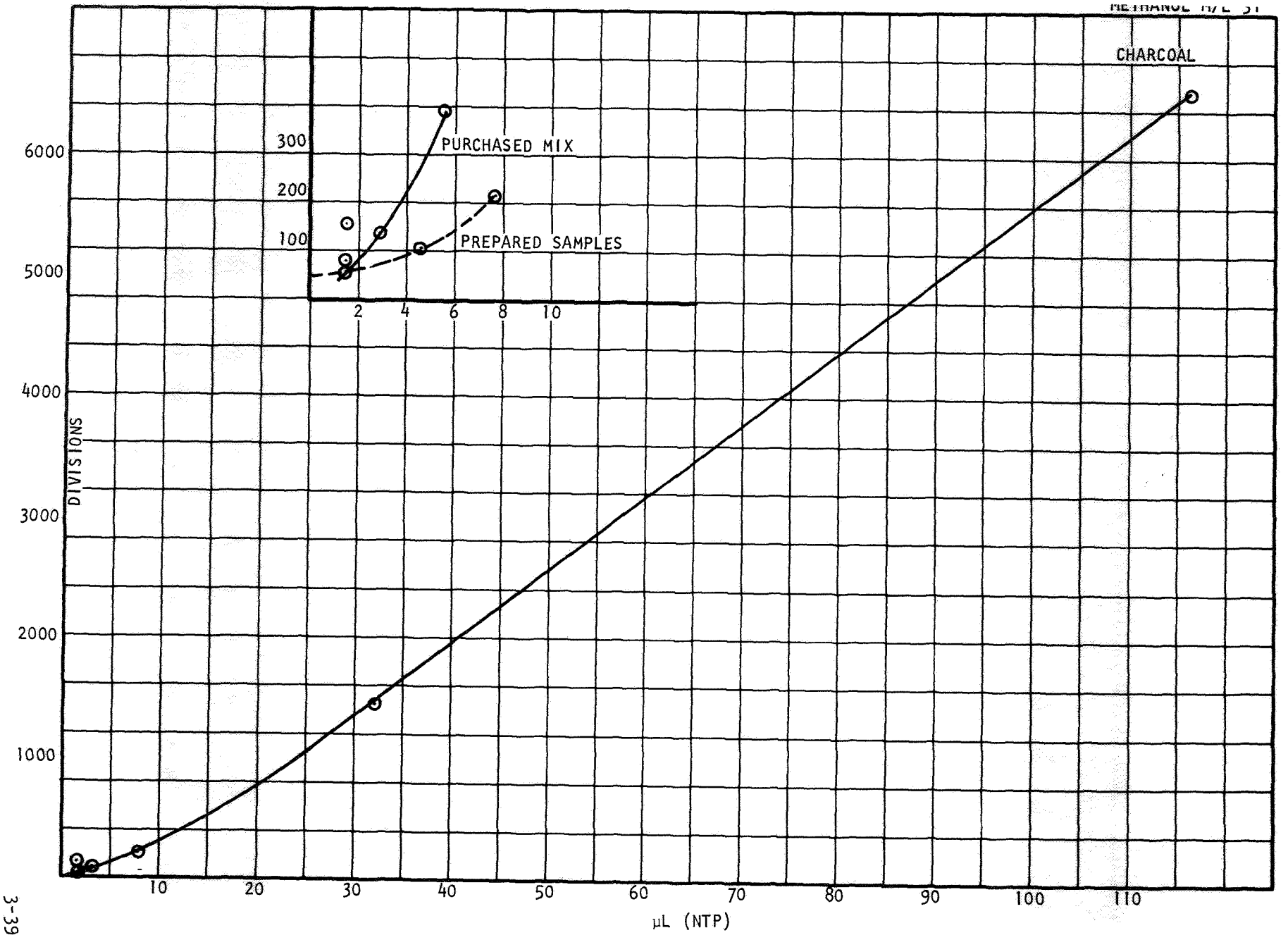

METHANOL H/C 31
CHARCOAL
PURCHASED MIX
PREPARED SAMPLES
DIVISIONS
µL (NTP)
6000
5000
4000
3000
2000
1000
300
200
100
2
4
6
8
10
10
20
30
40
50
60
70
80
90
100
110

FIGURE 3-15

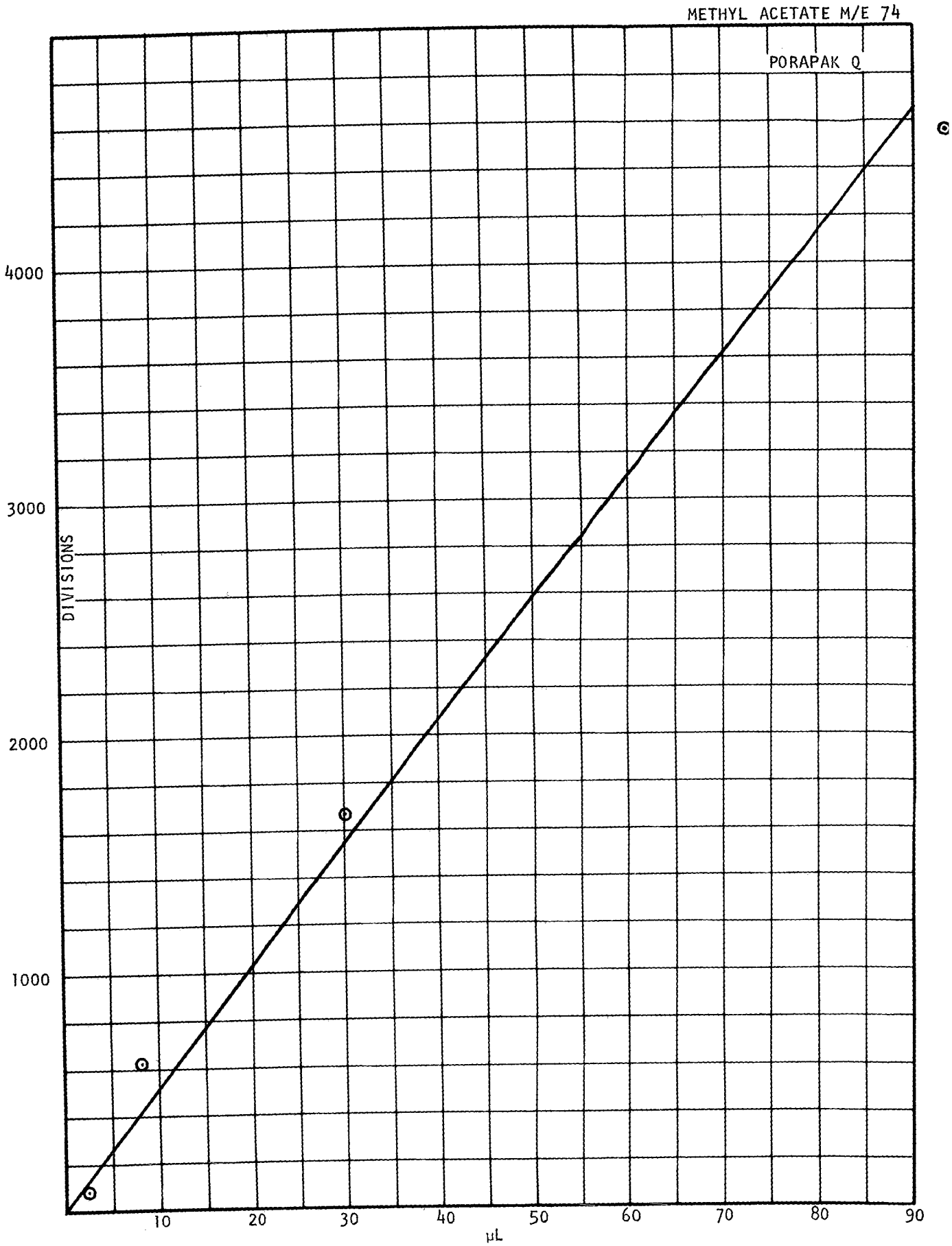

METHYL ACETATE M/E 74
POROPAK Q
4000
3000
2000
1000
DIVISIONS
10
20
30
40
50
60
70
80
90
µL

FIGURE 3-16

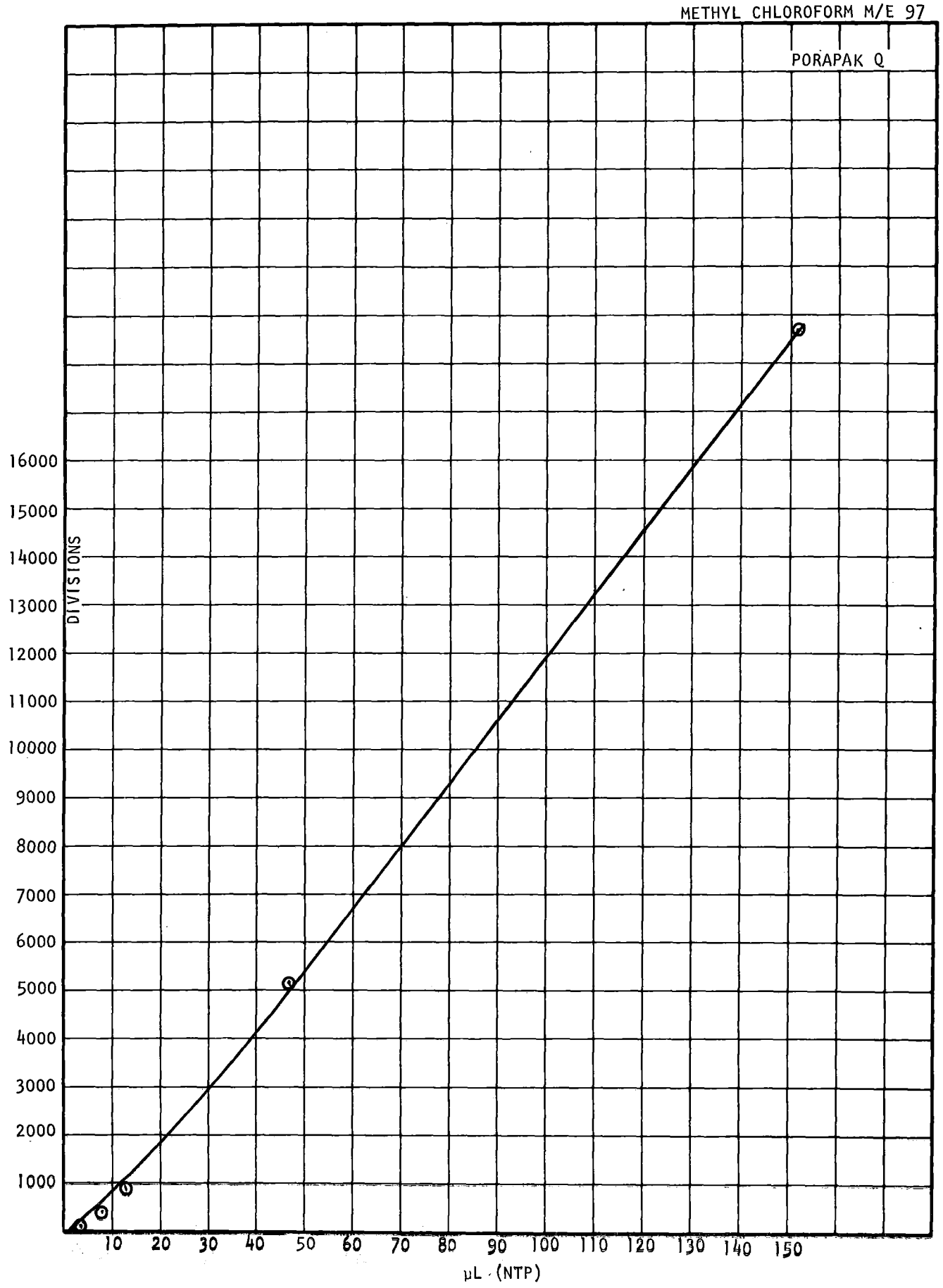

METHYL CHLOROFORM M/E 97
PORAPAK Q
DIVISIONS
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150
µL (NTP)

FIGURE 3-17

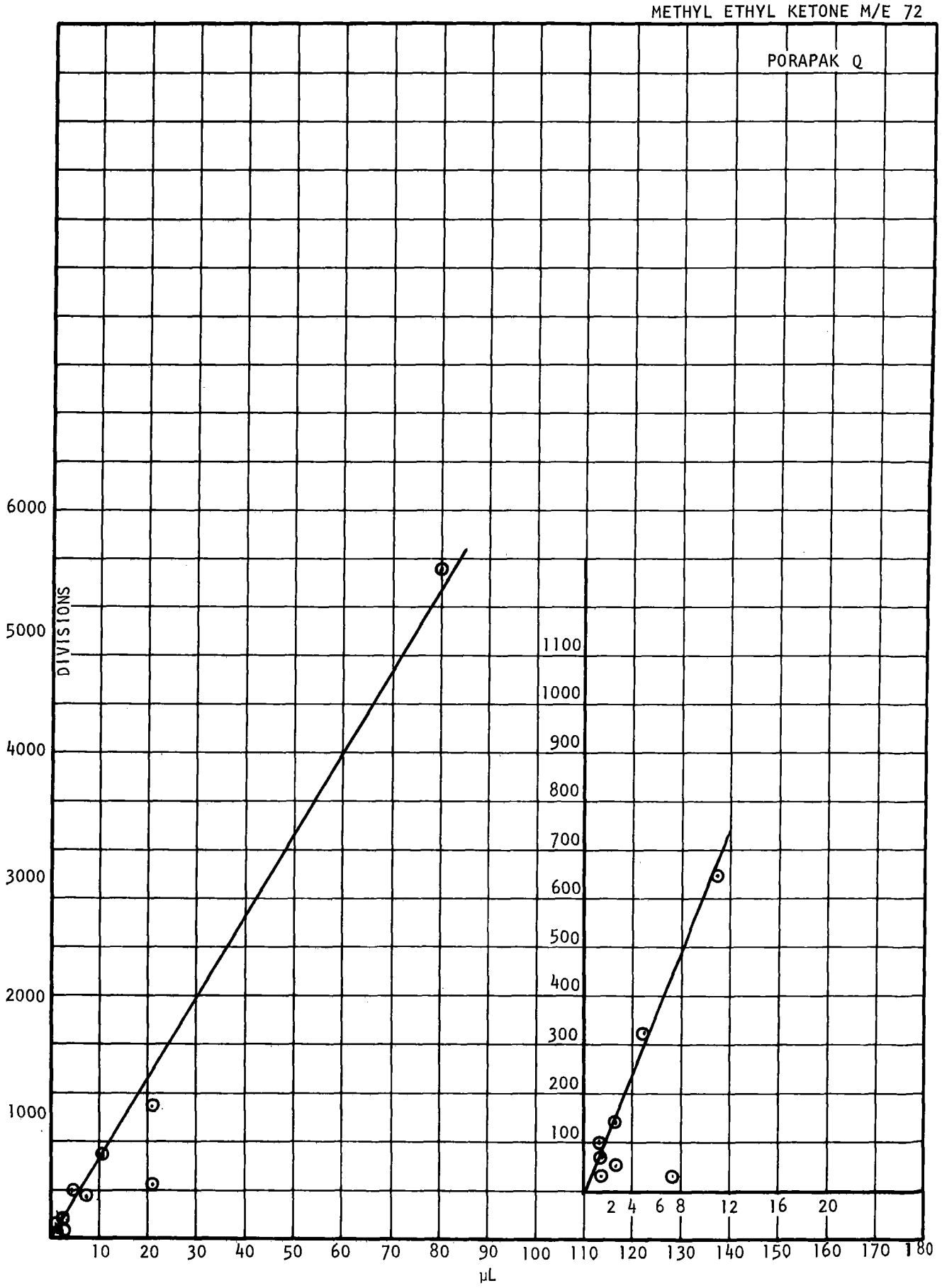

METHYL ETHYL KETONE M/E 72
PORAPAK Q
DIVISIONS
6000
5000
4000
3000
2000
1000
1100
1000
900
800
700
600
500
400
300
200
100
2 4 6 8 12 16 20
10 20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180
µL

FIGURE 3-18

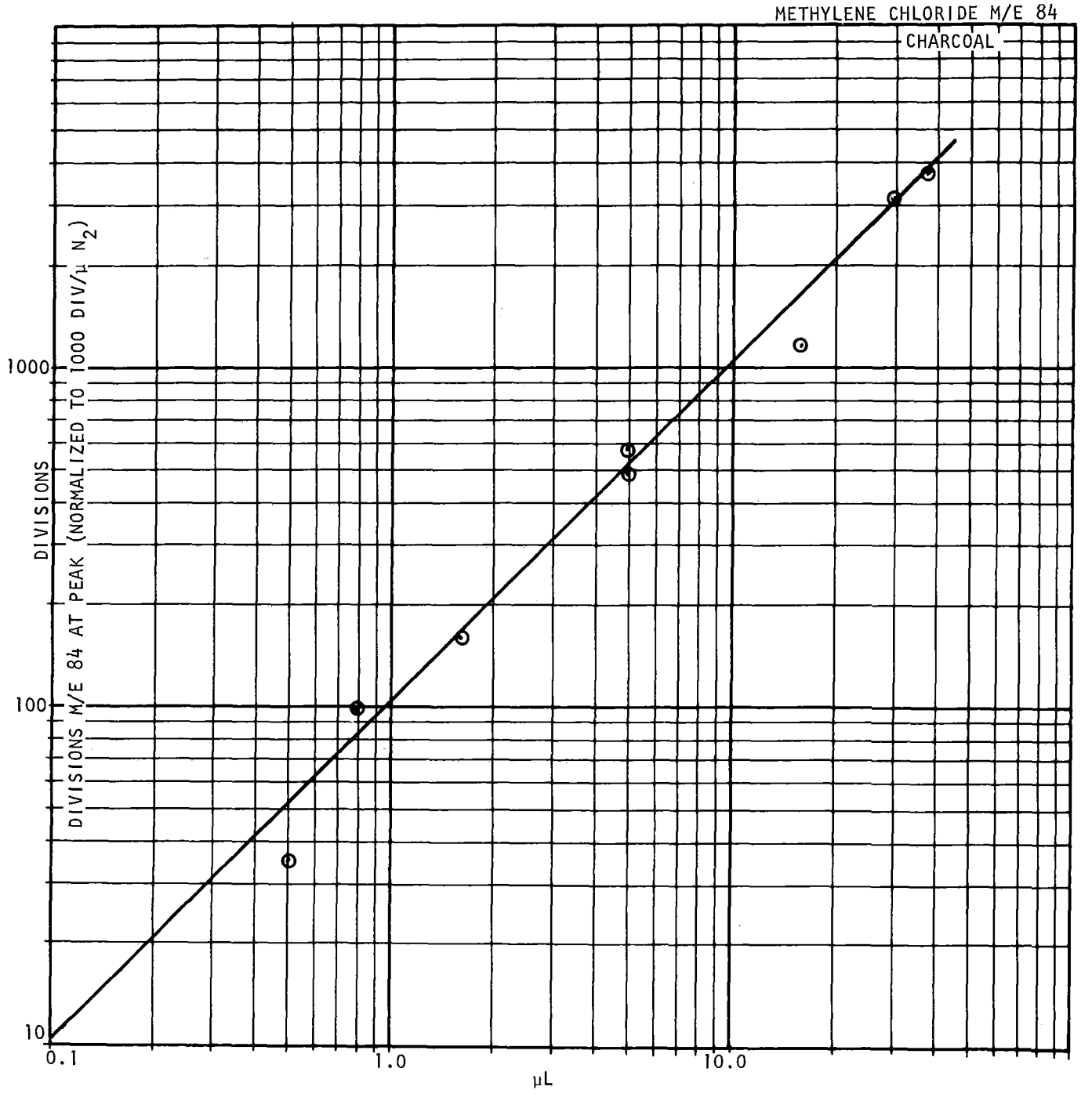

METHYLENE CHLORIDE M/E 84
CHARCOAL
DIVISIONS M/E 84 AT PEAK (NORMALIZED TO 1000 DIV/μ N2)
DIVISIONS
1000
100
10
0.1
1.0
10.0
μL

FIGURE 3-19

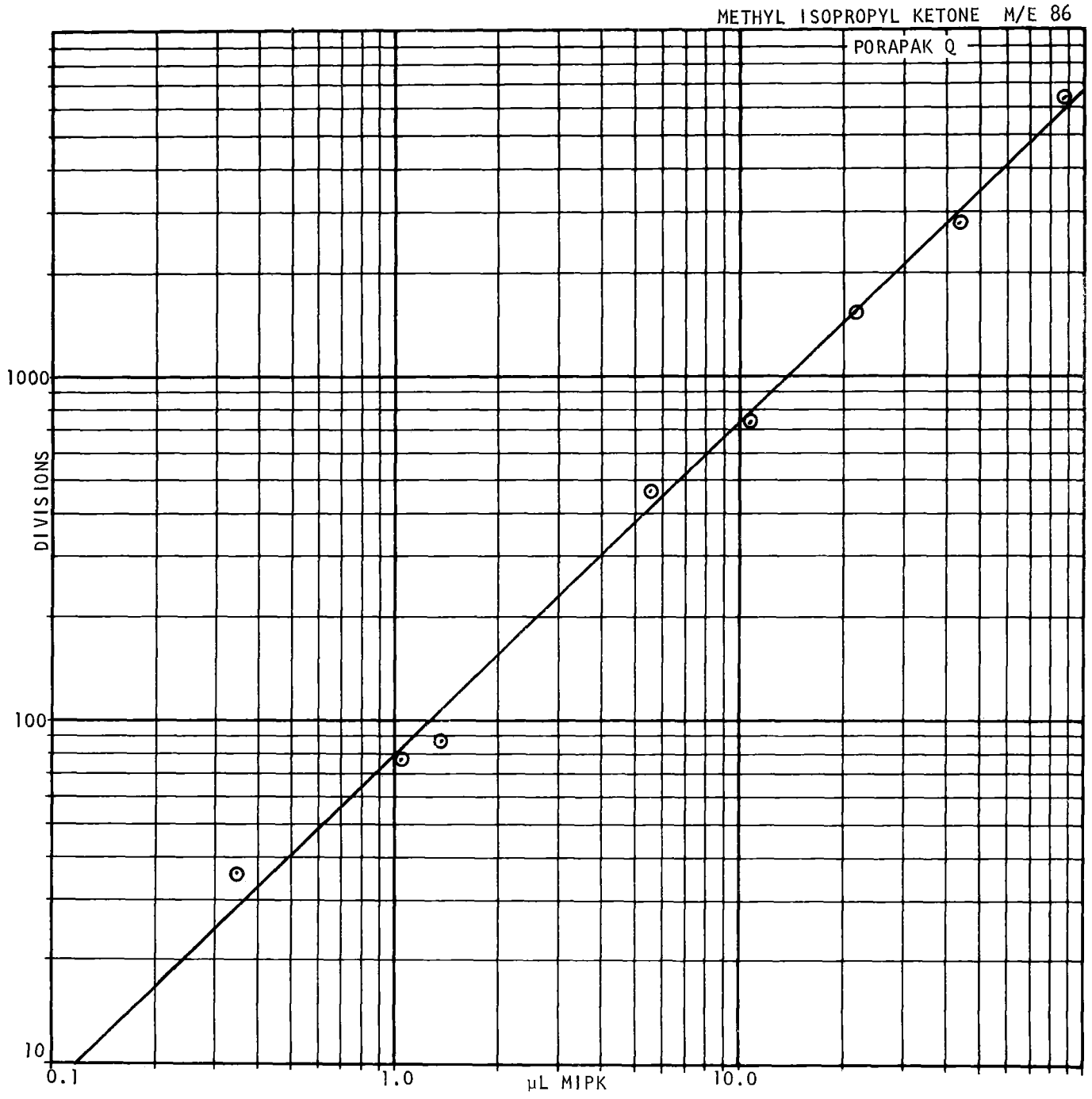

METHYL ISOPROPYL KETONE M/E 86
PORAPAK Q
1000
100
10
DIVISIONS
0.1
1.0
10.0
µL MIPK

FIGURE 3-20

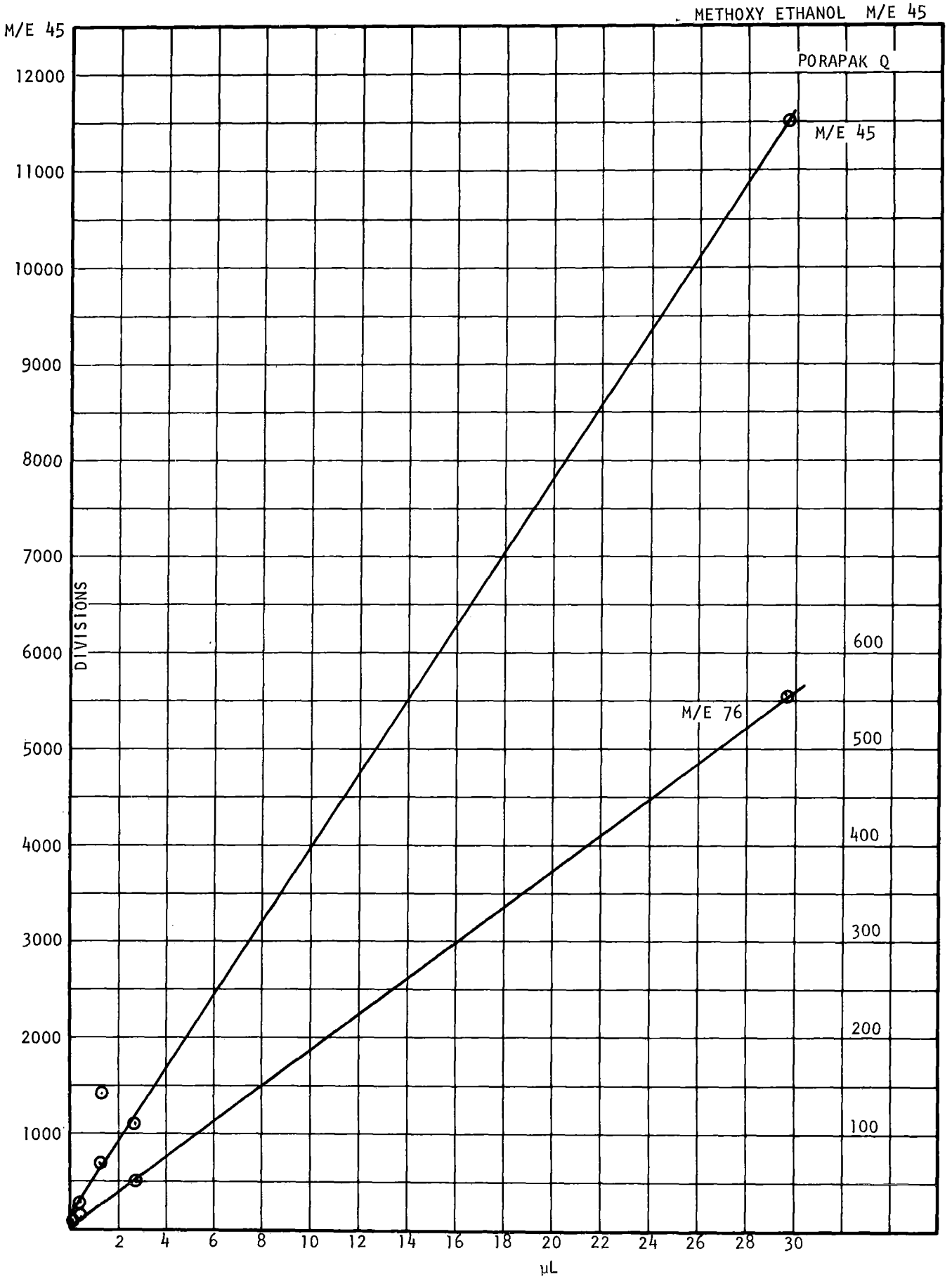

METHOXY ETHANOL M/E 45
M/E 45
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
DIVISIONS
PORAPAK Q
M/E 45
M/E 76
600
500
400
300
200
100
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
µL

FIGURE 3-21

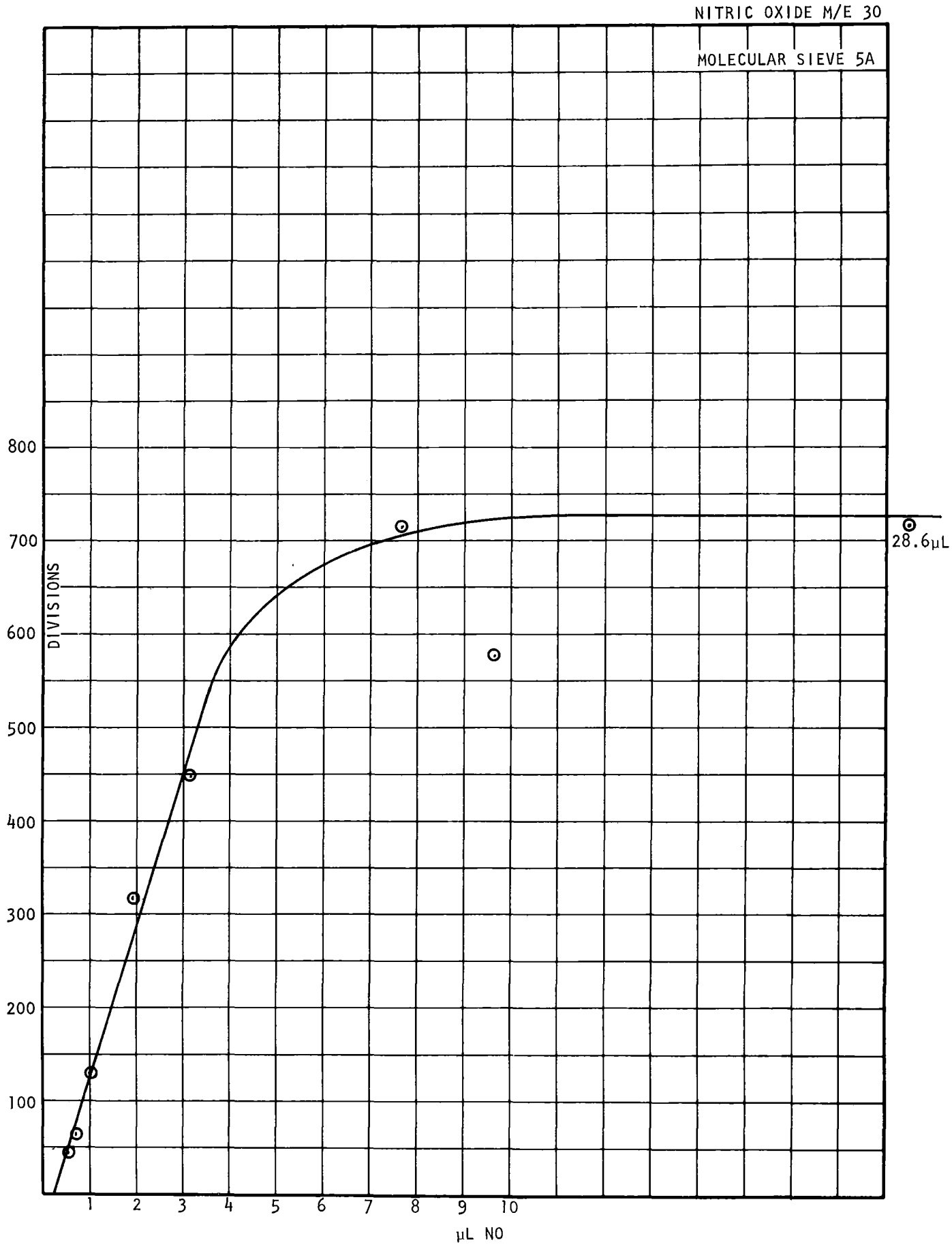

NITRIC OXIDE M/E 30
MOLECULAR SIEVE 5A
DIVISIONS
800
700
600
500
400
300
200
100
28.6µL
1
2
3
4
5
6
7
8
9
10
µL NO

FIGURE 3-22

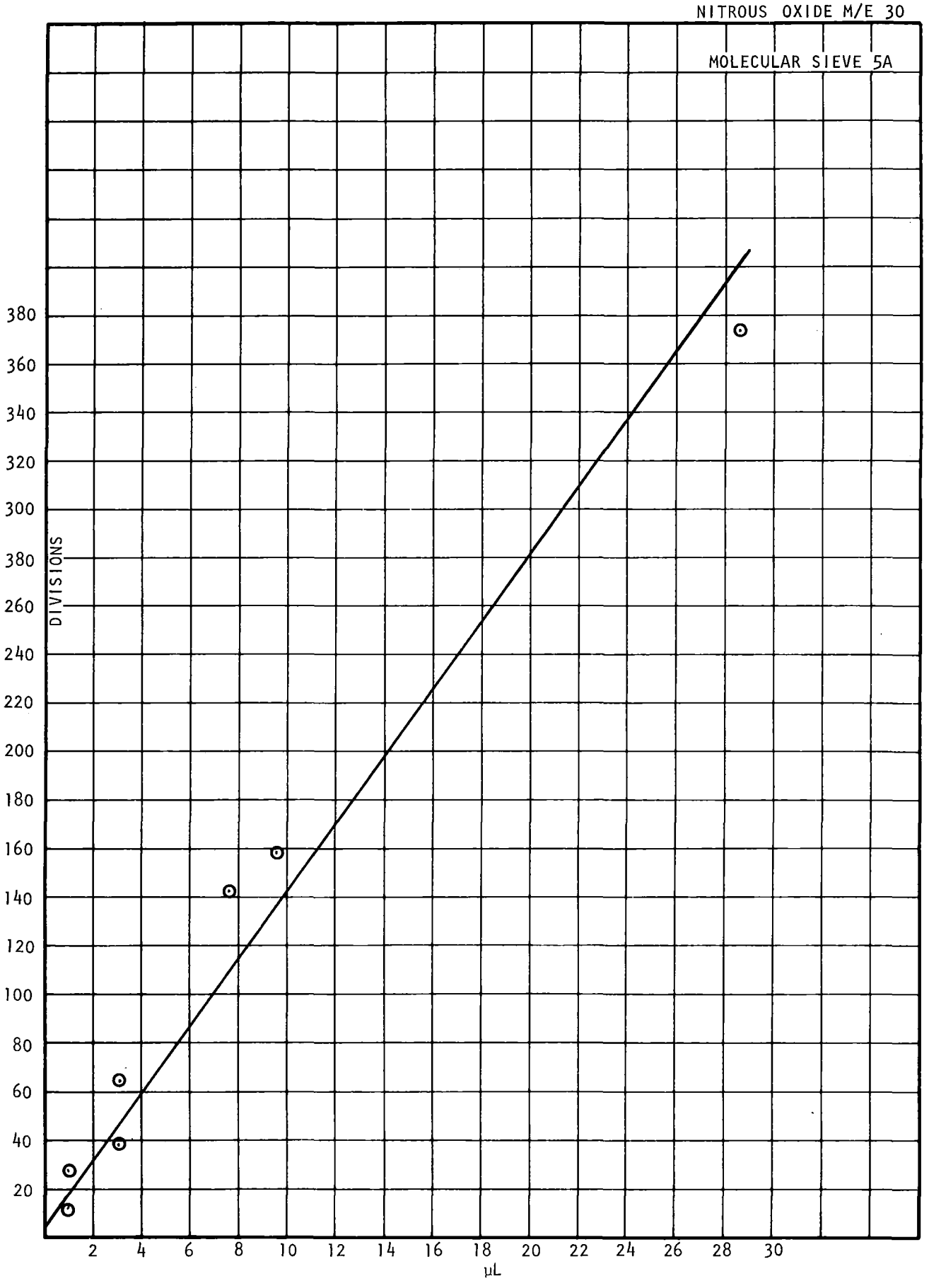

NITROUS OXIDE M/E 30
MOLECULAR SIEVE 5A
DIVISIONS
380
360
340
320
300
380
260
240
220
200
180
160
140
120
100
80
60
40
20
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
µL

FIGURE 3-23

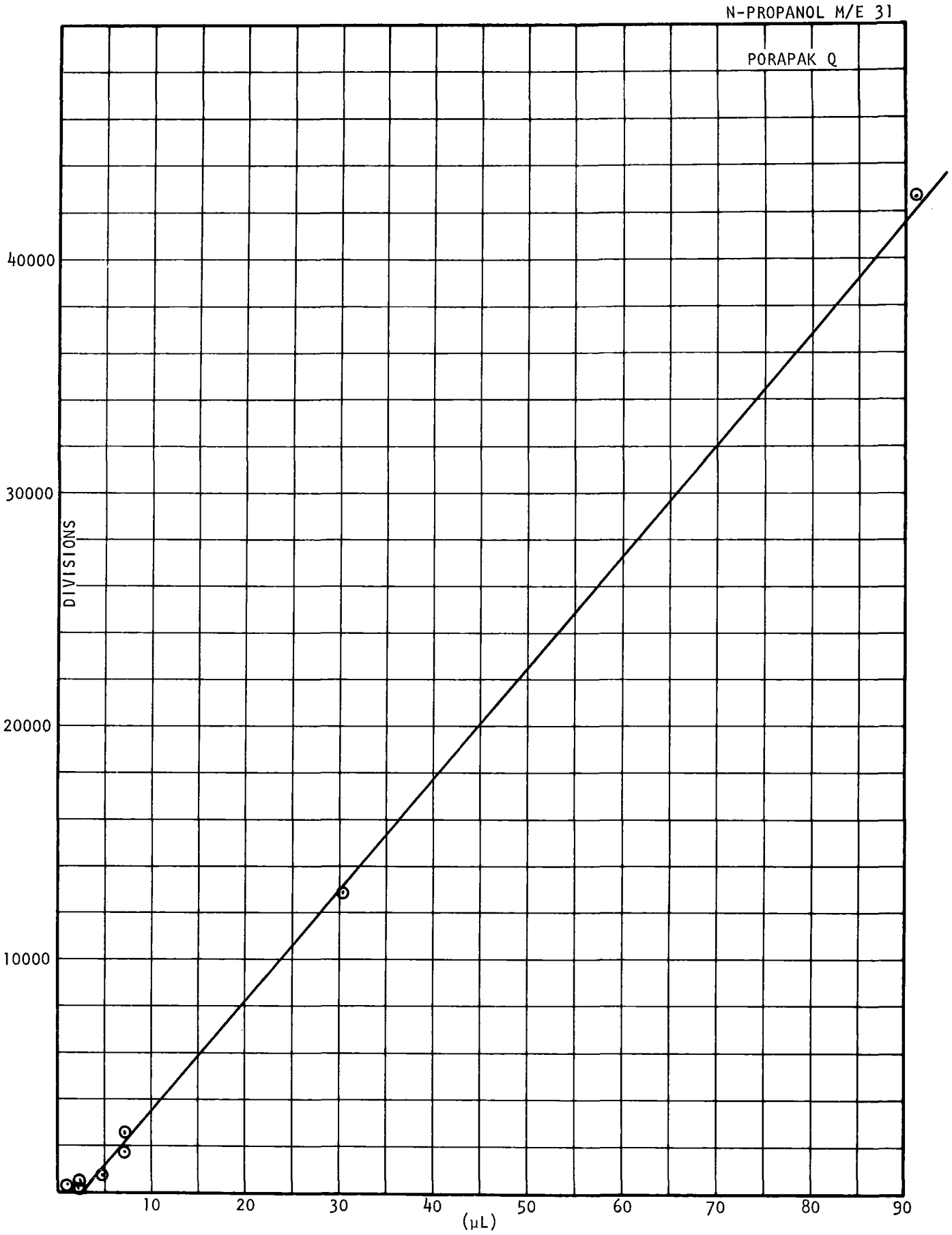

N-PROPANOL M/E 31
PORAPAK Q
40000
30000
20000
10000
DIVISIONS
10
20
30
40
50
60
70
80
90
(µL)

FIGURE 3-24

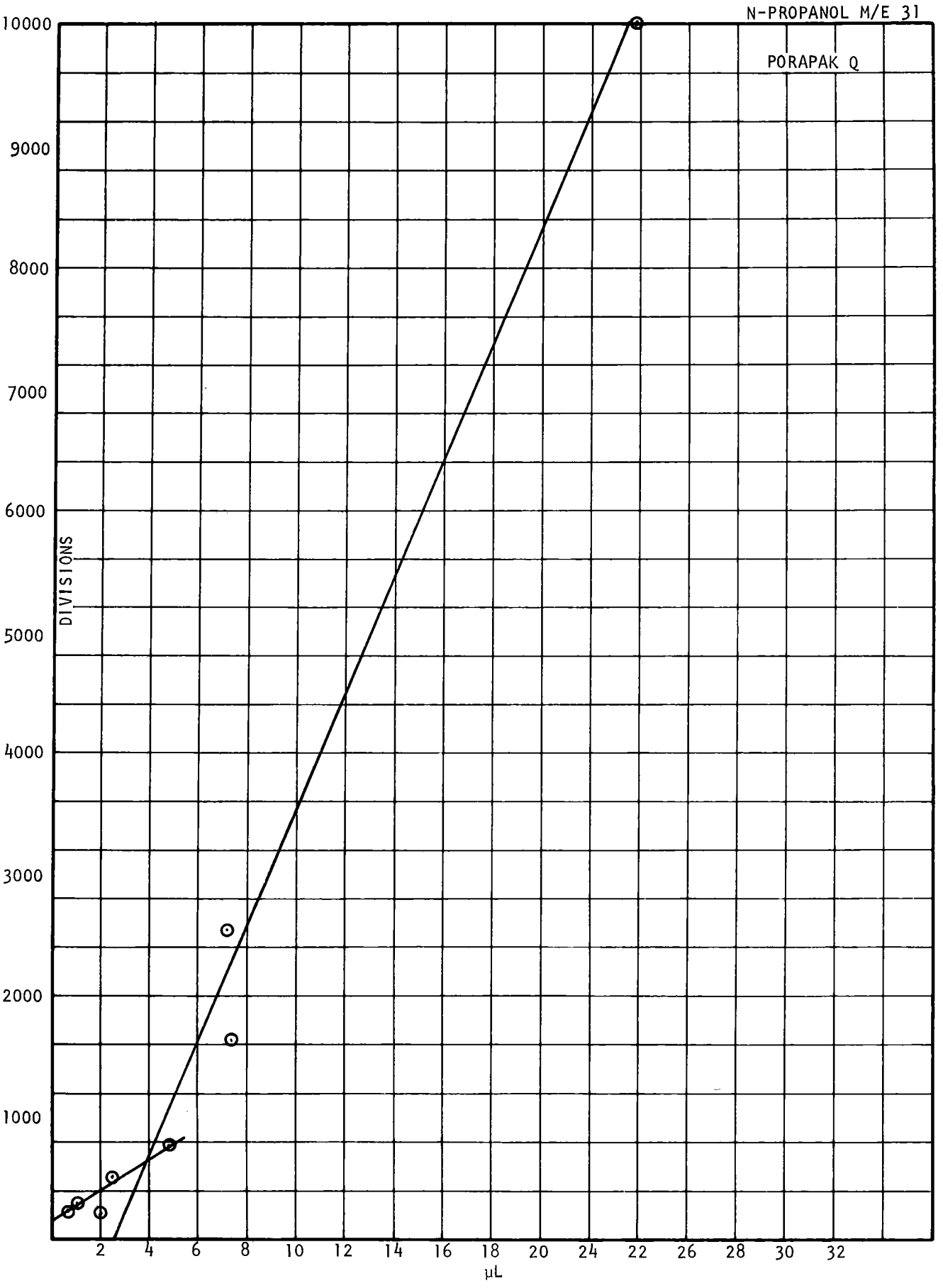

N-PROPANOL M/E 31
POROPAK Q
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
DIVISIONS
2
4
6
8
10
12
14
16
18
20
24
22
26
28
30
32
µL

FIGURE 3-24A

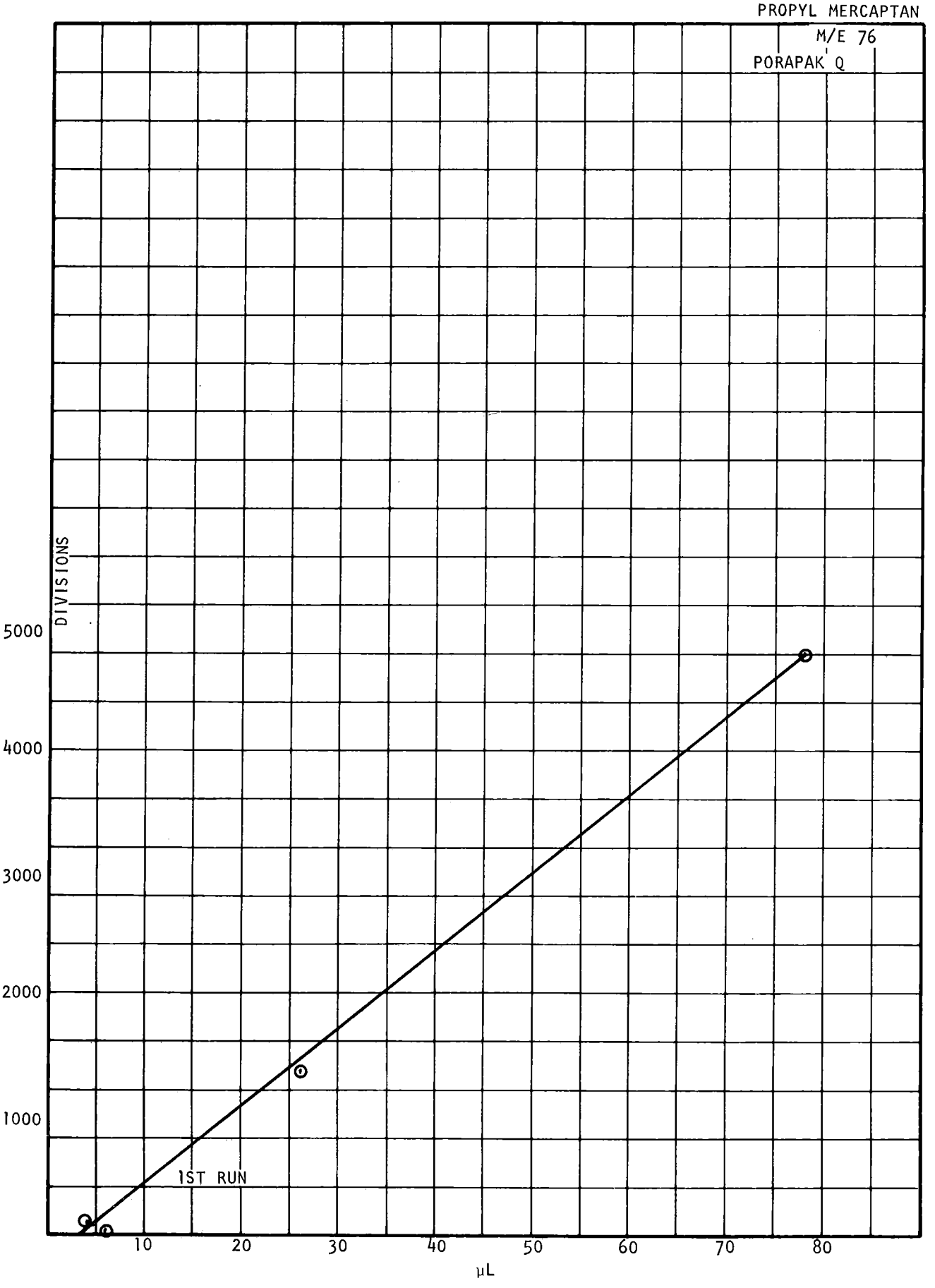

PROPYL MERCAPTAN
M/E 76
PORAPAK Q
DIVISIONS
5000
4000
3000
2000
1000
1ST RUN
10
20
30
40
50
60
70
80
µL

FIGURE 3-25

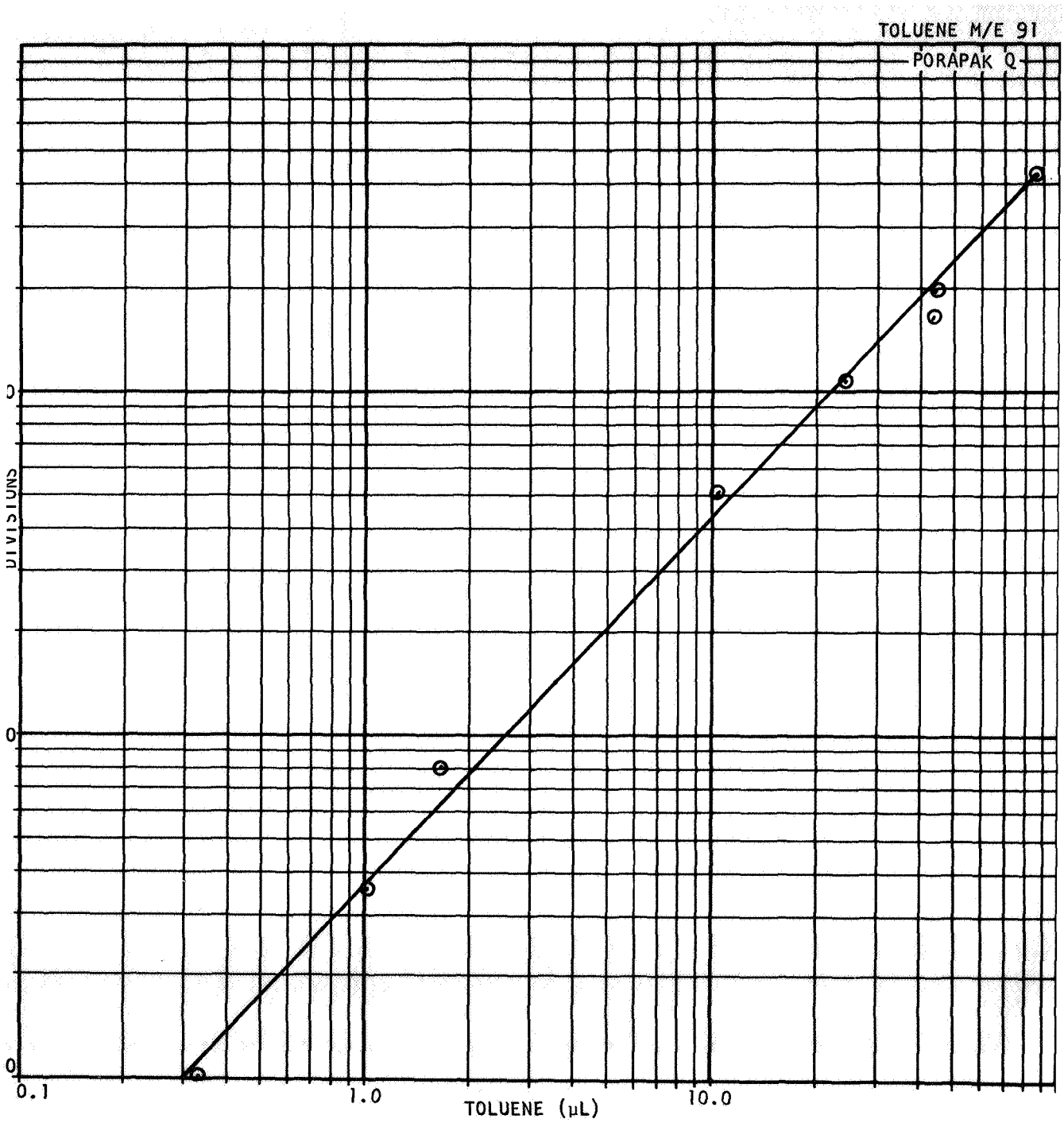


FIGURE 3-26

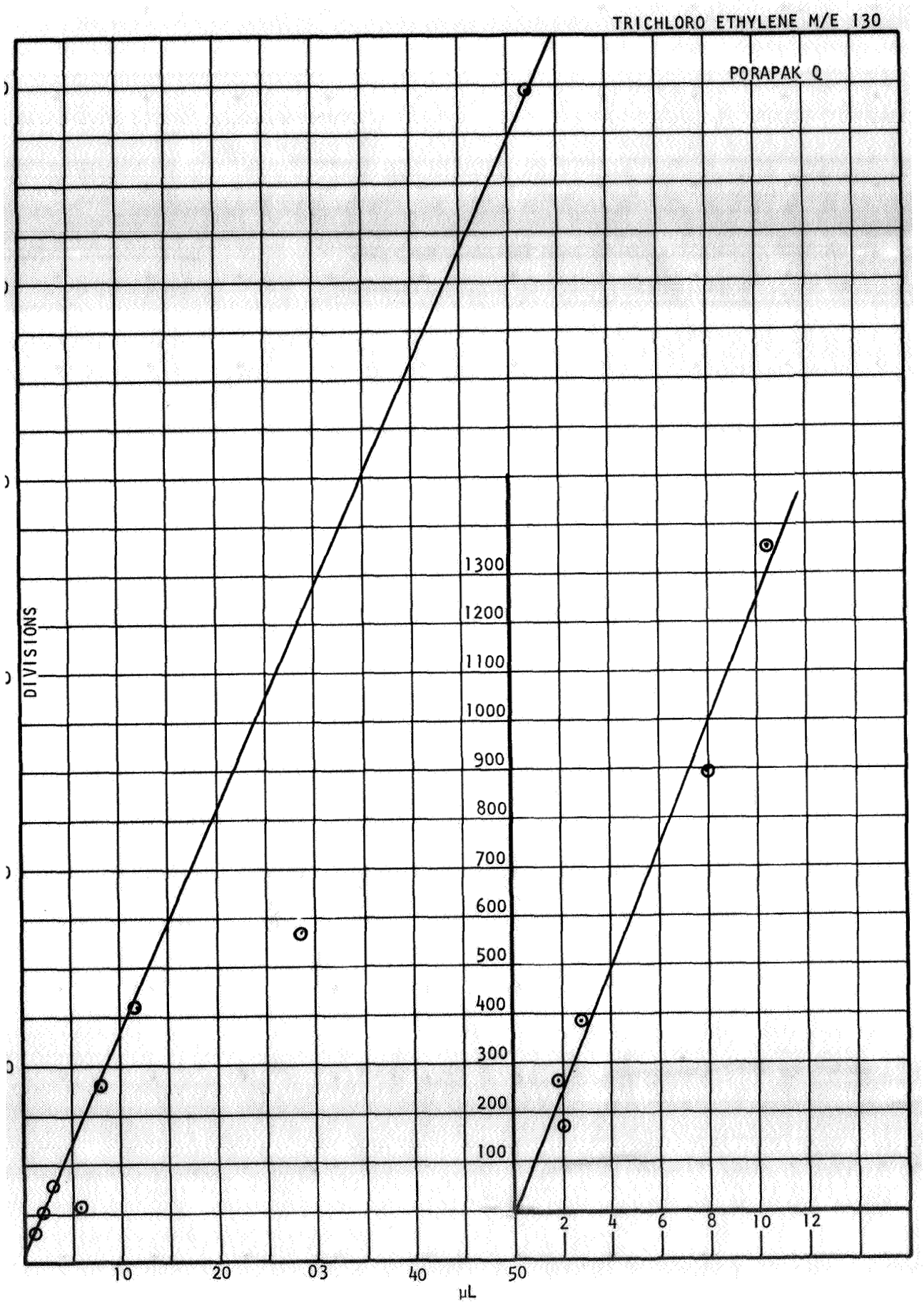

TRICHLORO ETHYLENE M/E 130
PORAPAK Q
DIVISIONS
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
10
20
03
40
50
µL
2
4
6
8
10
12

FIGURE 3-27

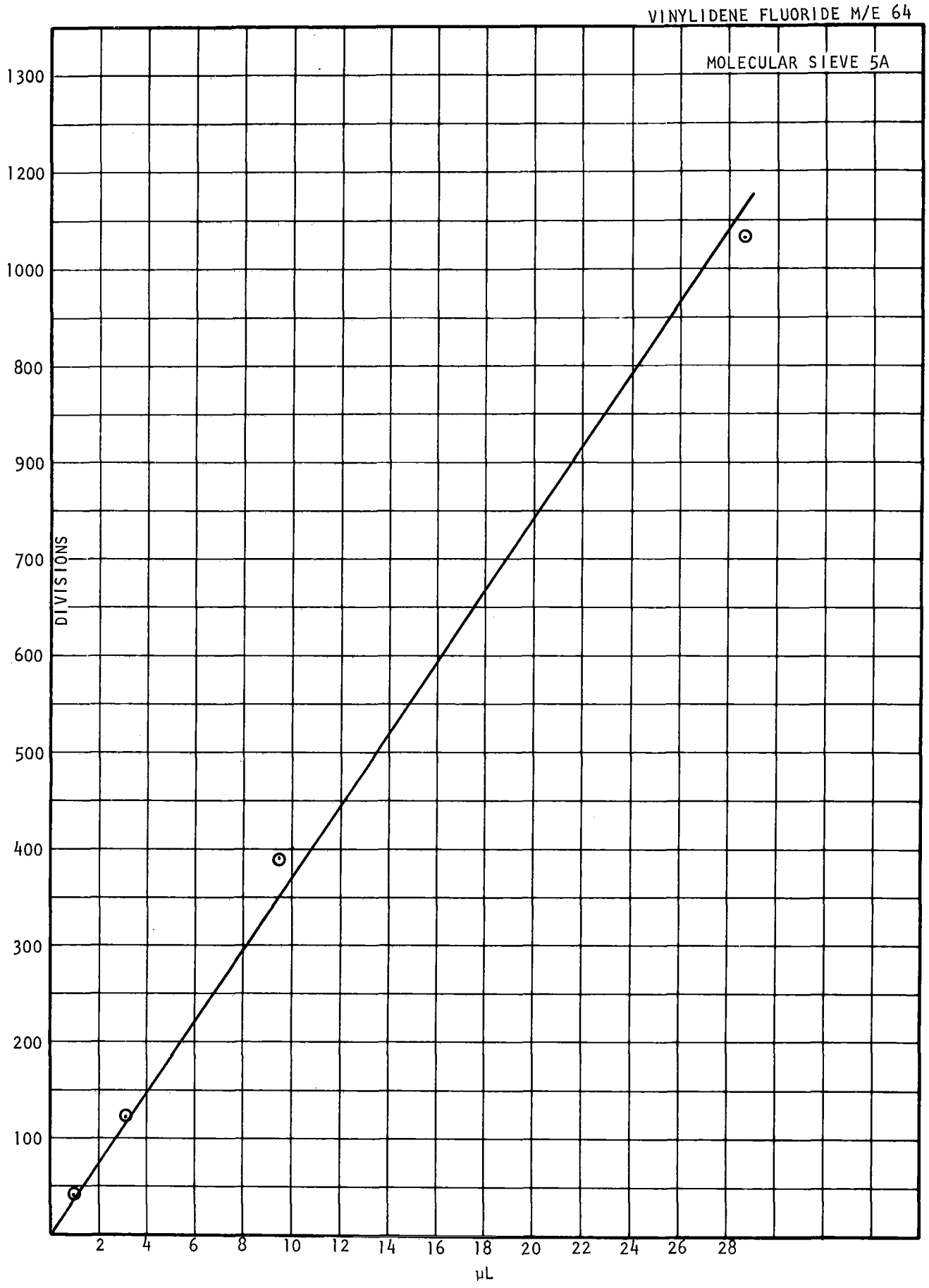

VINYLIDENE FLUORIDE M/E 64
MOLECULAR SIEVE 5A
DIVISIONS
1300
1200
1000
800
900
700
600
500
400
300
200
100
2
4
6
8
10
12
14
16
18
20
22
24
26
28
µL

FIGURE 3-28

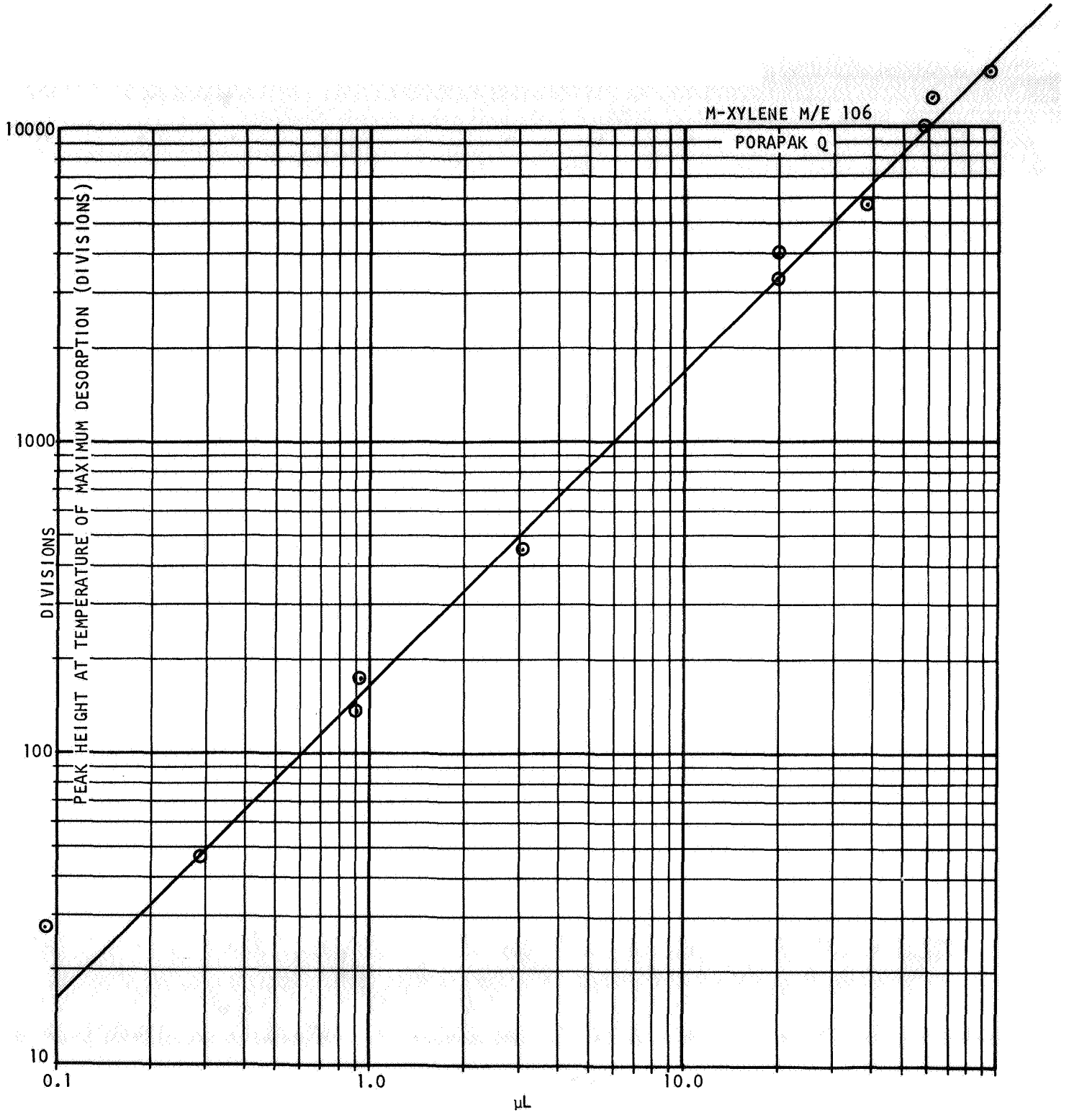

M-XYLENE M/E 106
PORAPAK Q
10000
1000
100
10
DIVISIONS
PEAK HEIGHT AT TEMPERATURE OF MAXIMUM DESORPTION (DIVISIONS)
0.1
1.0
10.0
µL

FIGURE 3-29

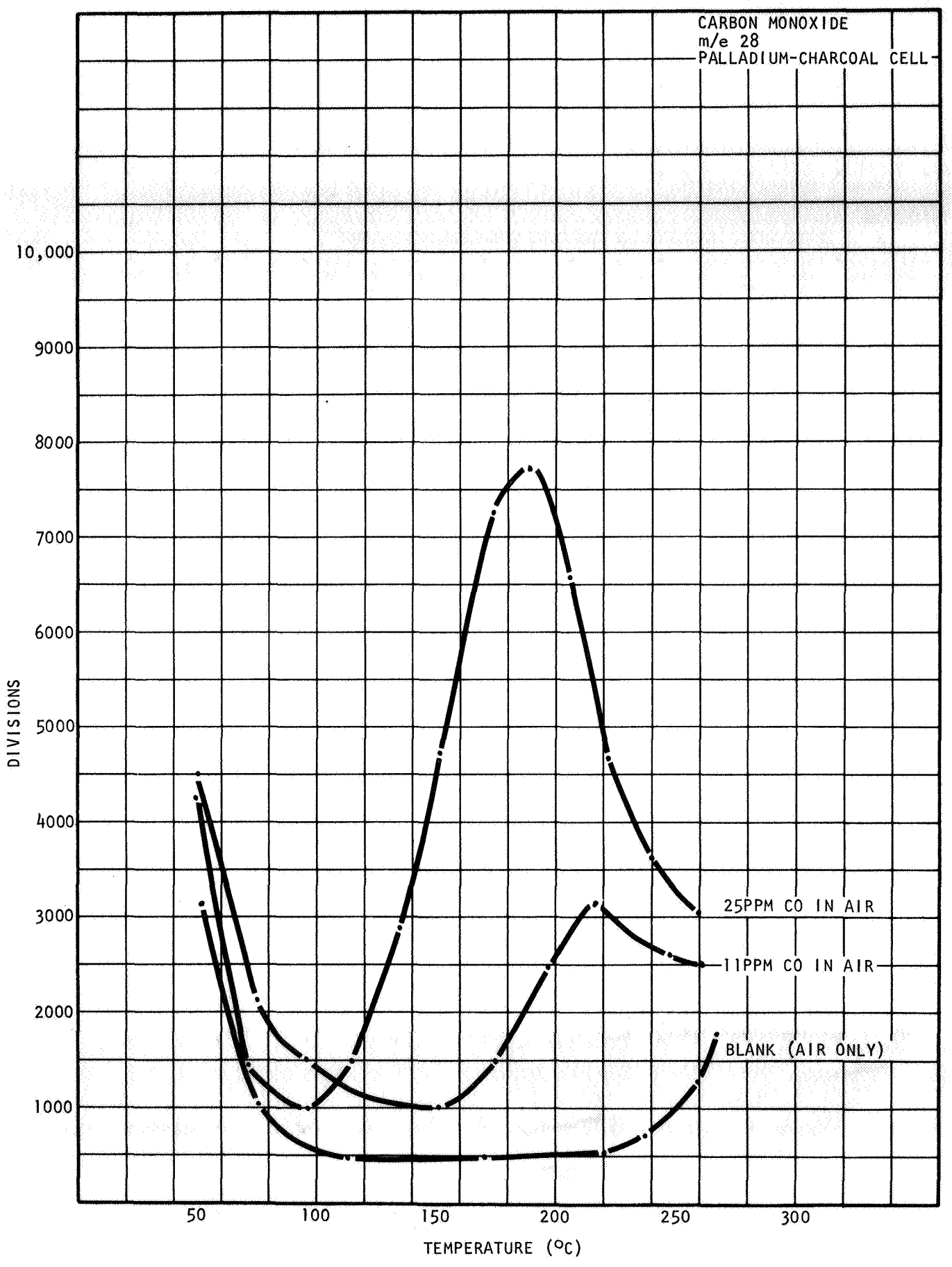

CARBON MONOXIDE
m/e 28
PALLADIUM-CHARCOAL CELL
10,000
9000
8000
7000
6000
5000
4000
3000
2000
1000
DIVISIONS
25PPM CO IN AIR
11PPM CO IN AIR
BLANK (AIR ONLY)
50
100
150
200
250
300
TEMPERATURE (°C)

FIGURE 3-30

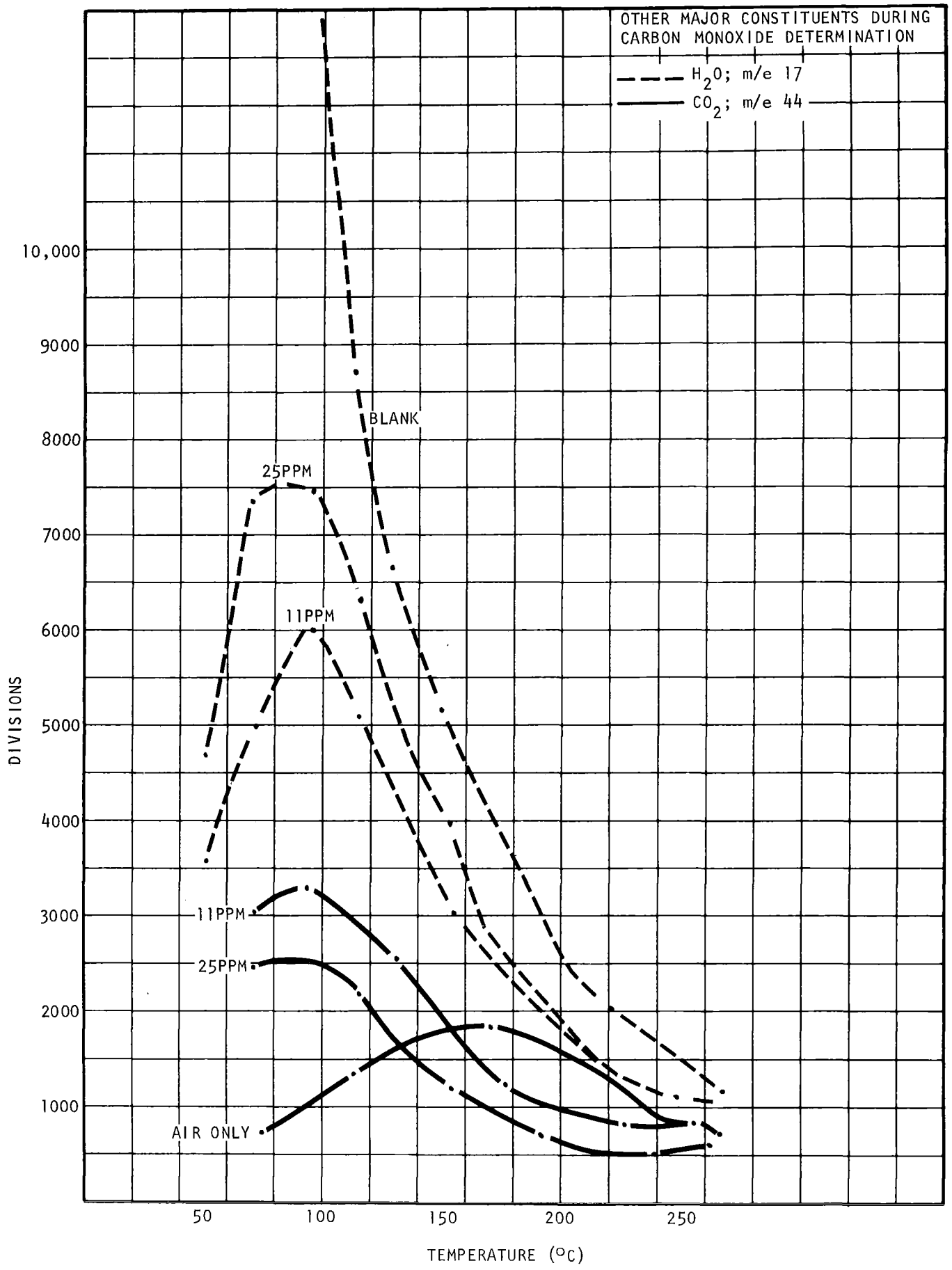

OTHER MAJOR CONSTITUENTS DURING CARBON MONOXIDE DETERMINATION
H_2O; m/e 17
CO_2; m/e 44
BLANK
25PPM
11PPM
11PPM
25PPM
AIR ONLY
10,000
9000
8000
7000
6000
5000
4000
3000
2000
1000
DIVISIONS
50
100
150
200
250
TEMPERATURE (°C)

FIGURE 3-31

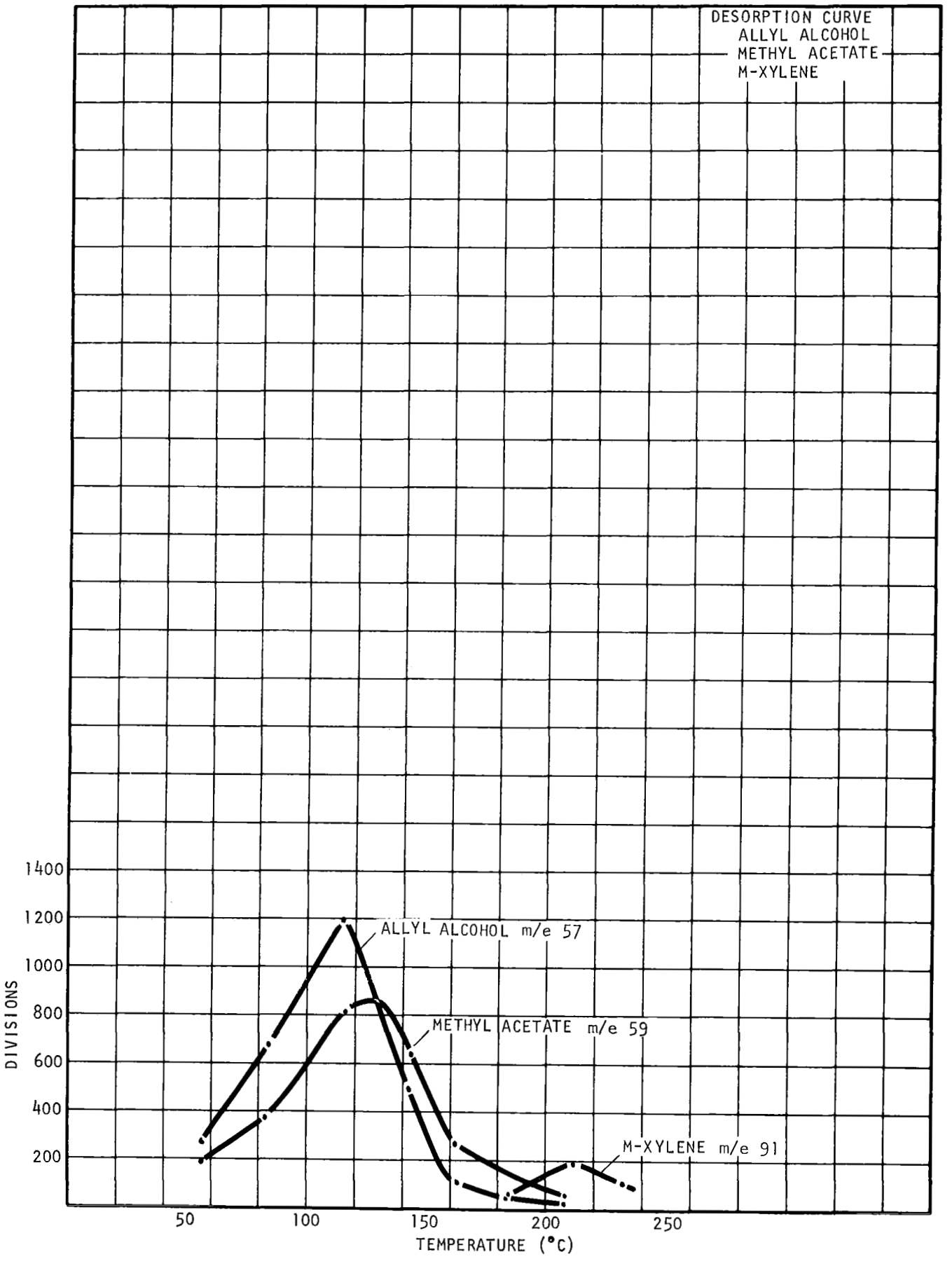

DESORPTION CURVE
ALLYL ALCOHOL
METHYL ACETATE
M-XYLENE
1400
1200
1000
800
600
400
200
DIVISIONS
ALLYL ALCOHOL m/e 57
METHYL ACETATE m/e 59
M-XYLENE m/e 91
50
100
150
200
250
TEMPERATURE (°C)

FIGURE 3-32

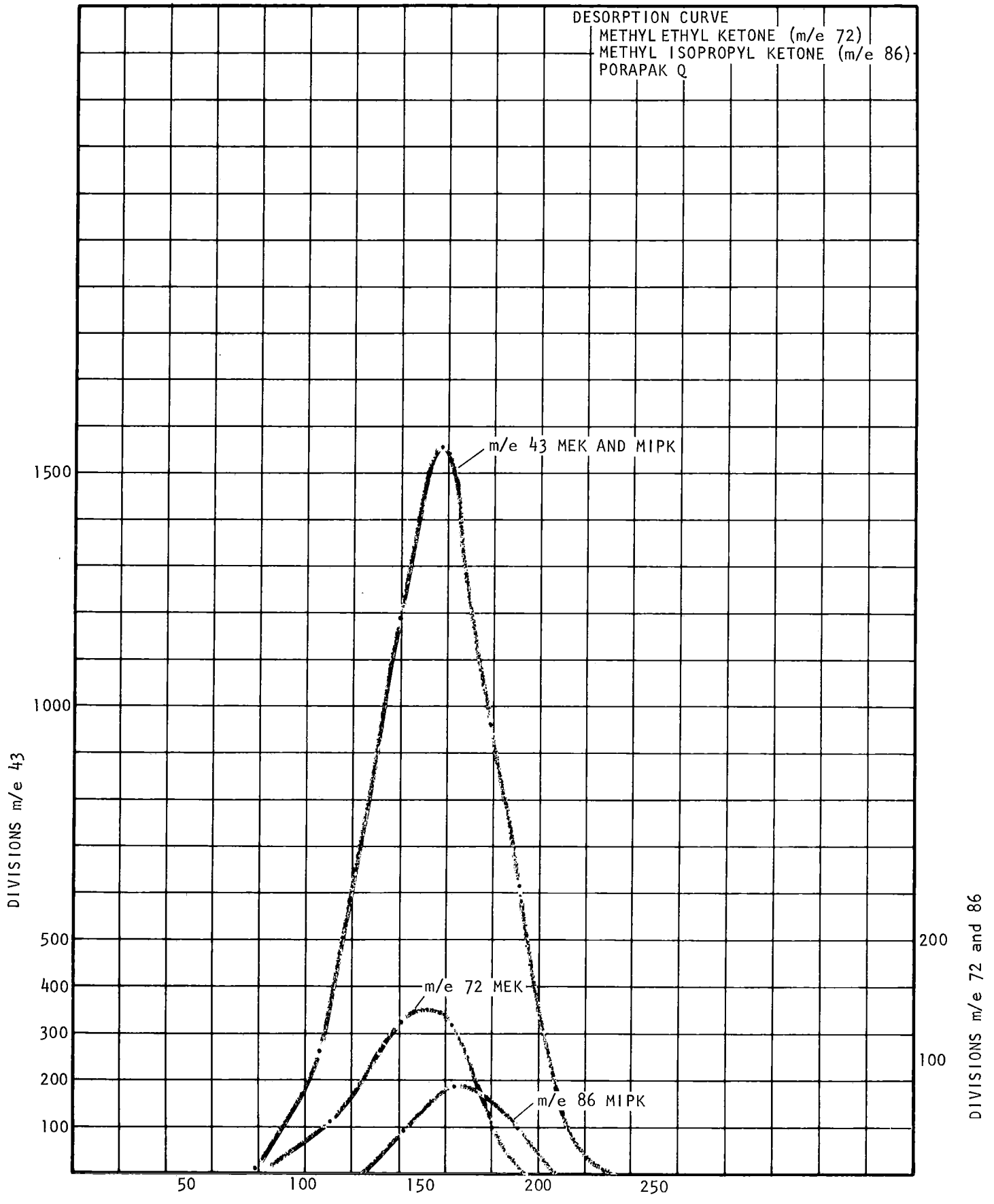

DESORPTION CURVE
METHYL ETHYL KETONE (m/e 72)
METHYL ISOPROPYL KETONE (m/e 86)
PORAPAK Q
m/e 43 MEK AND MIPK
m/e 72 MEK
m/e 86 MIPK
1500
1000
500
400
300
200
100
200
100
50
100
150
200
250
DIVISIONS m/e 43
DIVISIONS m/e 72 and 86
TEMPERATURE (°C)

FIGURE 3-33

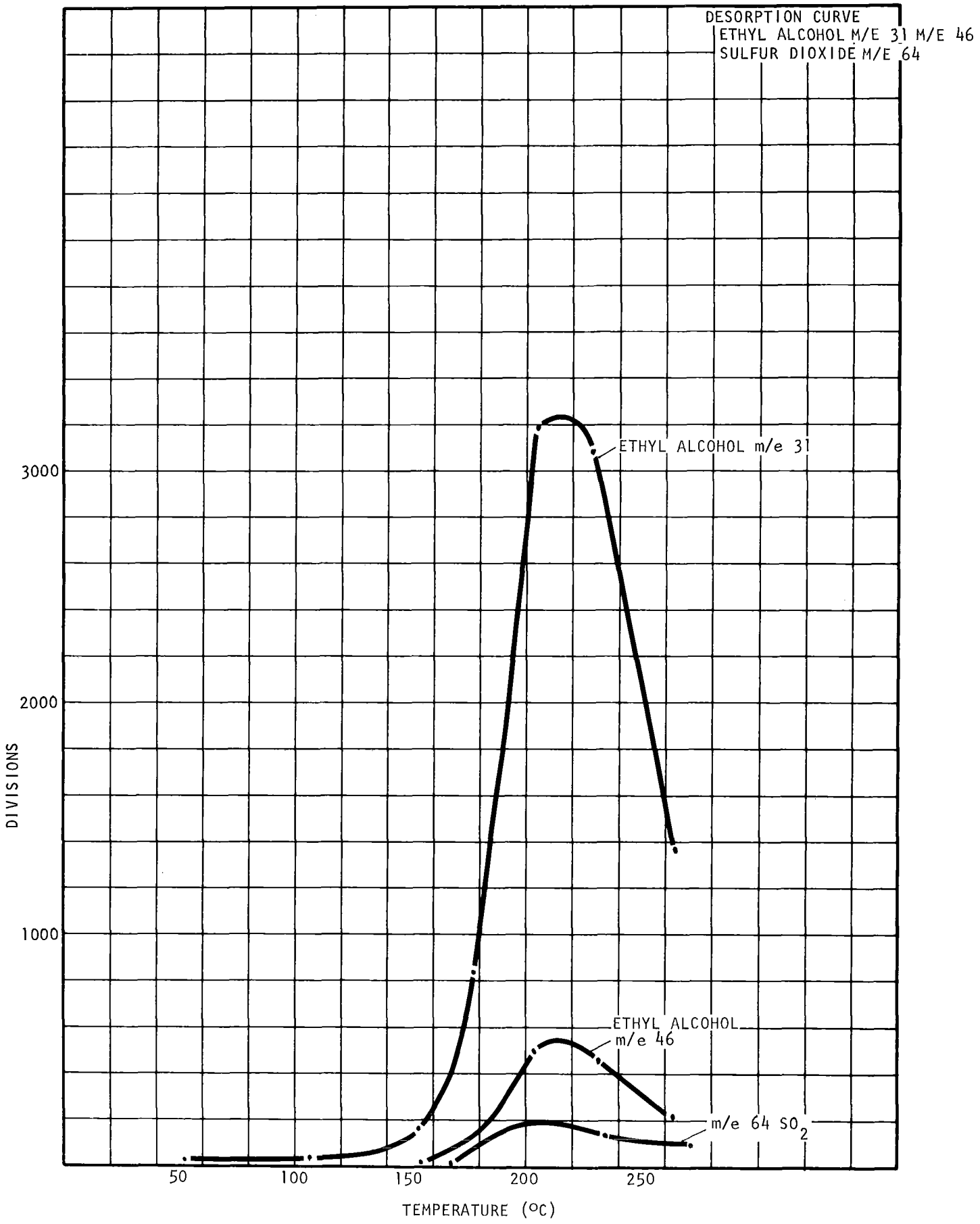

DESORPTION CURVE
ETHYL ALCOHOL M/E 31 M/E 46
SULFUR DIOXIDE M/E 64
ETHYL ALCOHOL m/e 31
ETHYL ALCOHOL m/e 46
m/e 64 SO2
3000
2000
1000
DIVISIONS
50
100
150
200
250
TEMPERATURE (°C)

FIGURE 3-34

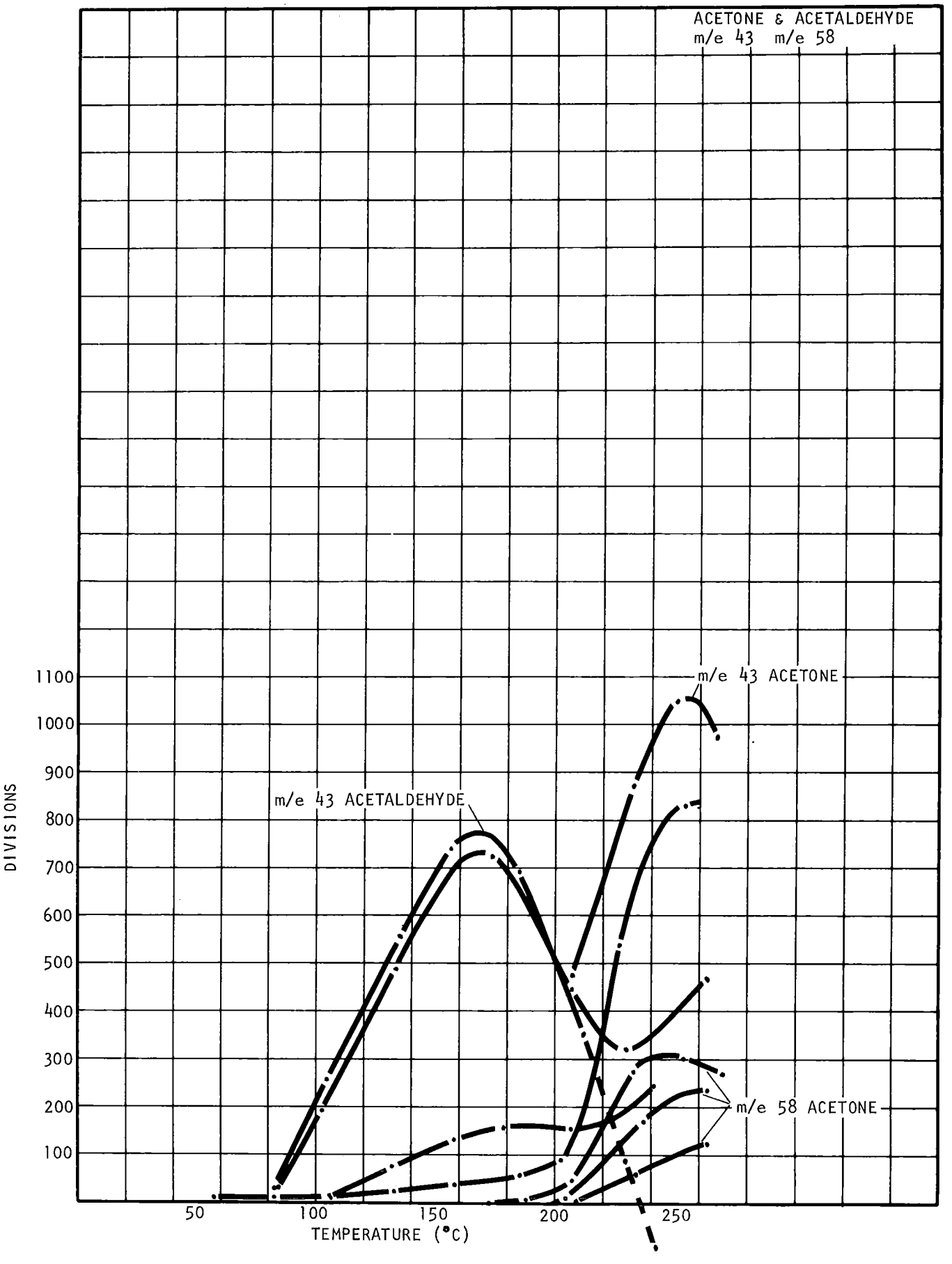

ACETONE & ACETALDEHYDE
m/e 43 m/e 58
m/e 43 ACETONE
m/e 43 ACETALDEHYDE
m/e 58 ACETONE
DIVISIONS
1100
1000
900
800
700
600
500
400
300
200
100
50
100
150
200
250
TEMPERATURE (°C)

FIGURE 3-35

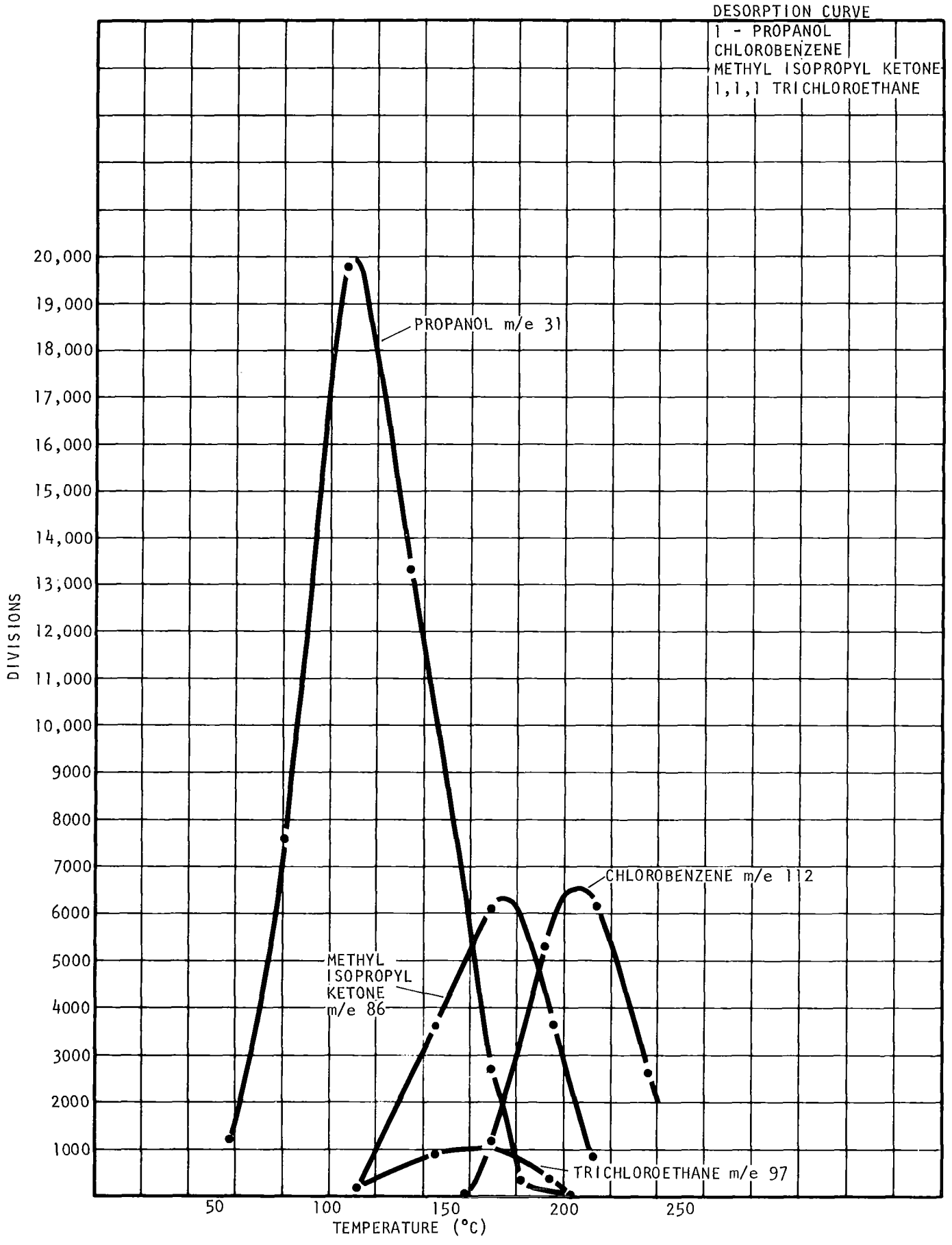

DESORPTION CURVE
1 - PROPANOL
CHLOROBENZENE
METHYL ISOPROPYL KETONE
1,1,1 TRICHLOROETHANE
DIVISIONS
20,000
19,000
18,000
17,000
16,000
15,000
14,000
13,000
12,000
11,000
10,000
9000
8000
7000
6000
5000
4000
3000
2000
1000
PROPANOL m/e 31
CHLOROBENZENE m/e 112
METHYL ISOPROPYL KETONE m/e 86
TRICHLOROETHANE m/e 97
50
100
150
200
250
TEMPERATURE (°C)

FIGURE 3-36

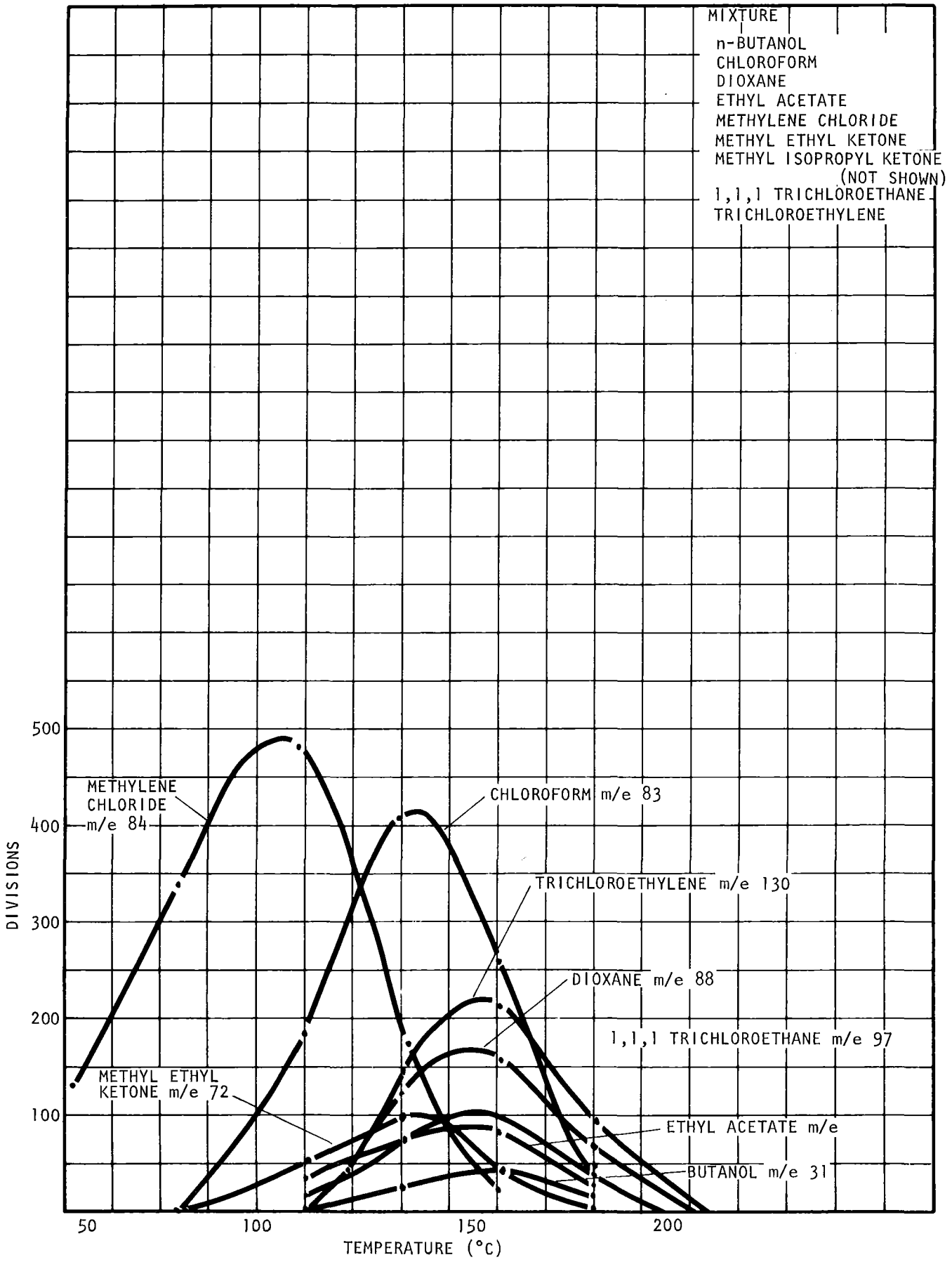

MIXTURE
n-BUTANOL
CHLOROFORM
DIOXANE
ETHYL ACETATE
METHYLENE CHLORIDE
METHYL ETHYL KETONE
METHYL ISOPROPYL KETONE
(NOT SHOWN)
1,1,1 TRICHLOROETHANE
TRICHLOROETHYLENE
METHYLENE CHLORIDE m/e 84
CHLOROFORM m/e 83
TRICHLOROETHYLENE m/e 130
DIOXANE m/e 88
1,1,1 TRICHLOROETHANE m/e 97
METHYL ETHYL KETONE m/e 72
ETHYL ACETATE m/e
BUTANOL m/e 31
DIVISIONS
500
400
300
200
100
50
100
150
200
TEMPERATURE (°C)

FIGURE 3-37

4. TEST RESULTS WITH CONTAMINANT SENSOR II

The second Laboratory Contaminant Sensor is essentially the same design as the original unit, except some modifications were made in the inlet system geometry to accommodate it to the configuration of the second CEC 21-621 mass spectrometer. A schematic of the new system is shown in Figure 4-1 and a photograph in Figure 4-2. The valves shown in the schematic are all mounted on the recessed panel (shown in the photograph) except for the sample flow control valve which is located behind the panel. A complete description of the system is provided in the System II Operations and Maintenance Manual.

Four accumulator cells; Porapak Q, Charcoal, Molecular Sieve 5A and Palladium-Charcoal, are provided with the system. These cells are described in Table 4-1. The Porapak Q, Molecular Sieve, and Palladium-Charcoal cells are shorter than those previously used, for convenience in attaching them to the inlet system. They contain the same amount of sorbent as the cells tested with the earlier instrument, and test results with the Porapak Q and Molecular Sieve cells indicate that the small change in geometry does not affect performance.

TABLE 4-1

Sorbent Cells System II

Cell	Geometry	Weight of Sorbent (meg)
Porapak Q	2.1" x 3/8" x 0.042"	785
Charcoal	2 x 3/8" x 0.065"	670
Molecular Sieve 5A	2.85" x 3/8" x 0.042"	≈2000
Palladium charcoal	2.85" x 3/8" x 0.042"	1400

After initial startup and pump down of the mass spectrometer and inlet system, the sensitivity of the new instrument to air was determined for comparison with the original instrument. The sensitivity of the new system, as measured by the ion current produced for a given pressure of air in the inlet system, was lower by about a factor of five. It was believed that this difference was due mainly to differences in conductance of the gold leaks, although this could not be verified from the pressure readings obtained from the ionization guage in the analyzer region. A rough measurement of the conductances indicated that the leak

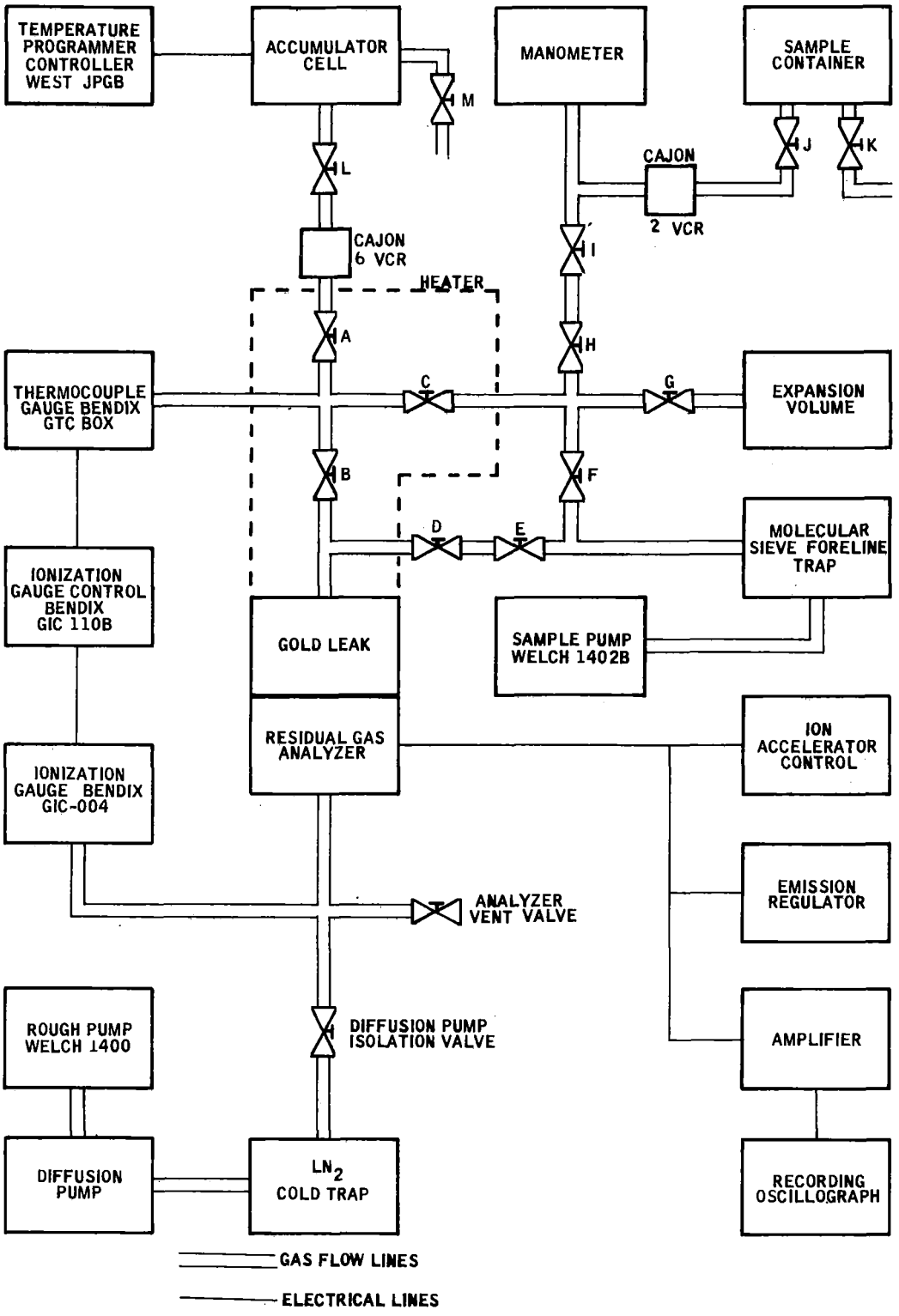
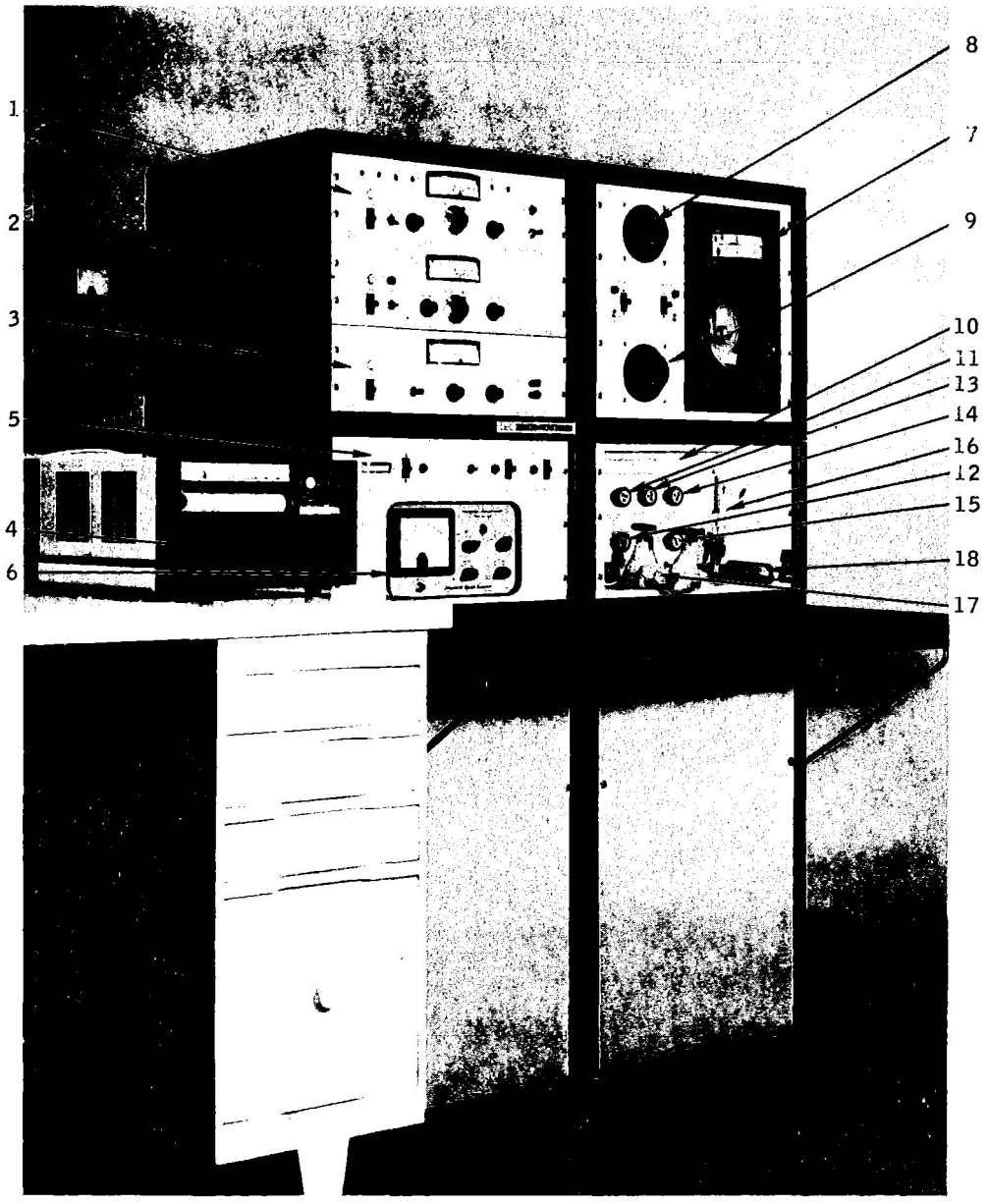


FIGURE 4-1
Laboratory Contaminant Sensor II Schematic Diagram



1. ION ACCELERATOR CONTROL
2. EMISSION REGULATOR
3. ION CURRENT AMPLIFIER CONTROL
4. RECORDING OSCILLOGRAPH (CEC 5-124A)
5. SYSTEM VACUUM CONTROL
6. IONIZATION GAUGE (BENDIX GIC 110B)
7. TEMPERATURE PROGRAM-CONTROLLER (WEST JPGB)
8. CELL CONTROL VARIAC
9. INLET SYSTEM VARIAC
10. INLET SYSTEM
11. VALVE C
12. VALVE E
13. VALVE G
14. VALVE H
15. VALVE I
16. MANOMETER
17. ACCUMULATOR CELL
18. SAMPLE VOLUME

FIGURE 4-2
Laboratory Contaminant Sensor II

in the old system was about three times as fast as that in the new instrument. In order to determine that the difference was due to the leaks, the high conductance leak from the old system was installed in the new unit. The sensitivity of the new instrument with this leak was comparable to that of the older unit.

This high conductance leak, one which was available at Perkin-Elmer Aerospace Systems, was installed in the Contaminant Sensor near the end of the previous development program. The conductance of the leak is a factor in establishing the lower limits of contaminants that can be detected. Use of the standard six-hole leaks for this instrument will decrease the detectability by a factor of three to five. A standard two-hole leak is available which has a conductance six times that of the standard six-hole leak (0.15 cc/seconds versus 0.025 cc/second). Use of this leak with smaller contaminant samples should result in the same sensitivity for detection of contaminants. If this leak is used, however, air precut time may need to be increased in order to avoid excessive pressures in the ion source.

Functioning of the entire contaminant sensor system was tested using the new accumulator cells and test mixtures of contaminants for which sensitivities had been established for the old system. Calibration curves for these contaminants are shown in Figures 4-3 to 4-8, at the end of this section. The calibration data are summarized in Table 4-2. Results for contaminants sorbed on the Porapak Q cell and the charcoal cell agree fairly well with those obtained on the older system. The values listed in Table 4-2 may be compared to those listed in Table 3-1, by dividing the sensitivity of the latter by 1.25, since the new system data are referenced to pure nitrogen while those for the old system are referenced to nitrogen in air. (Nitrogen was chosen as a reference gas for the new system because oxygen/nitrogen ratio for air was initially low for the new system. (No explanation is immediately available for this behavior. After the system is conditioned to air, it yields normal values.) For Porapak Q only the toluene data appear to be significantly different for the new system.

The data obtained for ethylene and nitrous oxide on the Molecular Sieve cell and carbon monoxide on the palladium-charcoal cell indicate a higher sensitivity for the new cells than for the old system. However, the data obtained for these cells is very limited and further tests should be performed with these cells before the difference in sensitivity can be verified. The Molecular Sieve cell appears to be more active for retention of carbon dioxide than the old cell. It is expected that with further use this will change.

Considerable difficulty was experienced in preparing the palladium-charcoal cell. Valves and fittings that were initially vacuum tight developed leaks on heating the cell. It was necessary to assemble the cell several times before it was leak tight, and the nitrogen background was sufficiently low to permit the carbon monoxide determination. During this interval, the sorbent apparently lost some of its capability for retention of carbon monoxide. The sorbent was replaced with a new batch of palladium-charcoal and the cell is shifted about 60°C higher. A test with the old palladium-charcoal cell on the new system

TABLE 4-2

Summary of Test Results, System II

Compound	Cell	Desorption Temperature (°C)	Sensitivity*	(m/e)	Table 3-1 Sensitivity $\left(\frac{1}{1-25}\right)$
Benzene	Porapak Q	160	272	(78)	268
Butene-1	Charcoal	220	198	(41)	195
Ethylene	Molecular Sieve 5A	135	100	(27)	64
Ethylene dichloride	Porapak Q	150	76	(62)	77
Methanol	Charcoal	210	40	(31)	36
Nitrous Oxide	Molecular Sieve 5A	130	18	(30)	12
Toluene	Porapak Q	190	267	(91)	344
Vinyl chloride	Charcoal	150	96	(62)	96
Carbon Monoxide	Palladium-Charcoal	240-260	100	(28)	72

*Divisions/ μℓ(NTP)/1000 Divisions/μN_2

also yielded a higher desorption temperature for carbon monoxide, and this, combined with the fact that the sensitivity is increased, suggests that the pumping speed through the metering valve is lower on the new system. However, it would be expected that the desorption temperatures for other cells would be affected in the same way, and this does not appear to be the case. The test data obtained with the new cell was necessarily limited because of the initial cell problems; it is necessary to obtain more information about this effect before it can be completely understood. Desorption curves for carbon monoxide on the new system are shown in Figure 4-9.

In summary, the test results with the new system show that for most contaminants the information on sensitivity and desorption temperature obtained with the earlier sensor is applicable. The data presented in Table 3-1 can be used in conjunction with the measured sensitivity to nitrogen or air (as described in Section 2) to obtain approximate contaminant concentrations. If more accurate standards for contaminant air mixtures are available, it would be advantageous to calibrate the system with these standards for best performance.

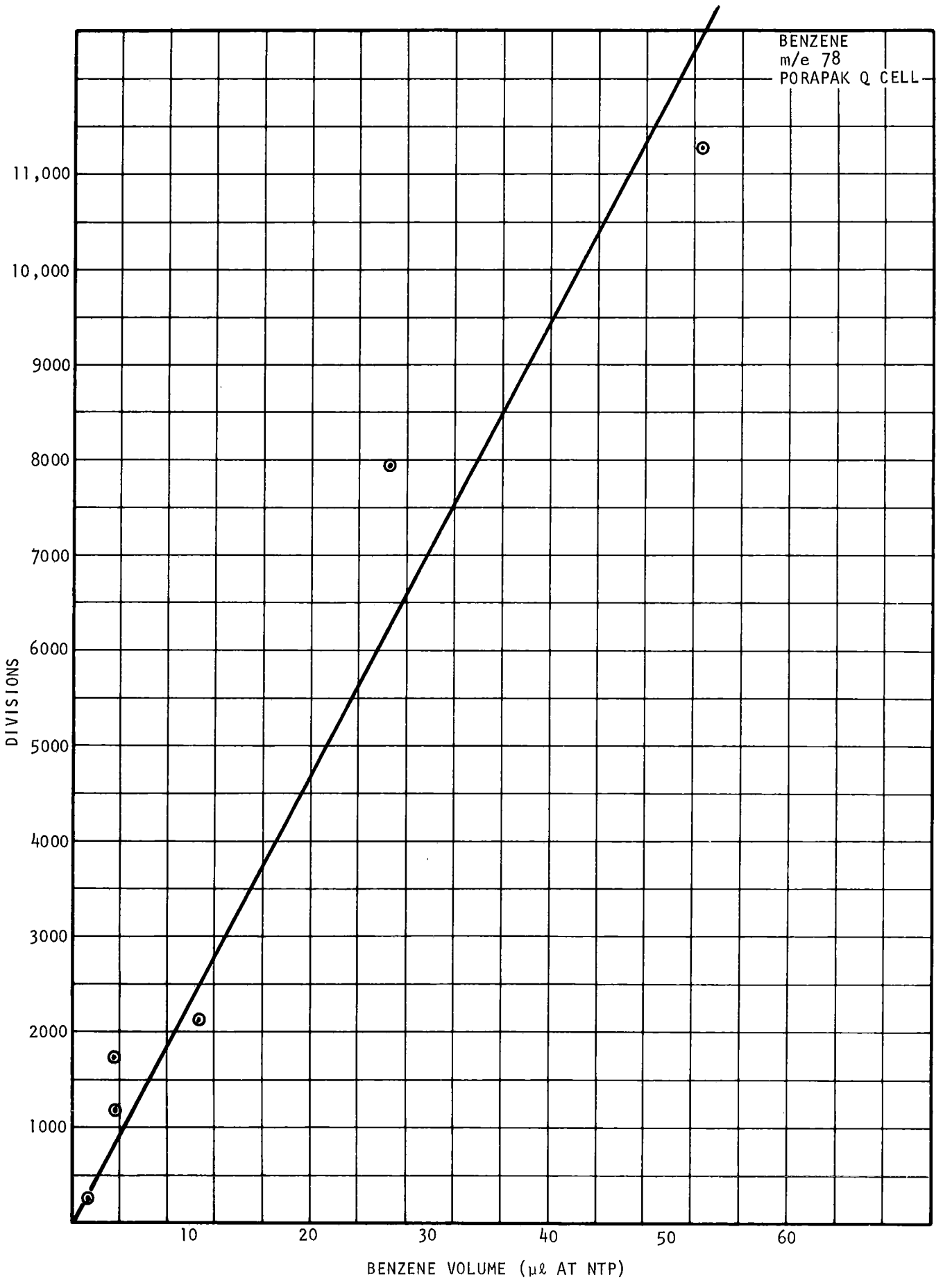

BENZENE
m/e 78
PORAPAK Q CELL
11,000
10,000
9000
8000
7000
6000
5000
4000
3000
2000
1000
DIVISIONS
10
20
30
40
50
60
BENZENE VOLUME (μℓ AT NTP)

FIGURE 4-3

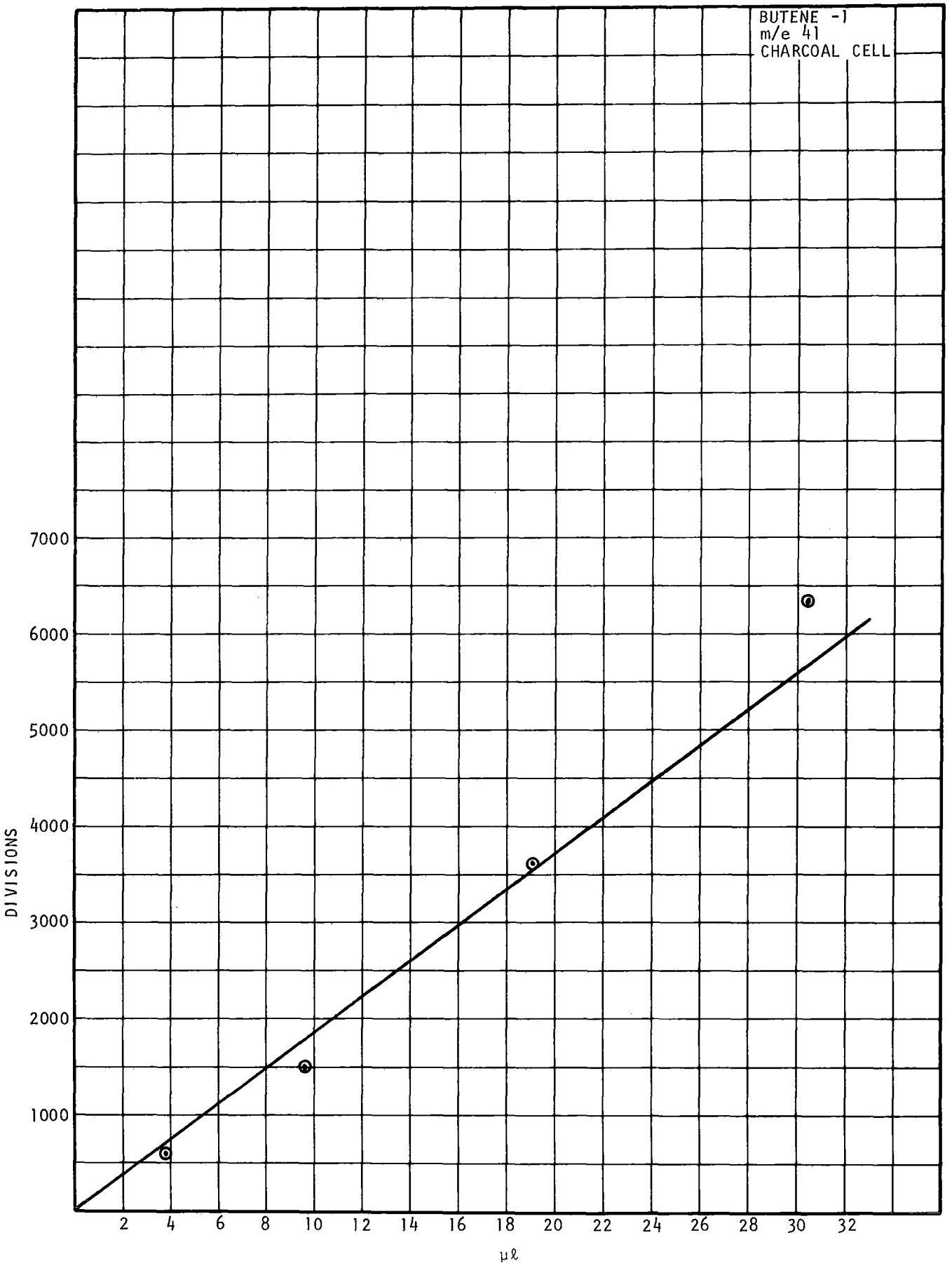

BUTENE -1
m/e 41
CHARCOAL CELL
DIVISIONS
7000
6000
5000
4000
3000
2000
1000
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
µℓ

FIGURE 4-4

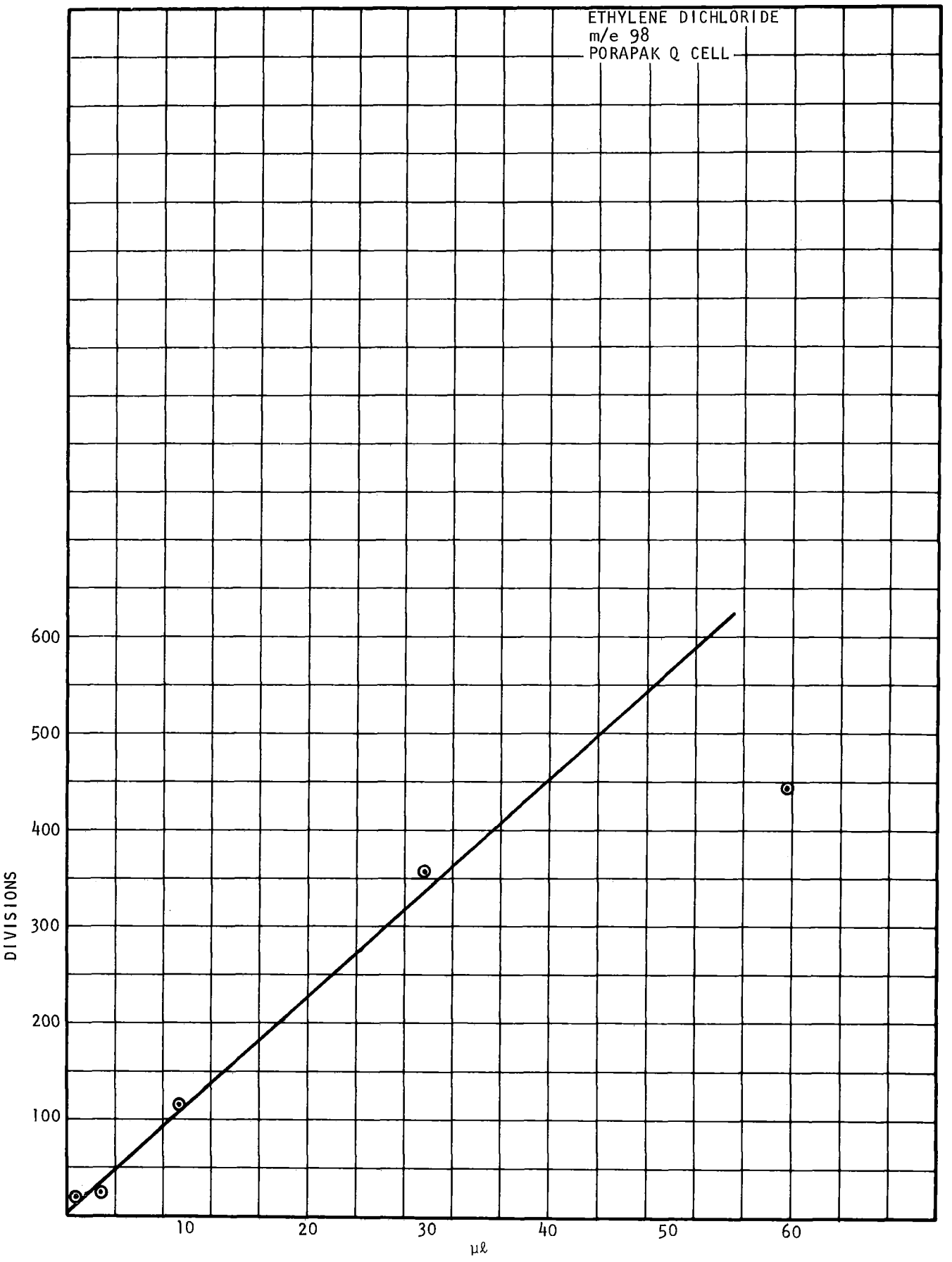

ETHYLENE DICHLORIDE
m/e 98
PORAPAK Q CELL
DIVISIONS
600
500
400
300
200
100
10
20
30
40
50
60
µl

FIGURE 4-5

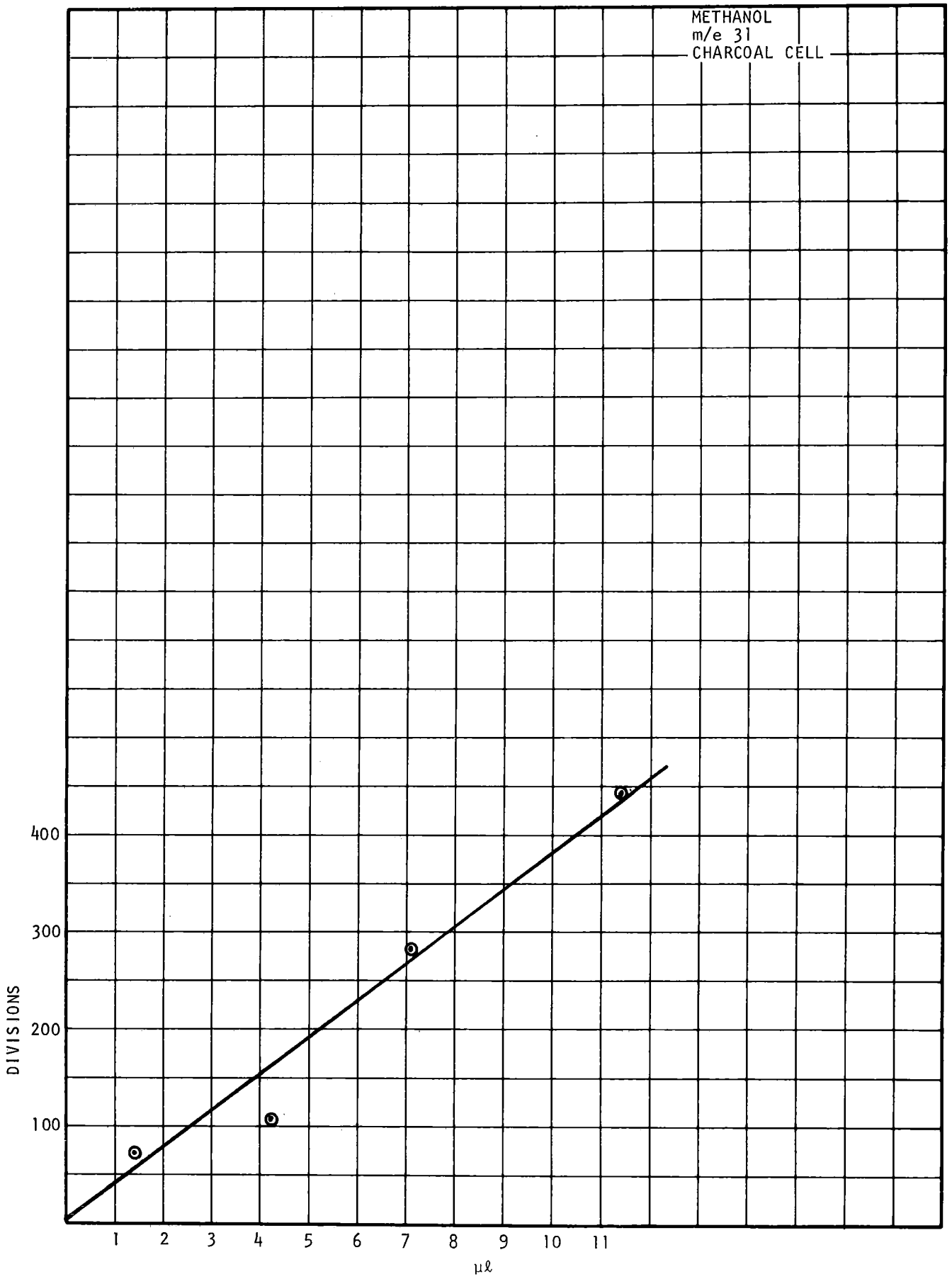

METHANOL
m/e 31
CHARCOAL CELL
DIVISIONS
100
200
300
400
1
2
3
4
5
6
7
8
9
10
11
µℓ

FIGURE 4-6

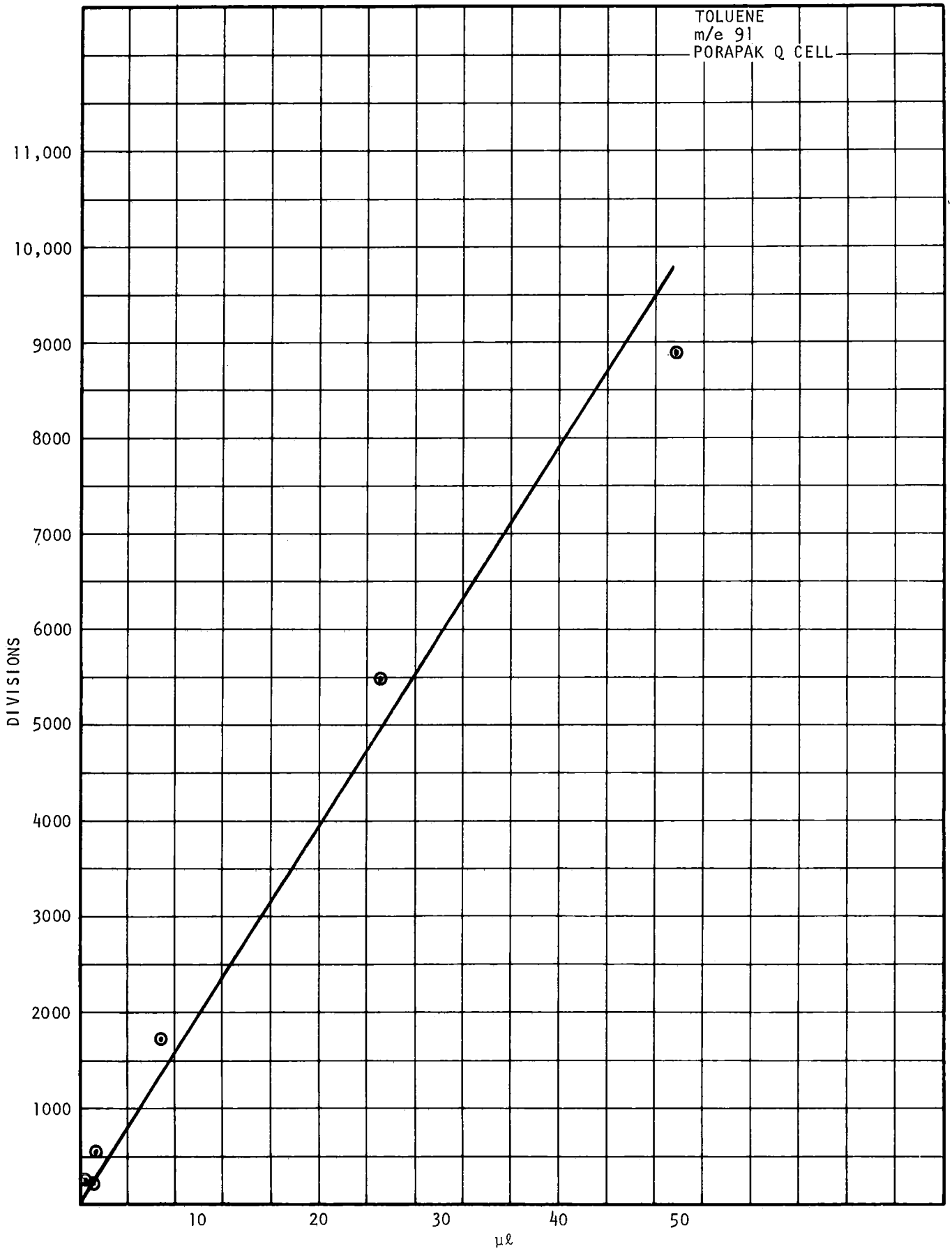

TOLUENE
m/e 91
PORAPAK Q CELL
11,000
10,000
9000
8000
7000
6000
5000
4000
3000
2000
1000
DIVISIONS
10
20
30
40
50
µℓ

FIGURE 4-7

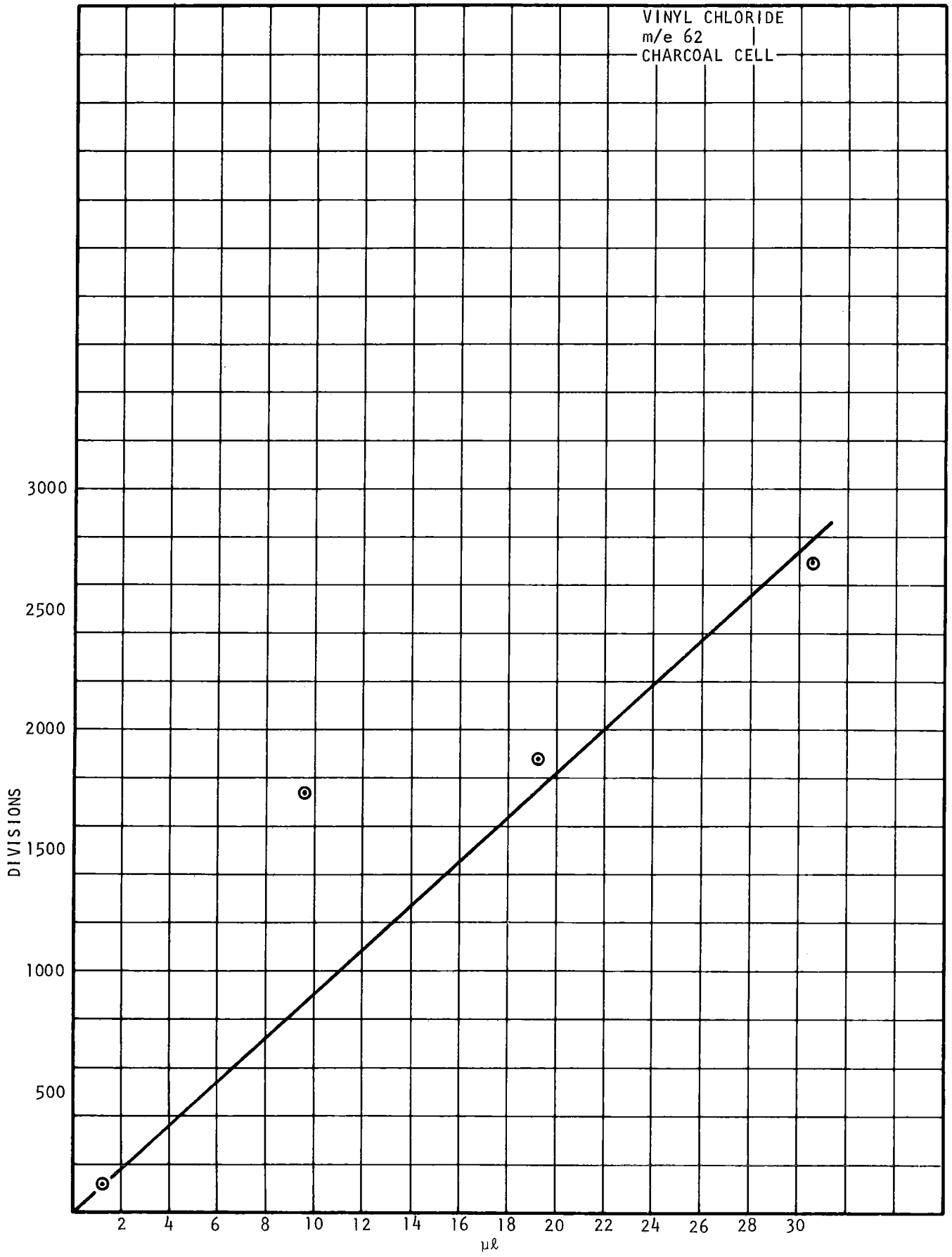

VINYL CHLORIDE
m/e 62
CHARCOAL CELL
DIVISIONS
3000
2500
2000
1500
1000
500
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
µℓ

FIGURE 4-8

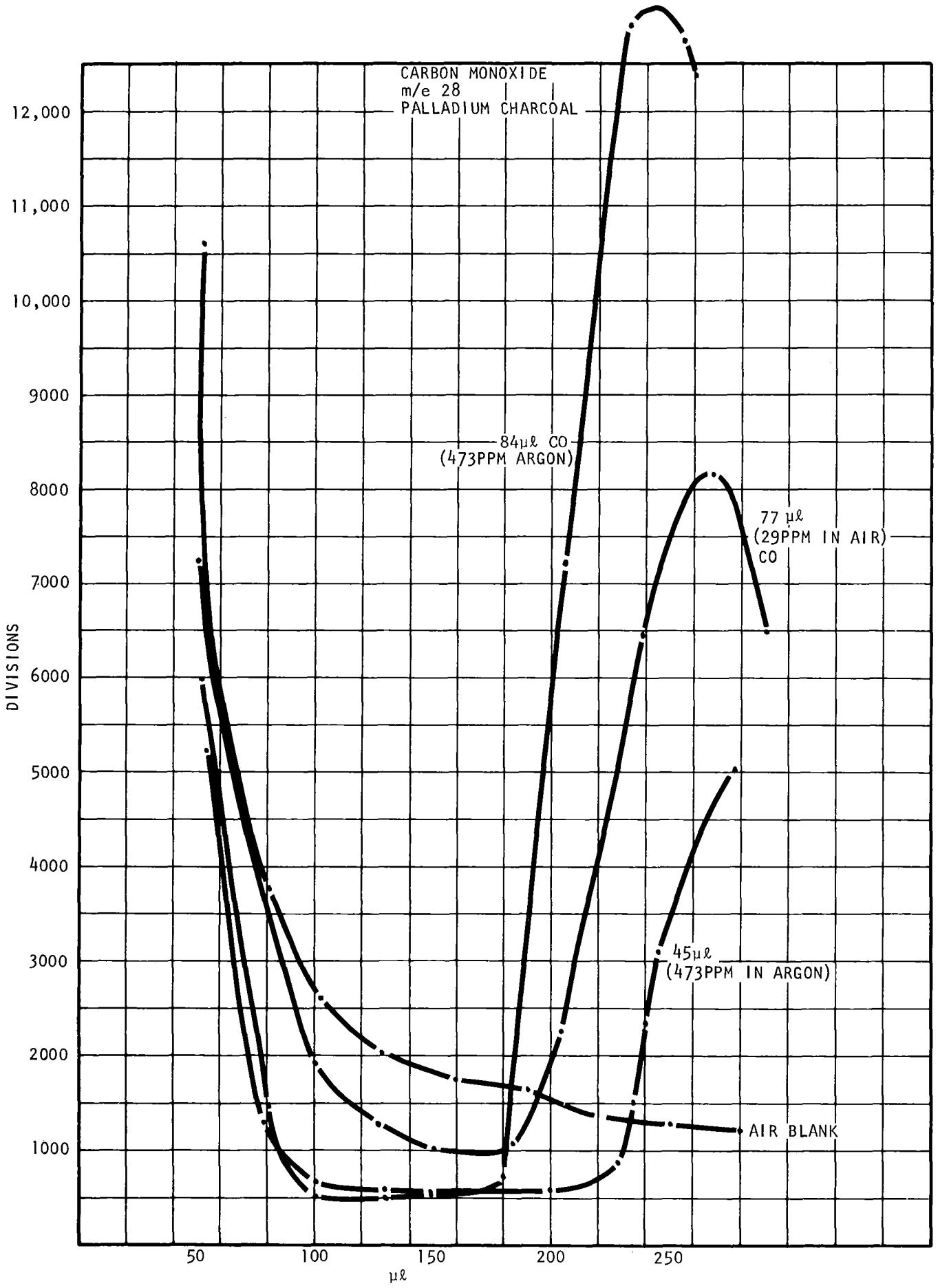

CARBON MONOXIDE
m/e 28
PALLADIUM CHARCOAL
84µℓ CO
(473PPM ARGON)
77 µℓ
(29PPM IN AIR)
CO
45µℓ
(473PPM IN ARGON)
AIR BLANK
DIVISIONS
12,000
11,000
10,000
9000
8000
7000
6000
5000
4000
3000
2000
1000
50
100
150
200
250
µℓ

FIGURE 4-9

5. SUMMARY

Results of this test program with the Laboratory Contaminant Sensor show that it is possible, using sorbent cells containing Porapak Q, charcoal, and Molecular Sieve 5A to extract a wide variety of contaminants from air samples and to effectively concentrate them for quantitative determination by mass spectral analysis. The mass spectra intensity at the maximum observed in the desorption curve appears to be linearly related to the amount of compound sorbed. This linear relationship holds down to concentrations of less than one part per million for many compounds. For certain compounds, notably the alcohols and some sulfur compounds, there appears to be some loss in the system so that the linear relationship fails at concentrations of the order of one to two parts per million.

The error of the overall process of preparing samples and analyzing them with the Laboratory Contaminant Sensor was estimated by calculating the standard deviation of the individual sensitivity measurements for each compound. The standard deviation is about twenty-five percent of the measured value, on the average.

Contaminants are identified by their mass spectral patterns and to a certain extent by their desorption characteristics. For simple contaminant mixtures, the various components can be identified usually by reference to the mass spectral patterns alone. In mixtures containing many contaminants, the mass spectra of the mixture must be interpreted in conjunction with the desorption characteristics of the various compounds. Low voltage ionization has potential use in simplifying the analysis of complex mixtures.

The second Laboratory Contaminant Sensor developed during this program was tested with a representative selection of compounds and appears to function in a manner very similar to the first unit. Comparison of test results on the old and new systems indicates the analytical technique appears well suited for the analysis of contaminants in laboratory environments and readily adaptable to the on-board analysis of contaminants in spacecraft.

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(3) A. Cornu and R. Massot, Compilation of Mass Spectral Data, Heydon and Son, Ltd., London, 1966.

APPENDIX A

CONTAMINANT MIXTURE ANALYSIS

APPENDIX A

CONTAMINANT MIXTURE ANALYSIS

The data generated by the Laboratory Contaminant Sensor - mass spectra of desorbing contaminants as a function of desorption temperature - requires interpretation in order to furnish information concerning the identity and concentration of contaminants in a sample. This interpretation may be relatively simple if only a few contaminants are present but can become quite complex as the number of contaminants increases. Although temperature programming affords some degree of separation between various contaminants, this separation is not enough to permit the mass spectrum at any particular temperature to be assigned to a single compound. Therefore, the analysis of the data is essentially the task of interpreting mass spectra of a mixture of organic compounds, which is changing in composition as the accumulator cell temperature increases. The behavior of a particular mass number or set of mass numbers throughout the temperature program is of some use in the interpretation, but the desorption pattern may become obscure if a large number of compounds are involved. Figures 3-32 and 3-36 show typical desorption curves for prepared mixtures of contaminants.

The interpretation of mass spectra of an unknown compound or mixture of compounds usually starts with the high mass end of the spectrum, by assigning molecular formulas to the most intense peak. If it is known that only a single compound is present, the correctness of the assigned molecular formula (or compound) can be verified by examination of the distribution of fragment ions. Certain fragments will be consistent with one compound but not with another. If a mixture of compounds is present, the choice between two assignments may be less clear-cut because of the presence of parent and fragment ions from other components in the mixture. Only by correctly identifying all the components can the mass spectrum of the mixture be resolved. Catalogs of mass spectra of numerous compounds are available[3] as an aid in interpretation of mass spectral data. Any other information that is available about the nature or origin of the sample can, of course, be of assistance in the analysis.

The analysis of typical mass spectral data generated by the Laboratory Contaminant Sensor is illustrated in the following paragraphs. The mass spectral data obtained on desorption for this particular sample is shown in Table A-1.* The headings at the top of the column show the temperature at which the mass scan was started and the pressure in the inlet system as indicated by a thermocouple gauge. The data for masses 12 through 18 have been omitted from the table, as well as the data for mass 28 and 32 which are due mainly to air in the system. A preliminary inspection of the data shows that most of the mass numbers reach their maximum at temperatures in the range from 130°C to 150°C. Also it may be noted that the

*All tables for this Appendix are included following the text.

most intense peak is that at m/e 43, which may be assigned to the fragment ions CH_3CO or C_3H_7. The acetyl fragment is characteristic of methyl ketones or acetic acid esters, while the C_3H_7 group is prominent in the spectra of many alkanes. The highest mass numbers in the spectra are 130, 132, and 134.

Considering the spectrum obtained at 54°C, the highest mass number observed is m/e 88, which is accompanied by mass numbers 86 and 84. The ratio of these three peaks suggests a compound containing two chlorine atoms. Assuming that mass 84 is the parent mass (masses 86 and 88 are isotope peaks), the difference between 84 and 70 should be representative of the rest of the compound, and this can be immediately recognized as CH_2Cl_2, methylene chloride. The peaks at 49 and 51 correspond to the fragment ions CH_2Cl^{35} and CH_2Cl^{37}. The remainder of the spectrum is consistent with this interpretation; some of the less intense peaks are probably due to other compounds but they cannot be identified at present. Following m/e 84 and 49 across Table A-1, it can be seen that they reach a maximum together in the 107°C scan. This is consistent with the known desorption characteristics of methylene chloride (see Table 3-5). It is also noted that the temperature maximum of m/e 47 (CCl) does not coincide with that of methylene chloride, which suggests the presence of some other compound with a fragment ion at mass 47. Furthermore, it may be noted that the ratios of m/e 84 to 86, and 84 to 88 change as the temperature increases above 107°C. This indicates the presence of other compounds with ions at mass 86 and mass 88.

There is some distortion in the spectrum obtained during desorption, since the temperature, and hence the pressure of the desorbing contaminant, changes during the mass spectral scan. In the initial part of the desorption, the pressure is increasing as the temperature increases and higher mass numbers in a scan are measured at a higher pressure relative to the lower mass numbers. Using a spectrum of methylene chloride obtained at constant pressure to calculate the intensity at mass 49 from the mass 84 peak, for example, will give too high a value for m/e 49. On the average, the temperature change that occurs, as the mass spectrometer scans from m/e 12 to m/e 130, is about 11°C. The change in temperature from the time m/e 49 is scanned until m/e 84 is passed, is about 2°C. The change in the spectrum is estimated to be approximately 2% of the maximum value per °C. Thus a discrepancy of about 40 divisions (4% of 940) is expected in the 49 peak and this is observed.

Proceeding to the next scan starting at 75°C (Table A-1), the methylene chloride spectra is increasing in intensity, and peaks appear at masses 57 and 31. These latter peaks are too close to the noise level to attach any significance to them at present.

In the scan at 107°C, new peaks appear at mass numbers 130, 132, and 134. From Table 3-5, these mass numbers can only be attributed to trichloroethylene. There are, of course, a large number of compounds which have fragment ions in this mass group. However, the desorption temperature is relatively low for such a high mass number; this is believed to be typical of halogenated compounds on Porapak Q. Many substituted aromatic compounds have fragment ions in this mass range but such compounds would be expected to have much higher desorption temperatures. Assuming these peaks are due to trichloroethylene, and represent the

start of the desorption of trichloroethylene, one expects peaks at 95, 97, and 99 and at 60, and these peaks are present. However, the ratio m/e 95/97 is less than expected for trichloroethylene. If there are 10 divisions at m/e 130 due to trichloroethylene one would expect to find about 10 divisions or less at m/e 95, depending on the desorption time. Since there are 10 divisions at m/e 95, one expects to find about 6 divisions at m/e 97, but instead there are 15. About 9 divisions of m/e 97 are due to some other compound. From Table 3-5, this could be due to 1,1,1-trichloroethane or furfuryl alcohol. However, for furfuryl alcohol there should be a peak at 98, but there is none. So it can be tentatively concluded that the spectra is due to trichloroethane. Subtracting the contribution to the spectra resulting from these two compounds and methylene chloride, which is still present (ignoring temperature effects for a first approximation and ignoring peaks less than 10 percent of the spectra for trichloroethylene and 1,1,1-trichloroethane), the residual spectra shown in Table A-2, column 5, is obtained. Methylene chloride contribution is based on the m/e 84 peak.

The residual spectra after subtracting the contribution attributed to methylene chloride, trichloroethylene, 1,1,1-trichlorothane has its major peaks at mass 43 and 83, with smaller peaks at 54, 57, 61, 70, 72 and 88. Mass 83 is assigned to chloroform since this is the only compound in Table 3-5 which is consistent with the rest of the spectra. After subtraction of the chloroform contribution, the spectra shown in the last column of Table A-2 results. Mass 43 peak is most intense in the residual spectra and could be due to a number of compounds. Considering only those listed in Table 3-5, acetone can be ruled out, since the 58 peak would be expected to be considerably larger and acetone should have appeared higher initially because its desorption curve has its maximum at about 110°C. Methylacetate, methyl ethyl ketone, 2-methoxyethanol, ethyl acetate, butyraldehyde, and possibly, n-hexane, are potential candidates. Methyl isopropyl ketone would not be expected to show up in the spectra at this low temperature. The intensity of the smaller peaks are consistent with several of these compounds and, therefore, no assignment is made at this time. Instead, it is more profitable to consider the next temperature scan to see how the intensities are changing as a function of temperature.

The original spectra, at 130°C, is shown in column 2 of Table A-3. After eliminating methylene chloride, trichloroethylene, 1,1,1-trichloroethane, and chloroform, the spectra presented in column 3 of Table A-3 remains. In this residual spectra masses 86 and 88 stand out clearly, as do the group at 70-73. The peak at 61 is significant, as are the peaks in the 54 to 59 group. The 43 peak stands out as the largest peak in the spectra. Starting from the high mass end of the spectra, the two compounds in Table 3-5 that have an 88 peak are ethyl acetate and dioxane. If the 88 peak were entirely due to ethyl acetate, the mass 61 peak should be roughly four times as large as mass 88. On this basis, mass 88 can be tentatively assigned to dioxane. Referring to Table A-1, the mass 88 peak appears to reach a maximum around 165°C; this would be expected for either ethyl acetate or dioxane. Subtracting the dioxane spectra on the basis of the 88 peak height leads to the spectra shown in column 4 of Table A-3. The large negative value at m/e 58 is suspicious that the assignment is wrong or that part of mass 88 comes from a compound which does not yield a 58 peak. Allowing the assignment to stand, the next mass to be considered is m/e 86.

Mass 86 can be due to either n-hexane or methyl isopropyl ketone from Table 3-5. Both compounds could contribute substantially to m/e 43; however, n-hexane would be expected to have large peaks at m/e 56 and 57 and these peaks are small relative to the 86 peak. If m/e 86 is to be attributed to methyl isopropyl ketone, then, there should be a peak at mass 71, about one-third its size, and the value of 29 is correct. Mass 43 is large enough to include methyl isopropyl ketone and some other compound. Eliminating the contribution of methyl isopropyl ketone to the spectra, the residual spectra is shown in column 5. (If mass 86 had been assigned to n-hexane, deficits at mass 56 and 57 would have been about 650 and 1200, respectively.)

Proceeding through the spectra, mass 73 is the next to be considered. There are nine compounds that can give rise to mass 73; of these benzene, chlorobenzene, and propyl mercaptan can be eliminated at once because of the absence of m/e 76, 77, and 78. Ethyl formate and diethyl ether should have shown up earlier in the desorption run and should not be peaking in this temperature range. Butanol, butyraldehyde, ethyl acetate, and tetrahydrofuran remain. Butyl acetate is considered unlikely since the m/e 73 reaches a maximum between 140 and 165°C and the maximum for butyl acetate would be expected at higher temperatures.

The possibilities to be considered are; butanol, butyraldehyde, ethyl acetate, and tetrahydrofuran.

The maximum amount of m/e 73 that could be assigned to butyraldehyde is (2.6/44.8) x 93, or 5 divisions, from the 72 peak. On the basis of m/e 56, none of 73 can be due to butanol. From m/e 61, 18 divisions of 63 can be ethyl acetate. From m/e 72, only 3 divisions of m/e 73 can be due to tetrahydrofuran. These considerations imply that ethyl acetate is the most likely candidate for m/e 73, although contributions from two other compounds, butyraldehyde and tetrahydrofuran, cannot be completely eliminated.

At mass 72, candidates are methyl ethyl ketone, butyraldehyde, tetrahydrofuran, and butanol. The absence of mass 71 implies that tetrahydrofuran is not a likely candidate. The ratio of 57/72 appears about right for either butyraldehyde or methyl ethyl ketone; the small value at m/e 41 casts doubt on butyraldehyde. The large 43 peak is consistent with either butyraldehyde or methyl ethyl ketone.

Tentatively then, the compounds in the m/e 70-74 group may be assigned to ethyl acetate and methyl ethyl ketone. Subtracting these compounds from the spectrum in column 4 of Table A-3 yields the spectrum shown in column 6. For most accurate results, the dioxane spectra should be refigured for the ethyl acetate contribution to mass 88, but for the moment, this minor correction (10 percent) will be omitted. The ethyl acetate subtraction is based on m/e 61 rather than 73, since the 61 peak is larger.

Many of the lower mass numbers now show deficit as a result of subtraction from higher mass numbers on the ascending side of the desorption curve. In other words, when the lower mass numbers were scanned, the pressure of the contaminants was increasing in the system. Conversely, it appears that methylene

chloride is undercorrected; that is, the large residuals at mass 49 and 51 are due to the fact that the partial pressure of methylene chloride had decreased when mass 84 was scanned. Basing the calculation for ethyl acetate on m/e 61 undercorrects the mass numbers greater than 61. This effect can interfere with detection of low concentrations of other contaminants.

Continuing the analysis of the scan started at 130°C, the remaining mass numbers which should be considered are mass 59, 56, 55, 45, 43, and 42. It is assumed that the 49 and 51 masses result from methylene chloride, although m/e 51 appears high for the chlorine isotope peak. Cyclohexane, butanol, and n-hexane all have major peaks at mass 56. But none of these will account for mass number 45. The only compound with a large m/e 45 is 2-propanol, but the maximum in its desorption curve is at 120°C. Thus, its maximum should appear to occur between 107 and 130°C. However, the peak at mass 45 appears to occur between 130 and 155°C scans, but the spectra is not symmetrical. At the 175°C scan, the value is 159 instead of 40-50 divisions, as might be expected for a single compound. It could be that this peak receives contributions from two compounds with different desorption temperatures, and that the residual at 130°C is due to 2-propanol. Thus, at this point, it is difficult to assign the residual spectra to any other compounds, but it appears that potential candidates are cyclohexane, n-hexane, n-butanol and 2-propanol.

Proceeding in the same manner for the mass scan at 155°C, the spectrum shown in Table A-4 results. Choice between butyraldehyde and methyl ethyl ketone for the assignment of mass 72 is not possible within this mode of identification. The only possible basis is the fact that with butyraldehyde assigned to m/e 72, the residual at 43 is relatively high and there are no other low molecular weight compounds available to account for the residuum within the framework of analysis. Acetone should have been recognized earlier. The other argument in favor of methyl ethyl ketone is that no additional negative numbers are introduced into the spectrum, and this is consistent with being on the descending side of this compound's desorption curve, noting that m/e 72 peaked in the prior desorption run.

Choice of butanol at mass 56 is also arbitrary. The temperature profile of mass 56 shows a maximum between the scan starting at 130° and the scan starting at 155°C; for mass 56, this means the peak is occurring in the region of 138°C to 163°C. This is low for butanol, but m/e 31, which is a strong indication of the presence of an alcohol, is reaching its maximum at too high a temperature to be any one of the three carbon alcohols or by diethyl ether. Ethylene glycol is the only other contaminant in this region which would yield a substantial peak at mass 31, but the intensity at m/e 33 is too low to attribute the 31 peak to this compound. If 31 is assigned to butanol, the spectra shown in the last column of Table A-4 results. The residual at masses 41 through 45 is higher than desirable; the values at masses 55 and 57 are consistent with background spectra. Assuming the residual at m/e 43 corresponded to an unknown methyl ketone, its concentration is expected to be of the order of 0.2 ppm.

The results of similar calculations for the scan 175°C are shown in Table A-5. The residuals in the mass 40-50 group are rather higher than desirable, but probably reflect the errors resulting from calculations based on higher mass

number, low intensity peaks which are on the trailing edge of the desorption curve. The mass numbers 85 and 87 in Table A-5 suggest that there is another contaminant present, which is not listed in Table 3-5. Small peaks appearing in the remaining scans are the end of the desorption curves. The peaks at m/e 63, 65, 91, 104, 116, and 136, which occur in the final scan at 230°C, are characteristic of the decomposition products of Porapak Q. The cell used had been heated above 230°C in earlier runs and the mass numbers appear to be associated with the divinylbenzene polymer degradation. The contaminants identified in the mixture are:

a. Methylene chloride

b. Trichloroethylene

c. 1,1,1-trichloroethane (Methylchloroform)

d. Chloroform

e. Dioxane

f. Methyl isopropyl ketone (MIPK)

g. Methyl ethyl ketone (MEK)

h. Ethyl acetate

i. n-Butanol

The amount of each contaminant present is calculated from the maximum value observed during the desorption using the sensitivity for each compound listed in Table 3-1. These calculations are summarized in Table A-6.

The greatest errors which appear in the analysis are those for trichloroethane and ethyl acetate. This particular set of errors suggests that the trichloroethane spectral data are in error since ethyl acetate is calculated from mass 61 after subtracting the trichloroethane contribution to this mass number. The other errors are believed to be within the accuracy with which sensitivities can be determined from prepared mixtures.

The method of qualitative identification is essentially the technique used for the analysis of mixtures by mass spectrometry. The additional information afforded by programmed temperature desorption from the cell is valuable to a certain extent in choosing between alternative compounds, but the mass spectral data itself provides the most important information.

The above discussion is confined for the most part, to considerations of compounds which were studied in the test program. Obviously, there are a large number of other potential contaminants which may be considered. The ability of this technique to provide for qualitative identification of these will depend on the complexity of the mixture in which they occur and their relative concentration in the mixture. These factors are discussed in Section 3 of this report.

TABLE A-1

Mass Spectral Data From A Mixture Analysis

Temperature °C		54	75	107	130	155	175	204	230
Pressure Inlet		52μ	12μ	14μ	20μ	20μ	14μ	9μ	9μ
m/e	24					14	8		
	25				27	64	39		
	26			16	99	150	62	10	10
	27	8	6	44	280	440	205	31	29
	29	40	42	135	480	560	240	93	93
	30	10	10	18	60	117	81	39	35
	31		4	12	96	171	87	18	16
	33				4				
	34	4		4	4				
	35	12	36	70	114	102	38		
	36	4	10	18	26	23	11		
	37		16	24	38	37	15		
	38			8	18	26	11		
	39			8	43	96	42	14	28
	40	60	54	64	105	41	36	34	38
	41	18	44	72	168	250	129	24	26
	42	12	28	60	144	153	57	17	15
	43	13	18	440	2325	2800	1035	108	42
	44	36	48	114	183	230	210	240	320
	45	6	8	42	183	183	159	23	25
	46	4	4		7	8			
	47	22	74	174	219	144	37		
	48	14	44	90	108	58	13		
	49	204	600	940	500	78	13		
	50	8	20	40	41	25	7		
	51	57	192	280	150	16	7	10	22
	52			8	6				
	53				7				
	54			10	11				
	55			5	14	19	12		
	56			5	32	40	17		
	57		8	20	62	70	29	16	17
	58			5	96	170	81	10	
	59			4	10	22	13		
	60			5	57	114	51		
	61			34	126	156	50		
	62				20	35	18		
	63				16	25	11		10
	64						6		11
	65					12	6		13
	66					10	7		
	70			18	61	47	9		
	71			5	29	44	20		
	72			42	93	38	8		
	73			12	36	30	8		
	74			3					
	77								19

TABLE A-1 (Continued)

Temperature °C		54	75	107	130	155	175	204	230
Pressure Inlet		52μ	12μ	14μ	20μ	20μ	14μ	9μ	9μ
m/e	82		4	10	18	16			
	83	4	12	192	410	260	35		
	84	126	340	480	195	18			
	85	4	10	132	260	183	24		
	86	78	222	300	204	156	52		
	87			24	42	37	18	14	
	88	14	34	58	153	183	72		
	91							10	28
	94					15			
	95			10	147	225	104	7	
	97			15	171	245	104	7	
	99			8	69	96	34		
	104								11
	106								12
	116								34
	117				23	26	17		
	118								168
	119				15	20	10		
	130			10	144	216	93		
	132			10	132	204	90		
	134			5	34	53	46		

TABLE A-2

107°C Scan

m/e	Original Spectra	Methylene Chloride (m/e 84)	Trichloro ethylene (m/e 130)	Trichloro ethane (m/e 97)	Chloro-form (m/e 83)
26	16				
27	44				
29	135	135	135	135	135
30	18	18	18	18	18
31	12	12	12	12	12
32	840				
34	4				
35	70	5	4	4	-30
36	18	3	3	3	- 1
37	24	5	5	5	- 2
38	8	3	3	3	3
39	8	8	8	8	8
40	64	64	64	64	64
41	72	-4	-4	-4	-4
42	60	18	18	18	18
43	440	399	399	399	399
44	114	114	114	114	114
45	42	42	42	42	42
47	174	41	40	40	-22
48	90	14	14	14	-17
49	940	-40	-40	-40	-60
50	40	12	12	12	4
51	280	-12	-12	-12	-12
52	8	8	8	8	8
54	10	10	10	10	10
55	5	5	5	5	5
56	5	5	5	5	5
57	20	20	20	20	20
58	5	5	5	5	5
59	4	4	4	4	4
60	5	5	1	0	0
61	34	34	34	29	29
63				-2	-2
70	18	18	18	18	18
71	5	5	5	5	5
72	42	42	42	42	42
73	12	12	12	12	12
74	3	3	3	3	3
82	10	5	5	5	0
83	192	180	180	180	-0-
84	480	0	0	-5	-10
85	132	119	119	119	7
86	300	0			
87	24	20	20	20	-1
88	58	57	13	13	13

TABLE A-2 (Continued)

m/e	Original Spectra	Methylene Chloride (m/e 84)	Trichloro ethylene (m/e 130)	Trichloro ethane (m/e 97)	Chloro-form (m/e 83)
95	10	10	-1	-1	-1
97	15	15	8	0	0
99	8	8	7	2	2
130	10	10	0		
132	10	10	0		
134	5	5	2		
136	5	5	5		

TABLE A-3

130°C Scan

m/e	Original Spectra (1)	Residual Spectra (2)	Dioxane (3)	MIPK (4)	Ethyl Acetate (5)	MEK (6)
25	27	-20	-15			
26	99	55	22	-4	-16	-23
27	280	250	190	80	23	-93
29	480	474	313	288	170	28
30	60	57	-14	-28	-14	-14
31	96	95	8	8	3	3
33	4	4	4	4	4	4
34	4	4	4	4	4	4
35	114	-5	3	3	3	3
36	26	3	11	11	11	11
37	38	4	-6	-6	-6	-6
38	18	14	18	18	18	18
39	43	43	43	-3	-3	-3
40	105	105	105	105	105	105
41	168	133	154	41	12	12
42	144	127	136	93	65	42
43	2325	2321	2271	1356	781	236
44	183	183	171	159	86	73
45	183	183	168	157	74	68
46	7	7	7	7	7	7
47	219	0	3	3	3	3
48	108	5				
49	500	50	50	50	50	50
50	41	9	9	9	9	9
51	150	32	32	32	32	32
52	6	6	6	6	6	6
53	7	7	7	7	7	7
54	11	11	11	2	-5	-5
55	14	14	14	14	14	14
56	32	32	32	32	32	32
57	62	62	32	29	29	-2
58	96	96	-33	-33	-33	-33
59	10	1	1	1	1	1
60	57	-12	-11	-11	-11	-11
61	126	50	69	69	0	0
62	20	-4	-1			
63	16	-8				
64		7				
65		-6				
66		-6				
70	61	61	61	61	28	28
71	29	29	29	1	1	1
72	93	93	93	93	78	0
73	36	36	36	36	21	21

TABLE A-3 (Continued)

m/e	Original Spectra (1)	Residual Spectra (2)	Dioxane (3)	MIPK (4)	Ethyl Acetate (5)	MEK (6)
82	18	-29				
83	410	0				
84	195	-12				
85	260	-5	-30	-30		
86	204	84	84	0		
87	42	-1	-7	-7		
88	153	136	0	0	-15	
95	147	-16				
97	171	-32				
99	69	-10				
117	23	0				
119	15	-7				
130	144	0				
132	132	-8				
134	34	-9				

TABLE A-4

155°C Scan

m/e	Original Spectra	Trichloro-ethylene	Trichloro-ethane	Chloro-form	Methylene Chloride	Dioxane	Methyl Isopropyl Ketone	Ethyl Acetate	Methyl Ethyl Ketone	Butanol
24	14	3	1	1	1					
25	64	12	0							
26	150	150	110	110	110	70	45	30	20	18
27	440	440	412	412	412	334	154	85	32	6
29	560	560	555	555	555	355	330	185	125	109
30	117	117	115	115	115	27	27	27	27	26
31	171	171	169	169	169	63	63	55	55	0
32	195	195								
35	102	71	58	21	13	13	13	13	3	
36	23	18	13	7	6	6	6	6	6	
37	37	27	22	12	10	10	10	10	10	5
38	26	26	24	24	24	24	24	24	24	22
39	96	96	96	96	96	96	20	15	15	8
40	41	41	41	41	41	41	41	41	41	40
41	250	250	250	224	248	248	63	51	51	18
42	153	153	153	153	153	147	78	43	32	15
43	2800	2800	2800	2800	2800	2738	1153	453	197	165
44	230	230	230	230	230	215	179	157	151	149
45	183	183	183	183	183	165	149	48	48	45
46	8	8	8	8	8	8	8	8	8	
47	144	117	112	23	6	8	8	8	8	
48	58	50	50	6	0					
49	78	69	67	-8	-24	22	22	22	22	
50	25	22	22	10	10	22	22	22	22	
51	16	16	16	16	11	10	10	10	10	
54						-15	-15	-15	-15	
55	19	19	19	19	19	19	19	19	19	14
56	40	40	40	40	40	40	40	40	40	-3
57	70	70	70	70	70	31	31	31	16	13
58	170	170	170	170	170	15	15	15	15	15
59	22	8	8	8	8	8	8	8	8	8
60	114	14	5	5	5	5	5	5	5	5
61	156	150	84	84	84	84	84	0		
62	35	8	2	2	2	2	2	2	2	2
63	25	25	3	3	3	3	3	3	3	3
65	12	2	2	2	2	2	2	2	2	2
66	10	1	1	1	1	1	1	1	1	1
67		-3	-3	-3						
70	47	47	47	47	47	47	47	7	7	7
71	44	44	44	44	44	44	-5	-5	-5	-5
72	38	38	38	38	38	38	38	38	0	0
73	30	30	30	30	30	30	30	11	11	11
82	16	12	12	4	3	3	3	3	3	
83	260	257	257	0						
84	18	16	16	8	0	0	0			
85	183	183	183	23	23	23	23	23	23	

TABLE A-4 (Continued)

m/e	Original Spectra	Trichloro-ethylene	Trichloro-ethane	Chloro-form	Methylene Chloride	Dioxane	Methyl Isopropyl Ketone	Ethyl Acetate	Methyl Ethyl Ketone	Butanol
86	156	156	156	156	151	149	0			
87	37	37	37	10	10	0				
88	183	183	183	183	182	18	18	0	0	
94	15	3	3	3	3	3	3	3	3	
95	225	-7								
97	245	91	0	0						
99	96	74	15	15	15	15	15	15	15	
117	26	5								
119	20	-2								
130	216	0								
132	204	-6								
134	53	-15								

TABLE A-5

175°C Scan

m/e	Original Spectra	Trichloro ethylene	1,1,1-Trichloro-ethane	Dioxane	MIPK	MEK	Ethyl Acetate	Butanol
24	8	3	3	3	3	3	3	3
25	39	16	11	11	11	11	11	11
26	62		45	28	20	18	14	12
27	205		193	159	92	85	69	47
29	240		238	151	146	133	99	86
30	81		81	42	42	42	42	42
31	87		87	41	41	41	41	0
33								-3
35	38	25	19	19	19	19	19	19
36	11	9	7	7	7	7	7	7
37	15	11	9	9	9	9	9	9
38	11		11	11	11	11	11	11
39	42		42	42	14	14	14	9
40	36		36	36	36	36	36	36
41	129		129	129	61	61	61	34
42	57		57	57	31	29	21	7
43	1035		1035	1007	454	398	231	206
44	210		210	208	195	195	191	191
45	159		159	151	146	146	122	120
47	37	25	23	23	23	23	23	23
48	13	10	13	13	13	13	13	13
49	13	9	8	8	8	8	8	8
50	7	6	7	7	7	7	7	7
51	7	7	7	7	7	7	7	7
54					-5	-5	-5	-5
55	12		12	12	12	12	12	8
56	17		17	17	17	17	17	-18
57	29		29	12	12	9	9	7
58	81		81	13	13	13	13	13
59	13	7	7	7	7	7	7	7
60	51	8	5	5	5	5	5	5
61	50	47	20	20	20	20	0	
62	18	7	4	4	4	4	4	4
63	11	11	2	2	2	2	2	2
64	6		6	6	6	6	6	6
65	6	2	2	2	2	2	2	2
66	7	3	3	3	3	3	3	3
70	9		9	9	9	9	-1	-1
71	20		20	20	3	3	3	3
72	8		8	8	8	0		
73	8		8	8	8	8	4	4
82		-1	-1	-1	-1	-1	-1	-1

TABLE A-5 (Continued)

m/e	Original Spectra	Trichloro-ethylene	1,1,1-Trichloro-ethane	Dioxane	MIPK	MEK	Ethyl Acetate	Butanol
83	4	3	3	3	3	3	3	3
84		-1	-1	-1	-1	-1	-1	
85	24	24	24	24	24	24	24	24
86	52	52	52	52	0	0		
87	18	18	18	14	14	14	14	14
88	72	72	72	0	0	0		
95	104	0	0					
97	104	38	0					
99	34	25	0					
117	17	7						
119	10	2						
130	93	0						
132	90	0						
134	46	18						

TABLE A-6

Calculation of Concentration of Contaminants

Compound	Sensitivity (m/e)		Peak Temperature Found	Peak Temperature (Table 3-1)	Peak Divisions	Amount (µl)
Methylene chloride	100	(84)	(112)		480	4.8
Trichloroethylene	120	(130)	162	160-170	216	1.8
1,1,1-Trichloroethane	84	(97)	162	160	91	1.1
Chloroform	144	(83)	140	150	403	2.8
Dioxane	76	(88)	160	165-170	164	2.2
Ethyl acetate	60	(61)	164	150-160	84	1.4
Methyl ethyl ketone	66	(72)	138	135-150	78	1.2
Methyl isopropyl ketone	70	(86)	163	165	149	2.1
n-Butanol	50	(31)	160	160	55	1.1

Compound	(Found)*	Concentration (Calculated)** ppm
Methylene chloride	1.6	1.7
Trichloroethylene	0.62	0.60
1,1,1-Trichlorothane	0.37	0.51
Chloroform	0.96	0.78
Dioxane	0.76	0.81
Ethyl Acetate	0.49	0.73
Methyl ethyl ketone	0.42	0.41
Methyl isopropyl ketone	0.73	0.59
n-Butanol	0.35	0.27

* Sample volume 2.9 liters

**Based on prepared mixture

APPENDIX B

TABLES OF MASS SPECTRAL DATA

TABLE B-1

Acetone

m/e	70 eV	8 eV
12	.009	
13	.022	
14	.089	
15	.410	
16	.006	
17	.007	
18	.026	
19	.004	
19.5	.003	
20	.002	
24	.004	
25	.012	
26	.054	
27	.081	.01
28	.032	.027
29	.048	.038
30	.003	
31	.007	
32	.003	
36	.004	
37	.016	
38	.017	
39	.031	
40	.007	
41	.018	
42	.068	.01
43	1.000	1.0
44	.025	.03
45	.003	.01
52	.002	
53	.003	
55	.002	
57	.008	
58	.305	.8
59	.013	.025
60	.002	
	*S = 1.3	

*Relative sensitivity to nitrogen (mass 28) in air.

TABLE B-2

Allyl Alcohol

m/e	70 eV	8 eV
12	.013	
13	.017	
14	.038	.009
15	.059	.110
16	.004	
17	.006	
18	.010	.021
19	.009	.007
19.5	.003	
20	.003	
24	.007	
25	.032	
26	.168	.012
27	.407	.053
28	.306	.461
29	.566	.636
30	.279	.901
31	.622	.246
32	.033	.045
33	.002	
36	.008	
37	.040	
38	.055	
39	.327	.026
40	.099	.127
41	.067	.024
42	.020	.013
43	.046	.033
44	.003	
45	.004	.002
52	.003	
53	.013	
54	.003	.005
55	.045	.002
56	.005	.006
57	1.000	1.000
58	.271	.506
59	.009	.003
60	.003	
	S = .58	**R = .064

**Relative sensitivity in the low voltage mode to high voltage mode

TABLE B-3

Benzene

m/e	70 eV	8 eV
12	.003	
13	.002	
14	.002	
15	.004	
16	.001	
17		.002
18		.016
24	.001	
25	.004	
26	.027	
27	.028	
28	.006	
31	.001	
36	.004	
36.5	.001	
37	.039	
37.5	.016	
38	.068	
38.5	.005	
39	.185	
39.5	.004	
40	.004	
43	.001	
48	.002	
49	.018	
50	.153	
51	.181	
52	.212	
53	.008	
60	.002	
61	.004	
62	.005	
63	.022	
64	.002	

TABLE B-3 (Continued)

m/e	70 eV	8 eV
72	.001	
73	.012	
74	.036	
75	.014	
76	.032	
77	.168	
78	1.000	1.000
79	.066	.061
80	.001	
	S = 1.7	R = .057

TABLE B-4

Butane

m/e	70 eV	8 eV
12	.001	
13	.002	
14	.009	
15	.038	.002
18		.008
25	.005	
25.5	.006	
26	.050	.002
27	.352	.085
28	.350	.458
29	.457	.355
30	.009	.006
32	.003	.001
36	.002	
37	.007	
38	.013	
39	.108	
40	.012	
41	.274	.042
42	.123	.128
43	1.000	1.000
44	.033	.032
49	.003	
50	.010	
51	.008	
52	.002	
53	.006	
54	.002	
55	.007	
56	.008	.003
57	.021	.008
58	.113	.079
59	.004	.005
	S = 1.6	R = .17

TABLE B-5

n-Butanol

m/e	70 eV	8 eV
12	.003	
13	.005	
14	.020	
15	.076	.014
16	.003	.002
17	.003	.001
18	.007	.019
19	.039	.053
25	.006	
26	.051	
27	.515	.127
28	.227	.166
29	.318	.113
30	.020	.009
31	1.000	1.000
32	.025	.016
33	.084	.160
34	.003	.002
37	.011	
38	.020	
39	.139	
40	.033	.011
41	.656	.273
42	.341	.263
43	.638	.405
44	.057	.045
45	.059	.018
46	.006	.005
51	.007	
52	.002	
53	.010	
54	.002	
55	.114	.042
56	.853	.825
57	.059	.041

TABLE B-5 (Continued)

m/e	70 eV	8 eV
58	.003	
59	.003	
69	.003	
70	.002	
71	.003	
72	.011	.008
73	.013	.005
74	.008	.004
	S = .92	R = .16

TABLE B-6

Butene-1

m/e	70 eV	8 eV
12	.004	
13	.005	
14	.012	.002
15	.034	.025
16	.001	
17	.001	
18	.003	.009
19	.001	
24	.001	
25	.010	
25.5	.012	
26	.092	.006
26.5	.002	
27	.265	.025
28	.304	.504
29	.138	.075
30	.003	.001
36	.002	
37	.019	
38	.035	
39	.314	.030
40	.051	.047
41	1.000	.985
42	.034	.030
43	.001	
48	.002	
49	.011	
50	.044	
51	.035	
52	.009	
53	.050	.001
54	.018	.017
55	.174	.068
56	.365	1.000
57	.015	.042
58		.001
	S = 1.4	R = 0.13

TABLE B-7

Butyl Acetate

m/e	70 eV	8 eV
12	.001	
13	.003	
14	.016	
15	.119	.077
16	.002	
18	.002	.018
19	.003	.009
26	.012	
27	.091	.004
28	.065	.055
29	.109	.044
30	.004	.004
31	.055	.142
32	.003	.012
33	.003	.024
37	.001	
38	.003	
39	.032	
40	.007	
41	.148	.071
42	.041	.033
43	1.000	.851
44	.025	.019
45	.009	.004
50	.001	
51	.002	
52	.001	
53	.002	
54	.002	
55	.058	.032
56	.319	1.000
57	.031	.047
58	.014	.022
59	.001	
60	.002	.006
61	.103	.213
62	.002	
63	.001	

TABLE B-7 (Continued)

m/e	70 eV	8 eV
70	.002	
71	.010	.009
72	.002	
73	.110	.067
74	.004	
75	.001	
86	.004	.006
87	.008	.010
88	.001	

(No parent peak observed)

S = 2.0 R = .018

TABLE B-8

Carbon Disulfide

m/e	70 eV	8 eV
12	.027	.014
16	.001	
17	.001	.001
18	.003	.011
25.3	.002	
26	.001	
27	.001	
32	.095	.016
33	.001	
34	.006	.002
38	.129	
38.5	.003	
39	.010	
44	.123	.002
45	.002	.001
46	.005	
64	.009	
66	.001	
76	1.000	1.000
77	.023	.024
78	.089	.085
79	.001	.002
80	.002	.002
	S = 2.1	R = .05

TABLE B-9

Carbon Tetrachloride

m/e	70 eV	8 eV
12	.142	
16	.002	
17.5	.005	
35	.381	
36	.013	
37	.099	
38	.006	
41	.020	
42	.014	
43	.006	
47	.409	
48	.006	
49	.114	
58.5	.077	
59.5	.074	
60.5	.024	
61.5	.005	
82	.303	
83	.005	
84	.168	
85	.004	
86	.028	
117	1.000	
119	1.000	
121	.338	
123	.023	
	S = .3	

TABLE B-10

Chlorobenzene

m/e	70 eV	8 eV
12	.007	
13	.003	
14	.002	
15	.003	
16	.001	
17	.002	
18	.007	.028
24	.001	
25	.006	
26	.020	
27	.030	
31	.001	
35	.006	
36	.011	
36.5	.001	
37	.060	
37.5	.024	
38	.188	
38.5	.009	
39	.032	
40	.002	
43	.002	
44	.001	
47	.005	
48	.007	
49	.032	
50	.208	
51	.248	
52	.021	
55	.008	
56	.091	
56.5	.002	
57	.027	
57.5	.001	
60	.009	
61	.013	
62	.012	
63	.010	
64	.001	

TABLE B-10 (Continued)

m/e	70 eV	8 eV
72	.005	
73	.028	
74	.055	
75	.058	
76	.041	
77	.604	
78	.040	.015
79	.001	
84	.008	
85	.011	
86	.011	
87	.003	
88	.003	
97	.003	
111	.003	
112	1.000	1.000
113	.011	
114	.299	.282
115	.007	.007
	S = 1.0	R = .037

TABLE B-11

Chloroform

m/e	70 eV	8 eV
12	.043	.316
13	.093	.860
14	.005	
15		.023
17	.001	.005
17.5	.003	
18	.005	.034
18.5	.001	
35	.146	
36	.023	.047
37	.040	
38	.007	.018
39	.002	
41	.008	.013
41.5	.007	
42	.005	.005
42.5	.005	
43	.025	
44	.006	
47	.345	
48	.171	
49	.115	
50	.047	
70	.005	
72	.009	
82	.030	
83	1.000	1.000
84	.030	
85	.623	.659
86	.008	
87	.105	.094
88	.001	
117	.008	
118	.013	.016
119	.004	
120	.013	.016
122	.005	
	S = .69	R = .019

TABLE B-12

1-Chloropropane*

m/e	70 eV	8 eV
12	.006	
13	.008	
14	.021	.001
15	.060	.021
16	.002	
17	.001	.001
18	.005	.007
19	.004	
19.5	.002	
20	.005	
20.5	.001	
24	.001	
25	.009	
26	.067	.002
27	.552	.235
28	.296	.204
29	.529	.658
30	.012	.012
31	.005	
35	.007	
36	.014	.002
36.5	.001	
37	.034	
37.5	.001	
38	.041	
39	.136	
40	.030	.006
41	.270	.061
42	1.000	1.000
43	.377	.327
44	.016	.011
45	.007	.004
48	.005	
49	.043	
50	.006	
51	.014	
52	.001	
55	.004	.001
56	.001	.001
57	.005	.001

*Impurity of Chlorobutane

TABLE B-12 (Continued)

m/e	70 eV	8 eV
59	.002	
60	.003	
61	.008	
62	.009	
63	.072	.008
64	.004	
65	.022	.003
69	.001	
72	.005	.002
73	.013	.006
74	.001	
75	.004	
76	.001	
77	.004	
78	.048	.012
79	.002	
80	.015	.004
	S = 1.1	R = .083

TABLE B-13

Cyclohexane

m/e	70 eV	8 eV
14	.005	
15	.033	.005
16	.002	
17	.003	.001
18	.013	.051
25	.001	
26	.030	
27	.246	.017
28	.120	.085
29	.118	.027
30	.002	
31	.002	
37	.006	
37.5	.001	
38	.017	
39	.216	
39.5	.001	
40	.047	.005
41	.606	.105
42	.310	.410
43	.154	.203
44	.006	.011
49	.002	
50	.014	
51	.021	
52	.009	
53	.033	
54	.050	.023
55	.330	.139
56	1.000	1.000
57	.041	.040
58	.001	
62	.001	
63	.003	
65	.005	
66	.003	
67	.021	
68	.015	.015
69	.222	.186

TABLE B-13 (Continued)

m/e	70 eV	8 eV
70	.010	.009
71	.002	
73	.001	
74	.001	
77	.005	
78	.002	
79	.004	
81	.003	
82	.002	
83	.033	.009
84	.589	.70
85	.035	.037
86	.001	
	S = 1.2	R = .069

TABLE B-14

Diethyl Ether

m/e	70 eV	8 eV
12	.002	
13	.006	
14	.034	.001
15	.090	.014
16	.005	.001
17	.002	
18	.007	.010
19	.024	.025
25	.002	
26	.041	
27	.213	.009
28	.117	.025
29	.491	.221
30	.018	.007
31	1.000	1.000
32	.021	.004
33	.002	.002
39	.002	
40	.001	
41	.030	.023
42	.009	.001
43	.060	.002
44	.012	.001
45	.284	.064
46	.006	.001
47	.001	
55	.001	
57	.002	
58	.001	
59	.315	.229
60	.009	.006
61	.001	.001
73	.016	.011
74	.167	.173
75	.007	.002
76	.001	
	S = 1.6	R = .17

TABLE B-15

1,4-Dioxane

m/e	70 eV	8 eV
12	.002	
13	.008	
14	.032	
15	.175	.178
16	.004	.001
18	.002	.005
19	.004	
25	.002	
26	.059	
27	.115	
28	1.000	1.000
29	.294	.161
30	.130	.225
31	.156	.281
32	.007	.007
39	.002	
40	.001	
41	.004	
42	.011	
43	.091	.010
44	.022	.044
45	.026	.033
46	.001	.002
57	.058	.022
58	.229	.214
59	.008	
60	.001	
61	.001	
87	.015	.007
88	.242	.333
89	.009	.009
90	.001	.001
	S = 1.2	R = .064

TABLE B-16

Ethyl Acetate

m/e	70 eV	8 eV
12	.003	
13	.011	
14	.051	.003
15	.180	.368
16	.004	.011
18	.001	.019
19	.005	.027
25	.002	
26	.022	
27	.099	.020
28	.040	.176
29	.206	.602
30	.008	.010
31	.011	.004
39	.001	
40	.001	
41	.004	
42	.050	.023
43	1.000	1.000
44	.025	.027
45	.144	.510
46	.003	.011
49	.001	.001
51		.007
57	.001	
58	.001	
59	.001	
60	.006	.015
61	.120	.340
62	.003	(.011)
63	.001	
70	.057	.142
71	.002	
73	.027	.041
74	.001	
87	.001	
88	.026	.043
89	.001	
	S = 1.9	R = .014

TABLE B-17

Ethyl Alcohol

m/e	70 eV	8 eV
12	.010	
13	.021	
14	.052	.005
15	.116	.084
16	.007	.003
17	.013	.006
18	.029	.042
19	.036	.062
24	.003	
25	.014	
26	.055	.004
27	.205	.043
28	.076	.039
29	.209	.053
30	.053	.051
31	1.000	1.000
32	.046	.060
33	.003	.003
38	.002	
40	.002	
41	.007	
42	.022	
43	.082	
44	.008	.003
45	.398	.286
46	.166	.143
47	.003	.004
	S = 0.9	R = .19

TABLE B-18

Ethylene Oxide

m/e	70 eV	8 eV
12	.030	
13	.061	
14	.288	
15	.801	
16	.091	
17	.004	
18	.011	
21	.003	
24	.004	
25	.018	
26	.035	.005
27	.029	.007
28	.072	.024
29	1.000	1.000
30	.016	.009
31	.012	.005
32	.005	.002
39	.001	
40	.004	
41	.013	
42	.121	.009
43	.180	.096
44	.744	.785
45	.017	.016
46		.002
	S = .66	

FIGURE B-19

Ethylene

m/e	70 eV	8 eV
12	.013	
13	.020	
13.5	.004	
14	.041	.006
15	.003	
17	.001	
18	.007	.006
24	.027	
25	.093	
26	.573	.108
27	.613	.051
28	1.000	1.000
29	.019	.021
	S = 1.2	R = .24

TABLE B-20

Ethyl Formate

12	.007	
13	.018	
14	.047	.001
15	.108	.029
16	.007	.002
17	.002	
18	.005	.003
19	.048	.040
24	.002	
25	.010	
26	.101	.003
27	.407	.040
28	1.000	1.000
29	.575	.175
30	.042	.019
31	.985	.466
32	.016	.007
33	.002	
39	.002	
40	.002	
41	.005	
42	.012	
43	.069	.004
44	.014	.003
45	.263	.060
46	.014	.005
47	.076	.024
48	.001	
49	.001	
50	.001*	
51	.001*	
52	.001*	
53	.002	
56	.020	.007
57	.002	
59	.010	.002
60	.001	.001

*Trace of Benzene

TABLE B-20 (Continued)

m/e	70 eV	8 eV
63	.001*	
64	.001	
65	.001	
72	.002	.0005
73	.011	.002
75	.069	.015
75	.002	
78	.006*	.002
	S = .9	R = .34

*Trace of Benzene

TABLE B-21

Ethylene Dichloride

m/e	70 eV	8 eV
12	.010	
13	.015	
14	.046	
15	.005	.005
16	.001	
17	.002	
18	.008	.040
24	.008	
25	.048	
26	.202	
27	1.000	1.000
28	.073	
29	.001	
30.5	.004	
31.5	.004	
32	.007	.002
35	.034	
36	.018	.006
37	.012	
38	.006	
39	.001	
41	.003	
43	.005	
44	.001	
47	.018	
48	.022	
49	.427	.035
50	.012	
51	.117	
52	.002	
59	.003	
60	.021	
61	.093	
62	.502	.168
63	.165	.038
64	.165	.043

TABLE B-21 (Continued)

m/e	70 eV	8 eV
65	.036	.008
66	.001	
83	.002	
84		.003
85	.001	
86		.003
96	.004	
97	.003	
98	.079	.008
99	.002	
100	.048	.008
101	.001	
102	.008	
	S = .69	R = .05

TABLE B-22

Freon-11

m/e	70 eV	8 eV
12	.078	.212
13	.001	
14	.004	
15	.001	
16	.002	
17	.002	.028
17.5	.004	
18	.013	.324
18.5	.001	
19	.008	
25	.001	
26	.002	
29	.006	
31	.209	
35	.242	
36	.007	
37	.064	
38	.004	
39	.002	
40	.001	
41	.017	
42	.010	
43	.006	
44	.006	
45	.001	
47	.148	
49	.040	
50.5	.044	
51.5	.029	
52.5	.005	
58	.005	
59	.004	
66	.185	
68	.050	

TABLE B-22 (Continued)

m/e	70 eV	8 eV
70	.007	
72	.008	.113
82	.045	
84	.029	
86	.005	
101	1.000	1.000
103	.624	.500
105	.092	.112
117	.020	
119	.019	
121	.006	
	S = .39	R = .005

TABLE B-23

n-Hexane

m/e	70 eV	8 eV
12	.001	
13	.001	
14	.007	
15	.049	.006
16	.002	
17	.002	
18	.007	.020
26	.030	
27	.395	.035
28	.095	.030
29	.598	.436
30	.012	.007
31	.001	
37	.005	
38	.013	
39	.179	
40	.027	.003
41	.737	.202
42	.423	.665
43	.806	.770
44	.024	.019
50	.007	
51	.010	
52	.003	
53	.016	
54	.007	.003
55	.092	.013
56	.560	.715
57	1.000	1.000
58	.039	.043
62	.002	
63	.002	
65	.002	
67	.004	
68	.004	.004
69	.035	.023

TABLE B-23 (Continued)

m/e	70 eV	8 eV
70	.008	.006
71	.044	.037
72	.003	
77	.001	
84	.012	.010
85	.003	.002
86	.123	.086
87	.007	.005
	S = 1.1	R = .09

TABLE B-24

Isobutylene

m/e	70 eV	8 eV
12	.004	
13	.005	
14	.014	.001
15	.033	.012
16	.002	
17	.002	.001
18	.008	.011
25	.007	
26	.044	.002
27	.182	.008
28	.228	.260
29	.117	.045
30	.003	.001
36	.004	
37	.027	
38	.052	
39	.382	.020
40	.091	.043
41	1.000	.578
42	.030	.019
43	.002	.001
49	.013	
50	.046	
51	.033	
52	.009	
53	.047	
54	.015	.003
55	.165	.042
56	.414	1.000
57	.016	.042
58		.001
	S = 1.6	R = .18

TABLE B-25

Methanol

m/e	70 eV	8 eV
12	.012	
13	.022	
14	.052	.044
15	.259	.454
15.5	.007	
16	.006	.004
17	.008	
18	.011	.010
19	.003	
28	.065	.001
29	.457	.012
30	.060	.017
31	1.000	.656
32	.702	1.000
33	.010	.011
34	.002	.002
	S = .73	R = .16

TABLE B-26

Methyl Acetate

m/e	70 eV	8 eV
12	.006	
13	.021	
14	.073	
15	.475	
16	.007	
25	.002	
26	.004	
27	.005	
28	.035	.023
29	.066	.012
30	.007	.005
31	.035	.045
32	.009	.015
33	.002	
40	.002	
41	.005	
42	.089	.020
43	1.000	1.000
44	.024	.022
45	.007	.005
59	.053	.023
74	.156	.113
75	.008	.010
	S = 2.0	

TABLE B-27

Methyl n-Butyrate

m/e	70 eV	8 eV
12	.002	
13	.007	
14	.034	
15	.494	
16	.007	
17	.001	
18	.003	
19	.001	
20	.001	
25	.002	
26	.035	
27	.354	.077
28	.093	.068
29	.127	.100
30	.010	.002
31	.049	.059
32	.007	.046
33	.014	.057
34	.001	
36	.001	
37	.008	
38	.016	
39	.122	
40	.017	
41	.281	.017
42	.162	.078
43	1.000	.907
44	.044	.024
45	.035	.009
46	.001	
49	.001	
50	.001	
51	.001	
52	.001	
53	.003	
54	.001	
55	.071	
56	.004	
57	.009	

TABLE B-27 (Continued)

m/e	70 eV	8 eV
58	.001	
59	.227	.029
60	.008	
61	.005	
68	.001	
69	.001	
70	.006	
71	.494	.467
72	.020	.015
73	.002	
74	.603	1.000
75	.019	.035
76	.003	
87	.126	.044
88	.005	
89	.001	
101	.006	
102	.010	.020
	S = .93	

TABLE B-28

Methylene Chloride

m/e	70 eV	8 eV
12	.020	.014
13	.039	.038
14	.037	.318
15	.001	.014
16	.001	
17	.001	
17.5	.002	
18	.002	.020
24.5	.003	
25.5	.001	
29	.001	
31	.001	
35	.066	
36	.015	.004
37	.019	
38	.005	
41	.078	
41.5	.003	
42	.043	
42.5	.002	
43	.007	
44	.001	
47	.136	
48	.076	.023
49	1.000	1.000
50	.029	.011
51	.298	.281
52	.003	
70	.002	
72	.001	

TABLE B-28 (Continued)

m/e	70 eV	8 eV
82	.004	
83	.012	
84	.490	.115
85	.013	
86	.304	.070
87	.004	
88	.044	.016
89	.001	
	S = .85	R = .02

TABLE B-29

Methyl Ethyl Ketone

m/e	70 eV	8 eV
12	.003	
13	.007	
14	.038	.005
15	.144	.305
16	.002	.004
18	.002	.003
19	.001	.002
24	.001	
25	.005	
25.5	.001	
26	.041	.001
27	.130	.035
28	.028	.012
29	.233	.482
30	.005	.009
31	.005	.007
33	.001	
36	.001	
37	.004	
38	.005	
39	.016	
40	.002	
41	.014	.002
42	.044	.010
43	1.000	1.000
44	.024	.029
45	.007	.005
48	.001	
49	.002	
50	.004	
51	.002	
52	.001	
53	.004	
54	.001	.001
55	.004	.001
56	.003	.004

TABLE B-29 (Continued)

m/e	70 eV	8 eV
57	.057	.127
58	.002	.004
59	.001	.001
71	.006	.002
71	.143	.326
73	.006	.013
74	.001	
	S = 1.9	R = 4.35

TABLE B-30

Methyl Isopropyl Ketone

m/e	70 eV	8 eV
12	.001	
13	.004	
14	.018	.002
15	.108	.079
16	.001	.001
17	.001	.001
18	.002	.010
19	.001	.001
25	.002	.001
26	.015	.002
27	.121	.050
28	.046	.057
29	.016	.010
30	.001	.002
31	.004	.005
32	.002	.001
36	.001	
37	.004	
38	.008	
39	.051	
40	.007	
41	.124	.020
42	.047	.020
43	1.000	1.000
44	.024	.028
45	.011	.010
49	.001	
50	.002	
51	.003	
52	.002	
53	.004	
54	.010	.003
55	.006	.002
56	.002	.001
57	.007	.008
58	.003	.007
59	.001	.001

TABLE B-30 (Continued)

m/e	70 eV	8 eV
67	.001	
69	.001	
70	.001	.001
71	.031	.072
72	.002	.003
84	.001	
85	.001	
86	.094	.132
87	.004	.006
	S = 2.7	R = .09

TABLE B-31

Monomethylamine

m/e	70 eV	8 eV
12	.009	
13	.012	
14	.023	.004
15	.139	.116
16	.017	.006
17	.011	.007
18	.016	.018
26	.025	
27	.126	.002
28	.606	.094
29	.155	.054
30	1.000	.775
31	.613	1.000
32	.012	.016
33	.001	.001
36	.001	
37	.001	
38	.002	
39	.005	
40	.002	
41	.012	.001
42	.053	.013
43	.012	.003
44	.010	.005
45	.001	.001
54	.001	
55	.003	
56	.006	.002
57	.020	.016
58	.002	
59	.003	.001
70	.004	.001
72	.004	.001
	S = .79	R = .29

TABLE B-32

Nitrous Oxide

m/e	70 eV	8 eV
14	.079	.089
16	.029	.236
17	.001	
18	.003	.024
28	.090	.024
29	.001	
30	.185	.022
31	.001	
32	.003	.006
44	1.000	1.000
45	.007	.007
46	.002	
	S = .92	R = .04

TABLE B-33

2-Propanethiol*

m/e	70 eV	12 eV
12	.003	
13	.005	
14	.016	
15	.058	.024
16	.004	
17	.026	.01
18	.110	.11
19	.001	
20	.001	
25	.005	
26	.046	
27	.492	.29
28	.098	.05
29	.074	.05
30	.002	
32	.023	.01
33	.024	
34	.017	
34.5	.001	
35	.070	.03
36	.005	
37	.021	
38	.032	
39	.202	.01
40	.043	.06
41	.576	.34
42	.528	.66
43	1.000	1.000
44	.038	.033
45	.179	.01
46	.182	.124
47	.661	.434
48	.075	.063
49	.029	.017
50	.003	
57	.013	
58	.028	
59	.024	
60	.006	
61	.070	.049

TABLE B-33 (Continued)

m/e	70 eV	12 eV
62	.002	
63	.003	
64	.005	
66	.036	.022
68	.006	
69	.010	

m/e	70 eV	8 eV
73	.017	
74	.016	.013
75	.010	.010
76	.538	.75
77	.022	.028
78	.023	.032
	S = .7	R = .4

*Spectra shows evidence of Dipropyl Disulfide impurity estimated at 10%.

TABLE B-34

1-Propanol

m/e	70 eV	8 eV
12	.001	
13	.003	
14	.009	
15	.026	.008
16	.001	
17	.001	
18	.002	.003
19	.008	.010
19.5	.001	
20	.001	
24	.001	
25	.004	
26	.025	
27	.118	.007
28	.058	.020
28.5	.001	
29	.117	.026
30	.017	.008
31	1.000	1.000
32	.022	.020
33	.010	.007
36	.001	
37	.004	
38	.006	
39	.023	
40	.006	
41	.046	.003
42	.076	.091
43	.017	.003
44	.003	.001
45	.010	.002
46	.001	
53	.001	
55	.002	
57	.006	
58	.001	
59	.079	.041
60	.051	.035
61	.002	.001
	S = 2	R = .089

TABLE B-35

2-Propanol

m/e	70 eV	8 eV
12	.003	
13	.008	
14	.033	.002
15	.130	.048
16	.005	.003
17	.003	.001
18	.009	.014
19	.092	.191
19.5	.001	
20	.002	
24	.001	
25	.004	
26	.017	
27	.154	.062
28	.022	.006
29	.087	.026
30	.004	.001
31	.066	
32	.003	.002
33	.001	.001
36	.001	
37	.007	
38	.013	
39	.045	
40	.007	
41	.064	.007
42	.030	.006
43	.152	.042
44	.034	.044
45	1.000	1.000
46	.020	.022
47	.002	.02
53	.001	
55	.001	
57	.004	
58	.002	.001
59	.033	.014
60	.005	.004
	S = 1.8	R = .14

TABLE B-36

Tetrahydrofuran

m/e	70 eV	8 eV
12	.003	
13	.007	
14	.025	.003
15	.064	.036
16	.004	.007
17	.001	.001
18	.003	.008
19	.003	.002
20	.002	
25	.003	
26	.030	.002
27	.207	.064
28	.053	.020
29	.127	.026
30	.006	.001
31	.033	.034
32	.002	.003
34	.003	
35	.002	
36	.001	
37	.008	
38	.019	
39	.134	
40	.087	.013
41	.418	.075
42	1.000	1.000
43	.177	.117
44	.036	.018
45	.009	.003
49	.001	
50	.002	
51	.001	
53	.003	

TABLE B-36 (Continued)

m/e	70 eV	8 eV
55	.001	
57	.002	
69	.002	
70	.001	
71	.223	.153
72	.241	.321
73	.010	.012
74	.001	.001
	S = 1.3	R = .13

TABLE B-37

Toluene

m/e	70 eV	8 eV
12	.002	
13	.002	
14	.003	
15	.007	
16	.001	
18	.001	.004
25	.002	
26	.014	
27	.045	
29	.001	
36	.002	
37	.019	
38	.038	
39	.187	.001
40	.019	
41	.021	
42	.002	
42.5	.002	
43	.026	.002
43.5	.005	
44	.009	
44.5	.008	
45	.093	
45.5	.034	
46	.059	
46.5	.004	
49	.006	
50	.048	
51	.093	
52	.020	
53	.010	
60	.002	
61	.014	
62	.031	
63	.079	.001
64	.017	
65	.132	
66	.012	

TABLE B-37 (Continued)

m/e	70 eV	8 eV
73	.002	
74	.008	
75	.005	
76	.003	
77	.010	
78	.002	
84	.001	
85	.004	
86	.007	
87	.004	
88	.001	
89	.032	
90	.013	
91	1.000	.003
92	.696	1.000
93	.049	.055
	S = 1.2	R = .10

TABLE B-38

Trichloroethylene

m/e	70 eV	8 eV
12	.044	.009
13	.021	.011
14	.005	
15	.002	
16	.001	
17	.002	.007
18	.007	.050
24	.047	
25	.216	
26	.006	
37	.004	.011
28	.006	
29	.004	.007
30	.002	.006
35	.128	
36	.019	.022
37	.040	
38	.006	.009
39	.003	
40	.001	
41	.006	
42	.009	.036
43	.011	.018
44	.003	.013
45	.001	
47	.114	
47.5	.008	
48	.032	
48.5	.003	
49	.036	
50	.012	
57		.007
58		.006
59	.058	
60	.414	
61	.026	
62	.113	
63	.003	
65	.041	

TABLE B-38 (Continued)

m/e	70 eV	8 eV
66	.038	
67	.011	
70	.004	
71	.003	.004
72	.005	.011
82	.016	
83	.013	
84	.010	
85	.009	
86	.004	
87	.002	
94	.050	
95	1.000	.049
96	.040	
97	.635	.030
98	.012	
99	.089	.007
130	.894	1.000
132	.868	.916
134	.271	.279
136	.025	.021
	S = .5	R = .045

TABLE B-39

1,1,1-Trichloroethane

m/e	70 eV	8 eV
12	.024	
13	.020	
14	.040	
15	.069	
24	.020	
25	.129	
26	.439	
27	.390	
28	.160	
29	.058	
30	.027	
31	.024	
35	.148	
36	.051	
37	.052	
38	.018	
39	.008	
41	.021	
42	.016	
43	.028	
44	.018	
45	.006	
46	.005	
47	.059	
48	.010	
49	.024	
50	.005	
57	.013	
58	.029	
59	.017	
60	.090	
61	.728	
62	.068	
63	.239	
70	.004	
71	.005	
72	.012	

TABLE B-39 (Continued)

m/e	70 eV	8 eV
82	.022	
83	.008	
84	.014	
85	.007	
86	.005	
87	.004*	
88	.033*	
94	.003	
95	.026	
96	.010	
97	1.000	
98	.016	
99	.645	
101	.091	
117	.229	
119	.217	
121	.060	
123	.007	

*Impurities - see text

S = .32

TABLE B-40

Vinyl Chloride

m/e	70 eV	8 eV
12	.020	.001
13	.026	.002
14	.020	.006
15	.005	.002
17	.001	
18	.004	.007
24	.023	
25	.111	
26	.294	.081
27	1.000	1.000
28	.018	.022
29	.002	.001
30	.002	
30.5	.006	
31	.004	
31.5	.002	
35	.029	
36	.013	.002
37	.010	
38	.005	
39	.002	
47	.025	
48	.011	
49	.008	
50	.003	
59	.013	
60	.044	
61	.075	
62	.947	.600
63	.039	.011
64	.294	.181
65	.007	.004
	S = .77	R = .25

TABLE B-41

Vinylidene Fluoride (1,1-Difluoroethylene)

m/e	70 eV	8 eV
12	.043	.006
13	.038	.007
14	.214	.261
15	.002	.002
17		.001
18		.022
19	.007	
20	.003	
22.5	.026	
24	.02	
25	.029	
26	.046	
27	.001	
31	.504	.067
32	.027	.002
33	.458	.088
34	.005	
43	.025	
44	.283	.010
45	.547	.007
46	.012	
50	.025	
51	.012	
62	.013	
63	.144	
64	1.00	1.000
65	.020	.020
	S = .43	R = .18

TABLE B-42

o-Xylene

m/e	70 eV	8 eV
14	.007	
15	.023	.007
16	.002	
26	.015	
27	.126	
28	.007	
29	.009	
30	.001	
31	.001	
36	.002	
37	.010	
38	.028	
39	.180	
40	.016	
41	.029	
42	.004	
43	.019	
44	.002	
45	.002	
45.5	.005	
49	.006	
50	.058	
51	.197	
51.5	.009	
52	.084	
52.5	.008	
53	.034	
54	.001	
55	.004	
56	.003	
57	.005	
58	.001	
59	.002	
60	.001	
61	.007	
62	.020	
63	.055	
64	.011	
65	.072	
66	.010	
67	.002	

TABLE B-42 (Continued)

m/e	70 eV	8 eV
71	.006	
72	.001	
73	.004	
74	.020	
75	.010	
76	.010	
77	.139	
78	.051	
79	.060	
85	.003	
86	.004	
87	.004	
89	.015	
90	.003	
91	1.000	.023
92	.057	.005
93	.003	
98	.004	
101	.002	
102	.007	
103	.043	
104	.013	
105	.214	
106	.506	1.000
107	.024	.039
	S = 1.4	R = .079

TABLE B-43

m-Xylene

m/e	70 eV	8 eV
13	.001	
14	.005	
15	.019	.003
16	.001	
17	.001	
18	.002	.009
26	.012	
27	.111	
28	.006	
29	.008	.003
30	.001	.003
37	.010	
38	.027	
39	.174	.003
40	.017	
41	.026	
42	.004	
43	.006	
44	.001	
45.5	.004	
49	.007	
49.5	.002	
50	.051	
51	.184	
51.5	.007	
52	.096	
52.5	.006	
53	.033	
54	.003	
55	.003	
56	.001	
57	.004	
59	.002	
60	.002	
61	.007	
62	.019	
63	.052	
64	.011	

TABLE B-43 (Continued)

m/e	70 eV	8 eV
65	.071	
66	.009	
67	.002	
73	.003	
74	.011	
75	.009	
76	.007	
77	.132	
78	.053	
79	.055	
80	.033	
85	.003	
86	.003	
87	.003	
88	.001	
89	.016	
90	.002	
91	1.000	
92	.072	.028
93	.001	
98	.002	
101	.002	
102	.006	
103	.039	
104	.010	
105	.187	
106	.353	1.000
107	.022	.035
	S = 1.6	R = .076