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FINAL REPORT
LABORATORY CONTAMINANT SENSOR

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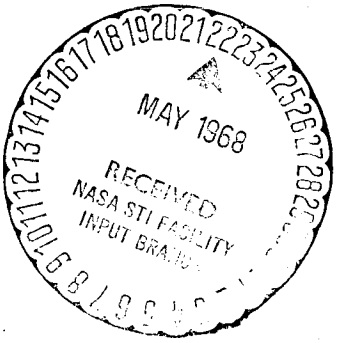

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ABSTRACT

This final report describes development of a Laboratory Contaminant Sensor, a prototype instrument which can be reduced to space flight hardware for detection of contaminants during manned space missions. The instrument design is based on the use of an accumulator cell which contains a sorbent for extraction of contaminants from air at room temperature. By heating the cell, contaminants are desorbed through a special inlet system to a mass spectrometer for identification and determination.

The performance of the instrument was evaluated by tests with typical contaminants. Three sorbents - Porapak Q, charcoal, and Molecular Sieve 5A - were used to sorb the various contaminants. A palladium-coated charcoal sorbent was prepared and successfully tested for the detection of carbon monoxide. Lower detectable limits for contaminants range from 0.5 to 5 ppm with the analytical conditions used. These conditions can be changed to permit detection of smaller concentrations. Identification of contaminants is facilitated by the use of three sorbents and programmed temperature desorption. A characteristic desorption temperature is determined for each contaminant. Correlation between boiling point and this desorption temperature, in addition to the mass spectra deduced from the desorption curves, provide information for identification of unknown contaminants.

The test results demonstrate that this instrument concept has considerable potential for detection, identification, and quantitative determination of atmospheric contaminants.

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1. INTRODUCTION

Instrumentation for monitoring atmospheric contamination is a requirement for life support systems used in manned space flights. Such instruments must have the capability of detecting and identifying a wide variety of contaminants which may be present at low concentrations in the confined atmosphere. This final report describes development of a prototype Laboratory Contaminant Sensor, which has the required capability and which is suitable for adaptation to the constraints of space flight instrumentation.

The usual analytical problems, identification and quantitative determination, present exceptional difficulty when the compounds are present in extremely low concentrations, in a complex mixture such as may be expected in a closed environment. In such environments, virtually the only limit on possible contaminants is one of volatility. In spacecraft, for example, numerous plastic materials containing residual solvents and volatile plasticizers may outgas (particularly under reduced pressure) for a considerable period of time, yielding noxious organic materials to the air. At high oxygen partial pressures, and under the influence of radiation, oxidation products of organic materials are readily formed. Volatile biological waste products also accumulate in the atmosphere. Toxicity limits for continuous exposure to such an environment need to be established and the effectiveness of atmospheric decontamination units need to be evaluated. An instrument for monitoring this type of atmosphere must have the capability of identifying unsuspected trace contaminants as well as those known to be present and determining their concentration at low levels with a reasonable degree of accuracy.

The goals of this program were to design and fabricate a prototype instrument for laboratory use, and to evaluate its capability for detection, identification and quantitative determination of atmospheric contaminants at low concentration.

The Laboratory Contaminant Sensor consists of a mass spectrometer coupled with an accumulator cell 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.

Preliminary experimental work was concerned with design of the accumulator cell and the inlet system which provides the interface with the mass spectrometer. A series of tests of various parameters were performed to establish optimum

conditions. Finally, the system was tested with a selected group of contaminants to evaluate its sensitivity for the selected contaminants as well as other aspects of its performance.

The instrument design and the test results are summarized in the following sections of the report.

2. LABORATORY CONTAMINANT SENSOR

Analysis of contaminants with the Laboratory Contaminant Sensor is accomplished by first extracting contaminants from air on sorbents contained in an accumulator cell at room temperature. The sorbed contaminants are subsequently desorbed by heating the accumulator cell at a fixed rate under vacuum. As the contaminants are vaporized, they are pumped past the gold leak entrance of a mass spectrometer where a portion of the sample enters the ion source for mass spectral analysis. The spectrum serves as a means of identifying the contaminant; the ion current or signal intensity is a measure of the amount of contaminant in the sample. The physical chemistry involved in sorption and desorption is reviewed briefly in the following section and a complete description of the apparatus and technique for analytical measurements is presented in Paragraph 2.2.

2.1 THEORY OF OPERATION

When a gas or vapor comes into contact with a surface, the concentration of the gas or vapor will be higher at the surface than in the bulk gas phase. This is a result of the attraction which exists between the surface and the molecules in the gas phase. In a mixture of gases, such as a contaminant air mixture, those components which are most strongly attracted to the surface of a sorbent will be preferentially concentrated on the sorbent, and there will be a reduction of the concentration of these components in the gas phase.

The forces of attraction involved in sorption vary in strength according to the mechanism involved. There are three generally recognized mechanisms: adsorption, chemisorption, and absorption. In adsorption, the attraction results from dipole or polarization interaction (Van der Waals forces) and is usually relatively weak. In chemisorption, actual chemical reaction occurs between the gas phase molecule and the surface. The forces are stronger, but reactions can only occur over a single molecular layer. In absorption, the gas phase molecules essentially dissolve in the bulk solid. This mechanism is more generally associated with gas absorption in liquids, but it appears to be relevant also to certain polymer sorbents. The gas phase molecules penetrate the surface and are surrounded by molecules of the sorbent in contrast to adsorption in which the adsorbed molecule experiences forces due to other adsorbed molecules as well as those due to the adsorbent. The general rules of solubility apply to absorbents.

Sorption by any of these three mechanisms is satisfactory for the Laboratory Contaminant Sensor. The only requirements for a sorbent are that the attractive forces between the contaminant and the sorbent are high enough that the

contaminant is essentially completely sorbed from a sample of air, and that the strength of these forces decreases with temperature in such a way that the contaminant can be desorbed at temperatures below the threshold temperature for thermal decomposition of the contaminant or the sorbent.

These requirements are described by the equilibrium constant and the heat of desorption. The equilibrium involved is defined as:

$$C(g,p,T) \rightleftharpoons C(s,c,T)$$

where C(g,p,T) refers to the contaminant in the gas phase, at pressure p, and temperature T, and C(s,c,T) refers to contaminant in the sorbed phase at concentration c, and temperature T.

The equilibrium constant K is defined as follows:

$$K = \frac{C_s}{C_g}$$

where C_s is the concentration in the sorbed phase in moles/gm and C_g is the concentration in the gas phase in moles/cm^3. The equilibrium constant, K, has the units of cm^3/gm with these definitions.

The relation between concentration (or pressure) in the gas phase and concentration in the sorbent is generally complex for sorption of mixtures of gases. However, in the case in which one component is present in very low concentration in the presence of a large and constant pressure of another, a linear relation can be derived from the Langmuir isotherm for mixed gases.*

The change in equilibrium constant with temperature is given by:

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

in which ΔH is the heat of sorption (calories/gm-mole), R is the gas constant in calories/gm-mole/°K, and T and K have their former meanings. The heat of sorption changes with temperature but for purposes of this discussion is considered constant.

The requirements for sorbents for the contaminant as described above will be satisfied then for values of K which are very large at room temperature, so that the equilibrium partial pressure of the contaminant is low, corresponding

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* D. M. Young and A. D. Crowell, Physical Adsorption of Gases, Buttersworth & Co., Ltd., 1962, pp 372-378.

to the condition in which the contaminant is essentially completely sorbed. The value of ΔH should be such that the equilibrium constant is very low at the upper limit temperature, which is 250°C for the contaminants and sorbents used in the experimental work.

A list of contaminants to be used for testing the Laboratory Contaminant Sensor is presented in Table 2-1. These contaminants are typical of those found in closed cabin atmospheres; they range from compounds which are gases at room temperature to high boiling organic liquids. It is highly unlikely that a single sorbent could be found that would be suitable for all compounds. Experimentally, it was possible to meet the sorbent requirements discussed above for most of the contaminants with three materials - Porapak Q, charcoal, and Molecular Sieve 5A.

A brief description of the desorption techniques is presented for the purpose of deriving the relation between the amount of contaminant sorbed and the experimental variables. Desorption of the extracted contaminants is accomplished by heating the accumulator cell containing the sorbent. After air is precut from the cell, the inlet system valves are adjusted in such a way that the desorbing contaminants flow past the gold leak entrance to the mass spectrometer ion source (see Figure 2-1). The pressure of a contaminant in the system during desorption depends on the balance between the rate at which it is desorbed and the rate at which it is pumped away through the micrometer needle valve. The mass spectrometer signal depends on the pressure of the contaminant in the inlet system. The maximum pressure reached is thus a function of the total amount of contaminant in the cell, the rate at which the cell is heated, and the speed at which the desorbed contaminant is pumped out of the system.

TABLE 2-1

Test Contaminants

CONTAMINANT	NORMAL BOILING POINT (°C)	REQUIRED SENSITIVITY (ppm BY VOLUME)
Acetone	56.2	100.0
Acetaldehyde	20.8	20.0
Allyl alcohol	97.0	0.2
Ammonia	- 33.35	5.0
Benzene	80.1	2.5
Butene-1	- 6.3	
Carbon dioxide	- 78.5 (sublimes)	500.0
Carbon disulfide	45.0	2.0
Carbon monoxide	-191.0	5.0
1,4-Dioxane	101.0	10.0
Ethyl acetate	77.06	40.0
Ethylene dichloride	84.0	
Formaldehyde	- 21.0	0.5
Freon-11	24.9	
Hydrogen chloride	- 84.9	0.5
Hydrogen sulfide	- 60.7	1.0
Methane	-161.49	
Methyl alcohol	64.96	20.0
Methylene chloride	40.1	50.0
Nitric oxide	-151.8	
Nitrous oxide	- 88.5	1.0
Phenol	182.0	0.5
Sulfur dioxide	- 10.0	0.5
Toluene	110.6	20.0
Vinyl chloride	- 13.9	50.0
m-Xylene	139.0	10.0

The amount of contaminant in the system is distributed between the vapor phase and the sorbed phase according to the following relation:

$$N = C_g V_g + C_s W$$

in which N is the total amount in the system in moles

C_g is the gas phase concentration (moles/cm^3)

C_s is the sorbed phase concentration (moles/gm)

V_g is the volume of the gas phase, and

W is the weight of sorbent.

The volume of the gas phase is considered in two parts; V_1 is the volume of the inlet system which is at constant temperature T_1, and V_2 is the volume of gas phase in the accumulator cell at temperature T_2 which varies with time as the accumulator cell is heated. Pressure is assumed isotropic throughout the inlet system and accumulator cell. From the perfect gas law and the definition of the equilibrium constant,

$$N = \frac{p}{R}\left(\frac{V_1}{T_1} + \frac{V_2}{T_2}\right) + \frac{KW}{V_1 + V_2}\left[\frac{p}{R}\left(\frac{V_1}{T_1} + \frac{V_2}{T_2}\right)\right] \quad \text{or}$$

$$p = \frac{NR}{\left[\frac{V_1}{T_1} + \frac{V_2}{T_2} + \frac{KW}{(V_1 + V_2)}\left(\frac{V_1}{T_1} + \frac{V_2}{T_2}\right)\right]}$$

V_1 is the volume of the gas phase in the inlet system

V_2 is the volume of the gas phase in the accumulator cell

T_1 is the average temperature of the inlet system

T_2 is the variable temperature of the accumulator cell

R is the gas constant

p is the pressure in the system

Differentiating with respect to time and remembering that the equilibrium constant is changing with respect to time because the temperature changes with respect to time leads to the following expression:

$$\frac{dp}{dt} = \frac{R\frac{dN}{dt} - p\left[\frac{W}{V_1 + V_2}\left(\frac{V_1}{T_1} + \frac{V_2}{T_2}\right)\frac{dK}{dT_2} - \frac{V_2}{T_2^2}\left(1 + \frac{KW}{V_1 + V_2}\right)\right]\frac{dT_2}{dt}}{\frac{V_1}{T_1} + \frac{V_2}{T_2} + \frac{KW}{(V_1 + V_2)}\left(\frac{V_1}{T_1} + \frac{V_2}{T_2}\right)}$$

For viscous flow out of the micrometer needle valve,

$$RT_1 \frac{dN}{dt} = -k \left(p^2 - p_o^2\right)$$

where k is a function of the viscosity of the gas and the geometry of the valve, p_o is the pressure on the pump side of the valve.

$$\frac{dK}{dT_2} = K \frac{\Delta H}{RT_2^2} = K_o \frac{\Delta H}{RT_2^2} \exp \left[- \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_o} \right) \right]$$

where K_o is the value of the equilibrium constant at some reference temperature T_o

V_1 is the volume of the gas phase in the inlet system

V_2 is the volume of the gas phase in the accumulator cell

T_1 is the average temperature of the inlet system

T_2 is the variable temperature of the accumulator cell

R is the gas constant

p is the pressure in the system

Making these substitutions and neglecting V_2 with respect to V_1,

$$\frac{dp}{dt} = \frac{- k \left(p^2 - p_o^2\right) - pW \frac{\Delta H}{RT^2} K_o \exp \left[- \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_o} \right) \right] \frac{dT_2}{dt}}{V_1 + WK_o \exp \left[\frac{-\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_o} \right) \right]}$$

in which ΔH is the heat of sorption.

At the pressures employed, the flow mechanism through the valve is probably in the transition range between molecular and viscous flow. For very small sample sizes, the flow may be molecular. In this case, the first term in the equation given above should be changed to reflect this fact.

The equation above was integrated numerically for selected values of K_o and ΔH calculated from gas chromatagraphic data to obtain the theoretical peak shape shown in Figure 2-2. The signal from the mass spectrometer is directly proportional to the pressure in the inlet system and should follow the same curve. The temperature at the maximum pressure differs from that measured experimentally by about 80°C. This discrepancy is attributed to differences in the calculated and true value of K_o and ΔH, and to neglect of the terms in V_2. The width of the peak (as measured at one half the peak height) was comparable to that measured experimentally.

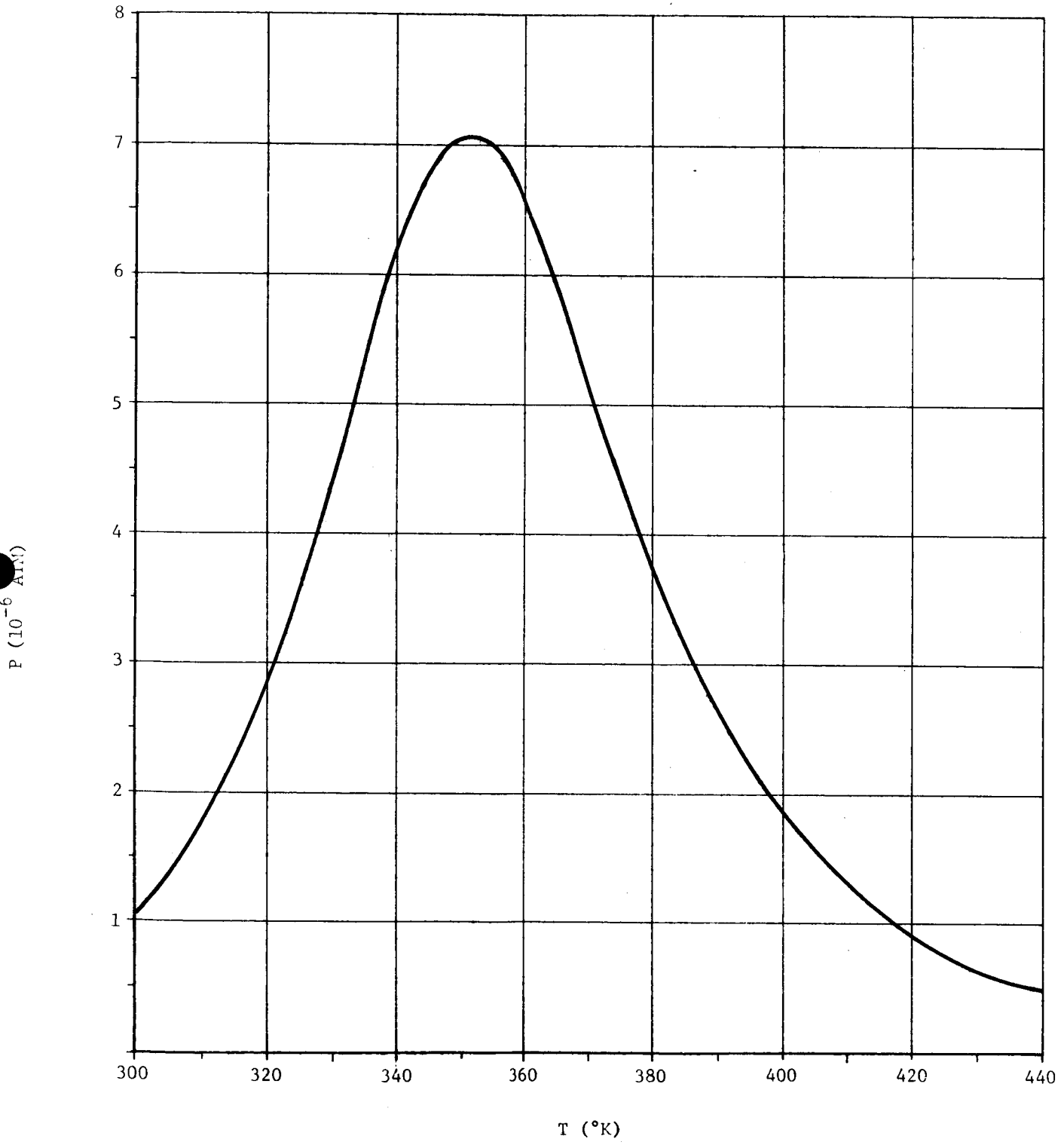


FIGURE 2-2
THEORETICAL PEAK SHAPE

One purpose in studying this equation was to determine the temperature spread which might be expected during desorption and to optimize the experimental variables to obtain maximum separation of contaminants. This equation would prove useful in selecting conditions for analysis if values for equilibrium constant and heats of sorption were accurately known. However, in the development program, in order to demonstrate the feasibility of proposed techniques, sorbents and analytical conditions were chosen on the basis of experimental results.

2.2 DESCRIPTION OF THE DESIGN OF THE PROTOTYPE LABORATORY CONTAMINANT SENSOR

The prototype Laboratory Contaminant Sensor consists of three basic components, (1) the mass spectrometer; (2) the sample inlet system; and (3) the accumulator cell assembly. A block diagram of the complete system is shown in Figure 2-3 and a photograph of the assembly is shown in Figure 2-4.

The system, with the exception of two Welch vacuum pumps, is housed in two 66" x 28" x 19" open racks. The system requires approximately 20 amperes of 110 VAC, 60 cycle power. Cooling water is required for the diffusion pump and liquid nitrogen for the cold trap.

2.2.1 THE MASS SPECTROMETER SYSTEM

The mass spectrometer selected for this program is a cycloidal focusing residual gas analyzer (CEC 21-614-1) modified by the addition of a vacuum system and a sample introduction system. It has a resolution of one part in 150 and two separate scan ranges, m/e 2-12 and m/e 12-200. The sensitivity in terms of inlet pressure is 20 divisions/micron N_2 under conditions normally employed for analysis - low sensitivity and 30 microamperes ionization current. This corresponds to an ion source sensitivity of 10^{-5} amps/torr/microampere ionization current in the low sensitivity mode. A factor of twenty increase in sensitivity is available in the high sensitivity mode, but its use is restricted to very slow scanning speeds.

The ionizing electron current is variable from 20 to 100 microamperes. A fixed electron accelerating voltage of 70 volts is standard on the instrument; a special modification permits selection of the electron accelerating voltage in the range from 6 to 22 volts.

The mass spectrometer vacuum system consists of a large liquid nitrogen cold trap and a diffusion pump (104 liters per second) backed by a mechanical pump (Welch 1400 B duo-seal). The vacuum system connects to the mass spectrometer through a 2 inch O. D. flanged tube. Pressure is monitored at the exit of the analyzer region by a Bayard-Alpert type ionization gauge (CIC-110B). This gauge is equipped with a filament protection circuit which turns off the filament of the mass spectrometer if excessive pressure develops in the instrument. The normal background pressure in this system is approximately 3×10^{-8} torr.

Modifications to the source region consist of addition of a small tube which connects the ion source to the inlet system through the gold leak assembly.

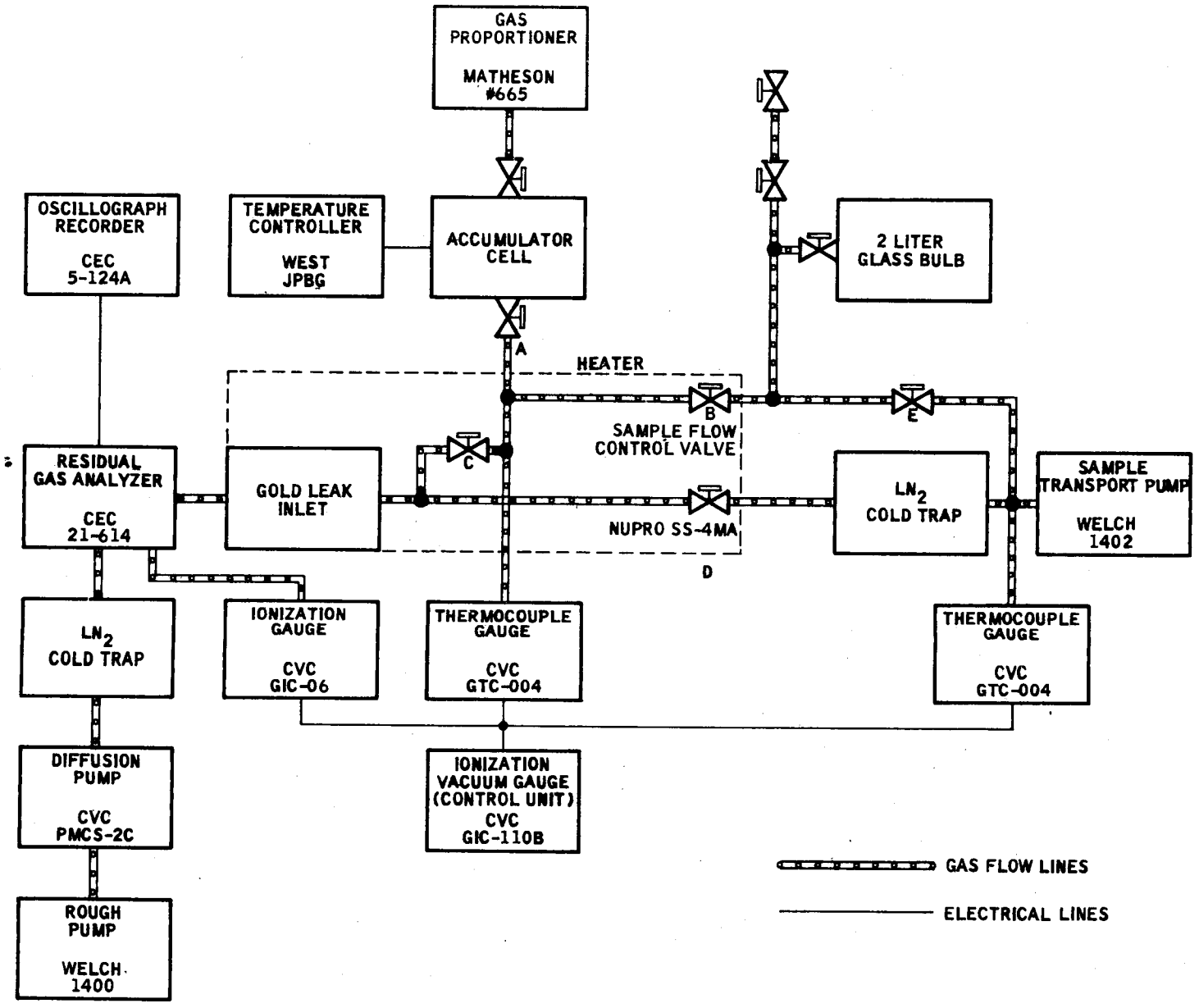


FIGURE 2-3
BLOCK DIAGRAM LABORATORY CONTAMINANT SENSOR

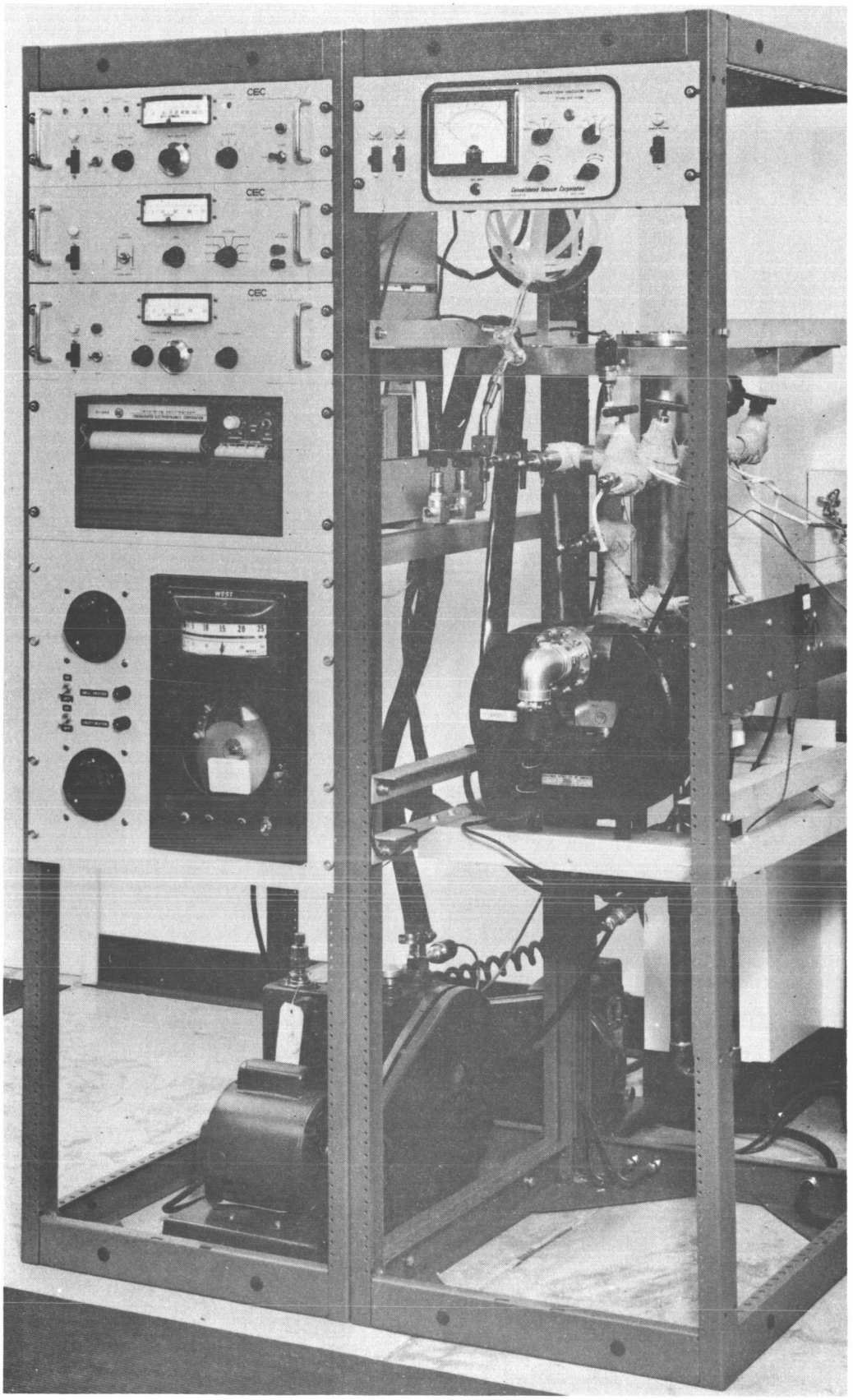


FIGURE 2--4

LABORATORY CONTAMINANT SENSOR

The gold leak assembly consists of a thin gold foil containing six small foil holes; the gold foil is welded to a stainless steel fitting which seals to the inlet system and the mass spectrometer with gold gaskets.

The analog output of the mass spectrometer is fed to an oscillograph recorder with five ranges, 100X, 30X, 10X, 3X, and 1X. The use of the five range oscillograph permits recording peaks over four orders of magnitude simultaneously throughout the scan range.

2.2.2 THE SAMPLE INLET SYSTEM

The sample inlet system provides the means for introducing the gases desorbed from the accumulator cell into the mass spectrometer. The main functions of the inlet system are as follows:

a. To control the pressure ahead of the gold leak at 300 microns and below.

b. To bypass the gold leak during the precut of air from the accumulator cell.

c. To permit direct introduction of sample gases.

d. To permit control of the pump-out rate of contaminant gases during desorption.

The sample inlet is operated from a separate vacuum pump (Welch 1402B) which is preceded by a cold trap to prevent backstreaming of pump oil to the mass spectrometer during sample analysis.

Inlet system pressure is monitored with a thermocouple gauge. The portion of the inlet system exposed to contaminant gases during desorption of the accumulator cell is maintained at approximately 125°C by external heaters. At the gold leak of the mass spectrometer the temperature is about 60°C because heat is lost to the mass spectrometer metal case. With the exception of the micrometer needle valve, the valves in this section are all metal, bakeable, high vacuum valves. The micrometer needle valve is stainless steel with Viton "O" ring seal. The rate of removal of air as a function of valve setting is shown in Figures 2-5A and 2-5B.

In operation, the accumulator cell is attached to the inlet system at (A), with valves (B) and (C) closed, valve (E) open. Air is pumped out of the upper section of the inlet system through (B) and (E) while the vacuum previously established at the gold leak is maintained by closing the flow control valve (D). When the upper section reaches background pressure, air is precut from the accumulator cells by opening the valve at the end of the cell for 15 seconds to reduce the pressure in the system to the level acceptable at the gold leak (less than 500μ). The accumulator cell valve is closed, valve (B) is closed, valve (C) is opened and the flow control valve (D) set at the desired opening. The temperature program is started on the accumulator

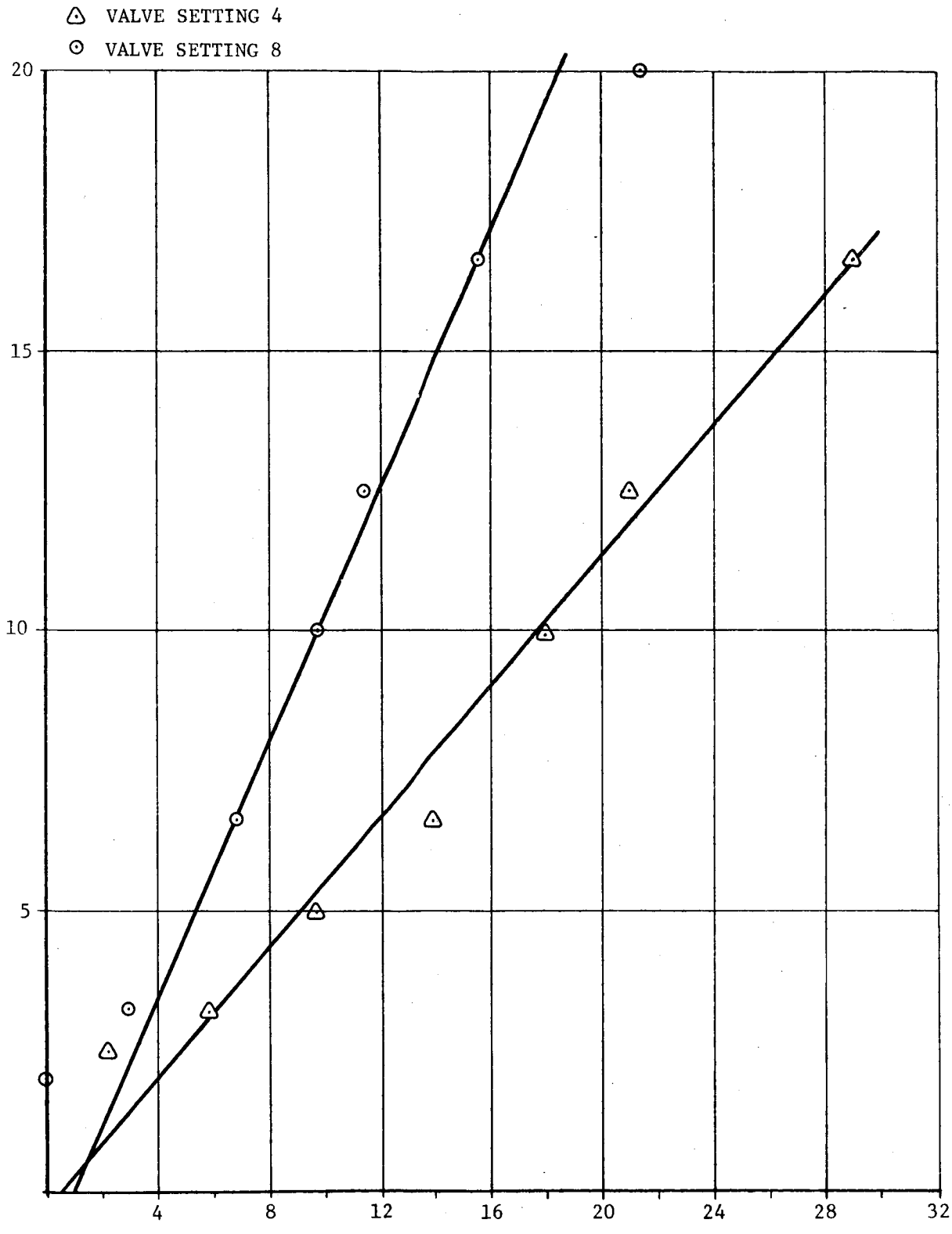


FIGURE 2-5A
PUMPOUT RATE THROUGH MICROMETER NEEDLE VALVE

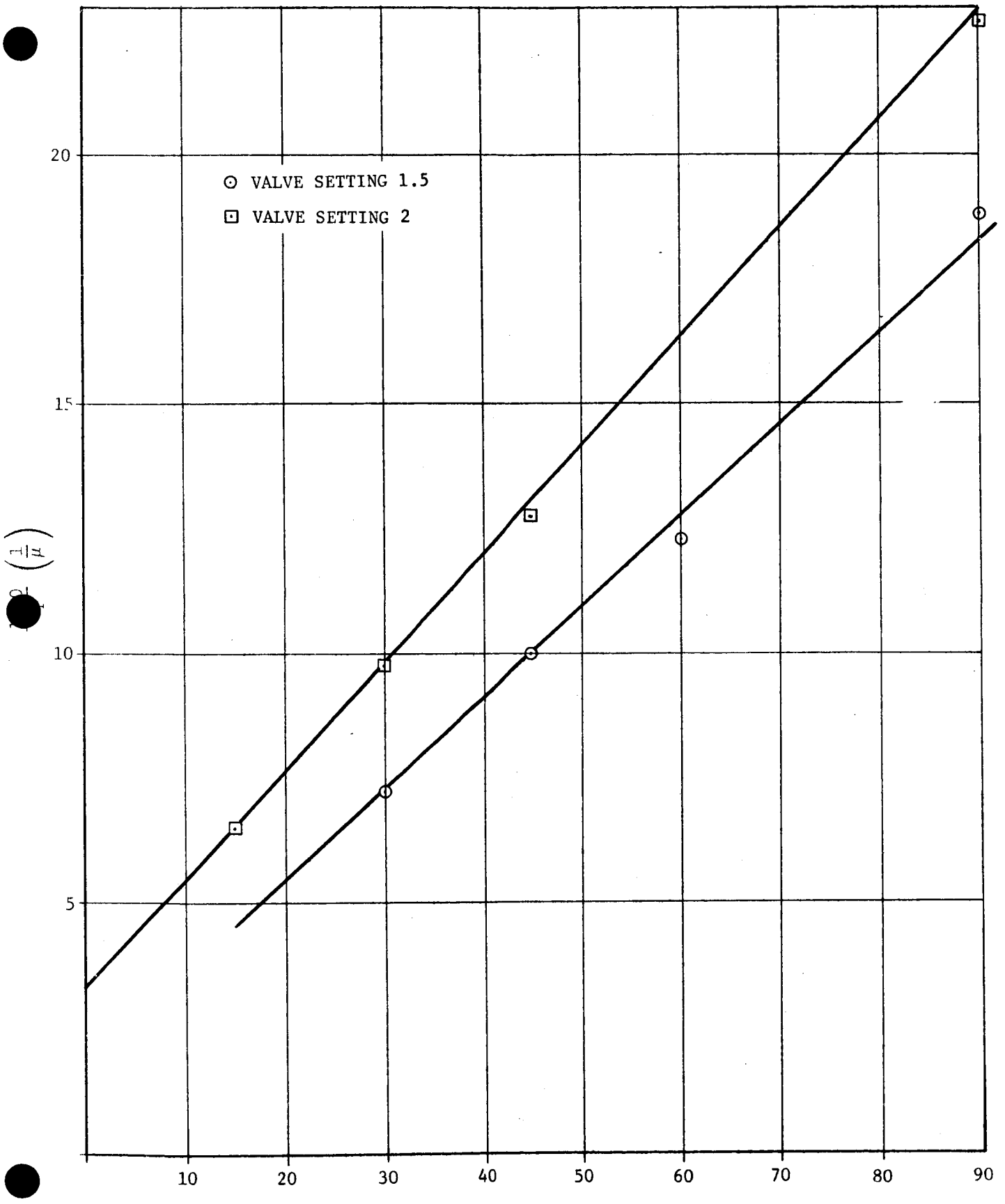


FIGURE 2-5B

PUMPOUT RATE THROUGH MICROMETER NEEDLE VALVE

cell, the cell valve is opened and the desorbed contaminants pass through the upper and lower inlet system sections to the cold trap ahead of the vacuum pump. A portion of the gases enters the mass spectrometer through the gold leak. Mass spectra are recorded at selected temperature intervals over the mass range, 12-120.

Mass spectral data obtained at two temperatures during desorption of a mixture of benzene, toluene, xylene and dioxane are shown in Figure 2-6. Note that m/e 88, due to dioxane, is decreasing with temperature in this portion of desorption, while m/e 91, due to toluene, is increasing.

When the upper temperature (250°C for charcoal or Molecular Sieve, 230°C for Porapak Q) of the desorption run is reached, valve (B) is opened and residual contaminants are pumped directly from the accumulator cell, bypassing the mass spectrometer.

In operation, the inlet system generally functioned satisfactorily with the exception that the gold leak occasionally plugged. The gold leak consists of six small holes in a thin gold foil, which permits molecular flow of the sample in the inlet system into the ion source of the mass spectrometer. Closure of the gold leak is evidenced by a decrease in the ratio of the pressure measured in the analyzer region to that in the inlet system and a corresponding decrease in sensitivity based on inlet system pressure. When leak closure are indicated, the vacuum systems are vented and the gold leak capsule removed for cleaning. Frequently, examination of the surface of the leak under a microscope (120x) showed nothing on the surface. Apparently, the holes of the gold leak are closed by a thin transparent film which is believed to form from vacuum pump oil either creeping through the system or swept up to inlet system as an aerosol when the cold trap is warmed. A Molecular Sieve trap used in place of the present liquid nitrogen trap should eliminate this.

2.2.3 ACCUMULATOR CELLS

There are three accumulator cells. Each consists of a teflon lined, stainless steel tube (3/8" diameter) wrapped with a nichrome heater and terminated on each end with a bellows type, stainless steel valve. The teflon coating is used to reduce sorption and possible reaction on metallic components. It is applied as an aqueous resin dispersion, dried and heated to 350°C to fuse the polymer.

The sorbent is retained in the tube by a 150 mesh stainless steel screen, inserted between the tube ends and the Swagelok fittings on the valves.

The assembly is wrapped with asbestos and glass tapes in order to provide heat distribution. A thermocouple attached to the wall of the cell furnishes a signal for the temperature programmer.

The Porapak Q cell consists of a 3 inch section of 3/8 inch tubing (.065" wall) containing approximately 750 mg of Porapak Q. The sorbent is conditioned by flowing ultrapure helium through the cell and heating it to 250°C. The final temperature is maintained for about thirty minutes after which the cell is

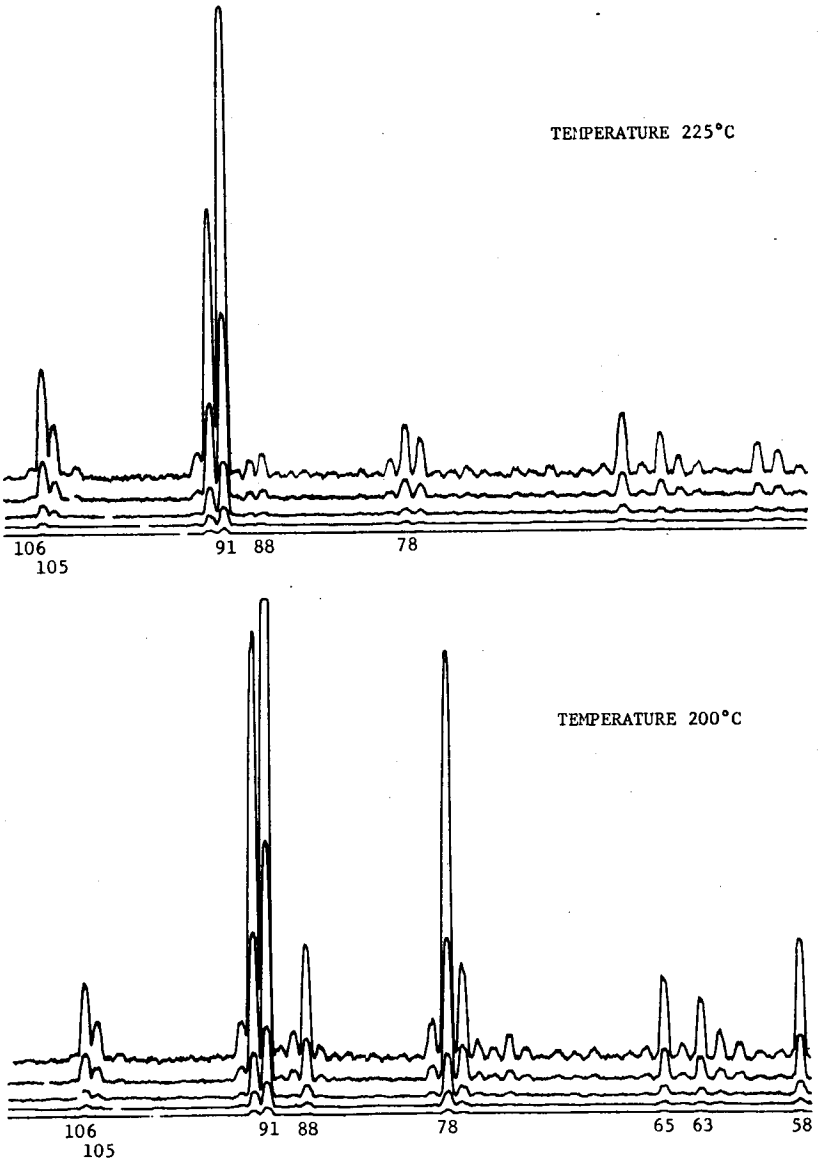


FIGURE 2-7
MASS SPECTRAL DATA

cooled under helium. The cell is attached to the inlet system and heated under vacuum as final conditioning procedure.

The charcoal cell consists of a 2 inch section of 3/8 inch tubing containing 700 mg of charcoal MI-1, which is a coconut charcoal of high adsorption capacity and activity. The same conditioning procedure is followed except that a temperature of 250°C is used.

The Molecular Sieve 5A cell consists of a 4 inch section of 3/8 inch tubing containing approximately 2 g of Molecular Sieve 5A. It is conditioned at 250°C.

A West Model JPGB temperature-programmer controller is used to control the temperature and the heating rate of the accumulator cell. The set point of the controller is mechanically driven upscale by a cam, cut to yield the desired heating rate and actuated by a clock-motor. When the cell temperature falls below the set point temperature, a light on the arm of the set pointer falls on a photoelectric cell which actuates the heater circuit through a relay. Heating rates of 1.8, 3.6 and 7°C/minute were used in preliminary experiments; a heating rate of 7°C/minute was selected for routine analysis of gas samples. The thermal lag in this system permits a temperature difference of approximately 5°C to occur between the programmed temperature and the actual temperature. Figure 2-7 shows the temperature as a function of time in a typical run.

The accumulator cell is charged by allowing a controlled gas mixture to flow through the cell from a pressurized source. The control of the flow is accomplished with the use of the gas proportioner. The flow rates of the sample gas and the diluent gas are adjusted for the desired concentration of contaminant.

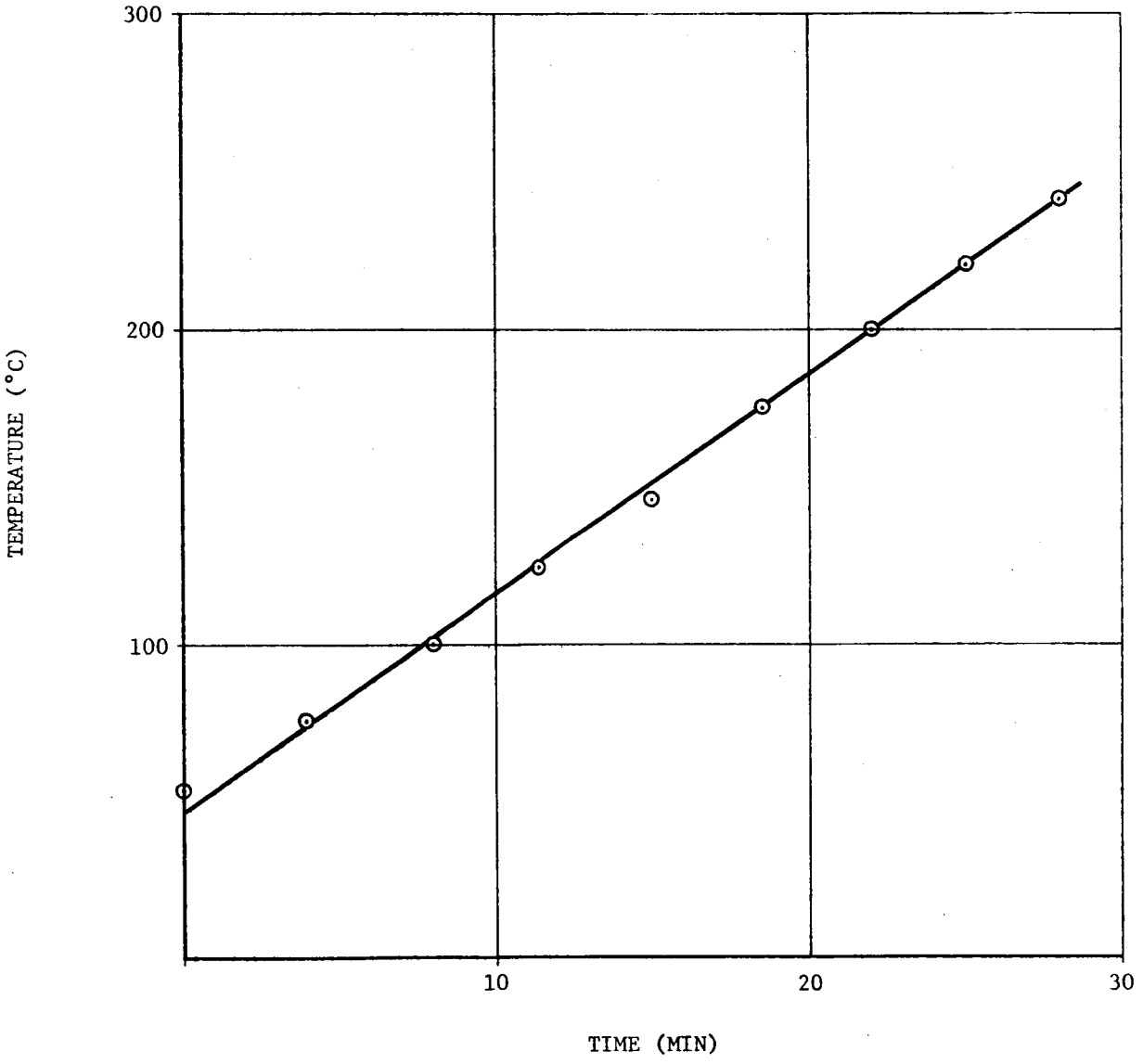


FIGURE 2-8
TYPICAL TEMPERATURE PROGRAM

3. CONTAMINANT AIR MIXTURES

Gas mixtures containing the contaminants at concentrations up to 0.1% by volume in air or nitrogen were purchased from a commercial vendor for test purposes. A list of the purchased mixtures is presented in Table 3-1. The table shows the diluent gas containing the contaminants as well as the analysis of the mixture composition reported by the vendor and that performed at Perkin-Elmer Aerospace Systems.

The mixtures are obtained in pressurized cylinders. For contaminants which are liquids at room temperature, the maximum partial pressure of the contaminant in the cylinder is adjusted to be less than the saturation vapor pressure at anticipated cylinder temperatures to avoid separation of a liquid phase. The total pressure in the cylinder is calculated to give the desired contaminant concentration. Cylinders are charged and discharged several times to equilibrate the walls with the gas mixture before finally filling the cylinder. Samples for analysis are taken from the charged cylinder. The vendor analyzes the mixture by gas chromatogrphy or wet chemical methods depending upon the nature of the contaminant; in one instance, mass spectrometry was employed.

Concentrated mixtures were used as received from the vendor for preliminary tests of inlet system design, in measurement of equilibrium constants (for two of the contaminants) and for experimental selection of sorbents to retain the components. For other experiments mixtures were diluted with air in a Gas Proportioner (Matheson Model 665). The Matheson Model 665 gas proportioner consists of two flowmeter tubes which discharge through a third mixing tube containing strands of glass wool. The glass wool provides turbulence for mixing the outputs from the two flowmeters. The flowmeter tubes (Matheson type #600 and #602) which were selected for the gas proportioner, permit a maximum dilution factor of approximately one hundred. With the purchased gas mixtures, dilutions to concentrations in the range from 1-20 ppm were obtained for testing. Extrapolation of test results permit evaluation of the test procedure at the required sensitivity limit at the lower concentrations.

The flowmeters making up the gas proportioner were calibrated with the use of a Brooks VOL-U-METER, Model 1074. The accuracy of this instrument is 0.1%. The results of these calibrations are shown in Appendix A, Figures A-1 through A-4.

The mixing accuracy of the gas proportioner was evaluated by preparing mixtures of oxygen and nitrogen with the gas proportioner and analyzing the mixtures with the mass spectrometer. A first series of measurements were performed with the capillary inlet system of the mass spectrometer and covered the O_2/N_2 ratio

TABLE 3-1

Purchased Contaminant-Gas Mixtures

MIXTURE NO.	CONTAMINANT	BULK GAS	CONCENTRATION OF CONTAMINANT (ppm) Vendor	Aerospace Systems
1	Acetaldehyde	Nitrogen	951	1250
2	Butene-1	Air	1090	1160
3	Toluene	Air	933	1050
4	Benzene	Air	390	418
	Toluene		350	453
	m-Xylene		170	401
	Dioxane		260	383
5	Benzene	Air	40	72
	Toluene		275	596
	m-Xylene		6	47
	Dioxane		0	48
6	Sulfur dioxide	Nitrogen	239	286
7	Hydrogen chloride	Air	122	125*
8	Methanol	Air	305	468**
	Methylene chloride		532	
	Acetone		501	430
	Ethylene dichloride		775	961**
9	Methane	Air	357	
	Methylene chloride		501	
	Acetone		561	
	Ethylene dichloride		569	
10	Carbon disulfide	Nitrogen	120	
	Hydrogen sulfide		90	
11	Carbon monoxide	Argon	473	
	Nitrous oxide		675	
12	Methane	Nitrogen	222	
	Nitric oxide		216	
	Carbon dioxide		202	
13	Allyl alcohol	Nitrogen	673	375
	Ethyl acetate		418	265
14	Vinyl chloride	Air	198	120
	Freon-11		501	

* Very small peak, less than 10 divisions

** Average of three values differing by more than 100 ppm

from 1 to 0.01 and total flow rates from 70 cc/ minute to 860 cc/minute. The standard deviation of the percentage difference was 4.0%. At maximum dilution, the error was approximately 10%.

Subsequent to this test, the glass wool in the mixing tube was replaced with Teflon strands to minimize surface adsorption. A check of the calibration system was carried out after this replacement, again using oxygen and nitrogen as the test gases. This calibration was accomplished using the inlet system described in Section 2. The standard deviation of the percentage difference was 7.35% for oxygen and 4.14% for nitrogen. These errors correspond to an error or uncertainty in the dilution factor of approximately 10% for the ratio (air/contaminant gas mixture) range from 73 to 0.46.

Data from these two calibrations are presented in Appendix A.

For tests at low concentration a sample of three liters, taken over a time period of five minutes or less, was used. This sample size and sampling rate are believed to be compatible with atmospheric sampling in closed systems. Before introducing the sample into the accumulator cell, the lines are purged for a minimum ten minute period. This purge is accomplished under conditions identical to those used during sampling. Precautions are taken throughout the sampling system to minimize the loss or hold-up of the contaminants. The lines connecting the gas sample cylinder, the gas proportioner and the sample cell are coated with a Teflon resin. The amount of contaminant sorbed in $\mu\ell$(STP) was calculated from the product of the concentration flow rate at STP, and time period of sampling.

In experiments to evaluate the effect of water on the analytical technique, two gas washing bottles were inserted in the line carrying diluent air to the gas proportioner unit. These bottles were partially filled with distilled water. The concentration of water in the sample gas mixture under these conditions should correspond to the saturation vapor pressure of water at room temperature, reduced by a small amount due to mixing with the contaminant gas mixture.

The vendor's analyses of most gas mixtures appeared satisfactory and were used as a basis for determining the sensitivity of the Laboratory Contaminant Sensor for the selected contaminants. However, in some instances discrepancies were observed between results obtained for two different samples containing the same component at different concentrations. It was suspected that these discrepancies might be due to a change in the composition of the gas in the cylinder from the time of the vendor's analysis to the time of sampling. In order to check for gross discrepancies of this nature, a temporary sample introduction system was designed and used to analyze the gas sample directly in the mass spectrometer. In interpreting the results of these analysis, published values for sensitivity and mass spectra were used, since these data are not available for our instrument.

The results of the analyses are shown in the last column of Table 3-1. The use of our analyses for mixtures 4 and 5 gave results which were more consistent than the use of the vendor's analysis. These results are discussed more fully in the following section.

4. EXPERIMENTAL RESULTS

Initial experiments were undertaken to evaluate a capillary inlet system, to test the sorption of contaminants and to establish acceptable cell designs and sample requirements for detection in the mass spectrometer. Results of this portion of the experimental program led to design of the inlet system described in Section 2 of this report and selection of a cell design. The effect of heating rate and pump out rate on the desorption curve were studied with this inlet system and cell design. Tests were conducted to establish a suitable sorbent for each of the contaminants listed in Table 2-1. For those contaminants for which suitable sorbents were found, the quantitative response of the instrument was determined for various concentrations or amounts of contaminant sorbed. The effect of water content of the sample on the analysis was evaluated to a limited extent. Simplification of the spectra obtained during desorption by the use of low voltage electrons for ionization in the mass spectrometer was also investigated.

The results of the experimental program are described in the following paragraphs and a discussion of the results and evaluation of the Laboratory Contaminant Sensor is presented in Section 5.

4.1 PRELIMINARY EXPERIMENTS

A capillary inlet system was designed for continuous sampling of gases at atmospheric pressures. A capillary tube of suitable length and diameter was used in conjunction with a mechanical vacuum pump to reduce the pressure from atmospheric or relatively high pressure to a value acceptable to the gold leak entrance to a mass spectrometer ion source - about one torr. (An extensive discussion of capillary inlet systems is presented in the Final Study Report, Contract NAS 1-5679, Development of a Two-Gas Atmosphere Sensor System.) This type of inlet system was chosen for initial design studies since it was not established at that time that air could be precut from the accumulator cell without significant loss of contaminants and it was therefore anticipated that it might be necessary to sample from a relatively high pressure source. The system used is shown schematically in Figure 4-1.

The capillary tube connects the inlet manifold to a flange assembly containing the gold leak to the mass spectrometer and a bypass line connected to a mechanical vacuum pump. Sample flow through the inlet system capillary is caused by the pressure differential maintained by the mechanical pump. In testing the gas dilution technique, the effluent gas from the gas proportioner unit flowed directly into the inlet manifold at atmospheric pressure. A small portion of the gas mixture is pumped through the capillary for analysis in the mass spectrometer. The remainder of the gas flows out through the ducts of the inlet manifold.

With the capillary inlet system it is also possible to obtain data on the equilibrium constants for sorption of contaminants by what is essentially a frontal analysis technique. Air containing a contaminant at low concentration is passed at a measured flow rate through a cell or tube containing a known amount of sorbent. This cell is connected to one duct of the inlet manifold. The gas emerging from the end of the cell is monitored with the capillary inlet for appearance of the contaminant in the mass spectrometer. From the concentration of contaminant in the air sample and the volume required to saturate the sorbent, an equilibrium constant for the contaminant on the sorbent can be calculated. Breakthrough curves for toluene on Porapak Q, and butene-1 on Porapak Q and charcoal (MI-1) are shown in Figures 4-2, 4-3 and 4-4.

Equilibrium constants calculated from these experiments are shown in Table 4-1 which includes later results obtained for acetaldehyde using the final inlet system design.

TABLE 4-1

Measured Equilibrium Constants

CONTAMINANT	SORBENT	CONCENTRATION (PPM)	EQUILIBRIUM CONSTANT ℓ(STP)/gm
Toluene	Porapak Q	933	25.6
Toluene	Porapak Q	32	74.0
Butene-1	Porapak Q	1090	0.87
Butene-1	Charcoal	1090	32.0
Acetaldehyde	Porapak Q	955	2.28
Acetaldehyde	Charcoal	955	14.15

The agreement of the measured equilibrium constant for toluene with that calculated from gas chromatographic retention times (34.6) is acceptable considering the differences in the technique used and the assumption involved in making the gas chromatographic calculations. (The difference in the toluene/Porapak Q equilibrium constant for different toluene concentrations is probably not significant since inherent inaccuracies in the technique are magnified at low concentrations.)

Preliminary desorption studies were also carried out with this inlet system. A vacuum pump was connected through a valved line to the inlet manifold through one duct; a charged accumulator cell was attached at another, and the remaining ducts were sealed off. Air was precut from the cell by opening the valve to the vacuum pump, and the accumulator cell valve for a short period of time. The valve to the accumulator cell was closed and the temperature raised in 20°C increments. At each temperature, the vacuum pump was valved off and the accumulator cell opened to the inlet manifold. A sample of the desorbed gases passed through the capillary and was analyzed in the mass spectrometer. The cell was valved off again and heated to the next temperature

while the remainder of the desorbed gases was pumped out of the inlet manifold with the manifold vacuum pump. At each temperature, the background spectrum in the inlet system was determined before the desorbed gases were admitted to the inlet manifold. These background spectra showed the necessity for placing a cold trap ahead of the inlet capillary vacuum pump to prevent backstreaming of contaminants from the relatively high conductance bypass line connecting this pump to the gold leak.

Experiments were carried out to establish the relationship between the total amount of toluene sorbed on Porapak Q and the mass spectral signal. The preliminary results were encouraging. A relatively constant (±25%) relation between the amount of toluene sorbed and the m/e 91 peak height was observed. The feasibility of detecting toluene concentrations near the required sensitivity of 20 ppm was demonstrated. However, when improvements were made in the system to reduce air leakage into the capillary sampling block, the results became erratic and appeared unrelated to the total amount of toluene sorbed. The explanation of these results appears to lie in the fact that air leaking into the system serves as a carrier gas to move the desorbed toluene through the capillary. In the original experiments, the amount of air leaking into the system was relatively reproducible and high enough for the results to be relatively independent of total pressure at the capillary. (For lower pressures, the concentration of contaminant is higher in the "carrier gas" but the total pressure at the leak is lower; for higher pressures, the reverse is true so that the effects of total pressure variation are small.) In later experiments, the total pressure at the capillary was much lower due to greatly reduced leakage; under these conditions small variations in pressure have a much larger influence on the amount of contaminant transported through the capillary, and hence in the mass spectrometer signal. These observations led to design of an inlet system described in Section 2, eliminating the capillary.

In summary, these preliminary experiments showed that:

a. Sorbents were available which would effectively remove small concentrations of contaminants from air samples.

b. At least for toluene on Porapak Q, it was possible to precut residual air from the system without loss of significant amounts of toluene.

c. Background spectra from Porapak Q and charcoal were negligible at temperatures up to 230°C and 250°C respectively.

d. A cold trap is required ahead of the inlet system vacuum pump to prevent backstreaming from the pump at low pressures in the inlet system.

As a result of these experiments it was concluded that the capillary inlet system could be used satisfactorily when a relatively high pressure differential existed between the capillary inlet and the gold leak, but that such a high pressure differential was neither necessary nor desirable for analysis of contaminants. Pressure in the accumulator cell could be reduced to values acceptable to the gold leak directly without significant loss of contaminants with the sorbents tested.

A large accumulator cell with a metal honeycomb section for heat distribution was originally designed for use with the capillary inlet system. It was designed to hold approximately ten grams of sorbent and to provide the pressure and amount of sample required for flow through the capillary. As the experimental work progressed, it became apparent that such a large cell was unnecessary with either the capillary inlet system or the direct inlet system, and this cell design was discarded in favor of the short tube cells described in Section 2.

4.2 ANALYTICAL CONDITIONS - EFFECT OF VARIATION IN HEATING RATE AND PUMP-OUT RATE

Effects of heating rate and pump-out rate were investigated with the inlet system described in Section 2 to select the best conditions for analysis. Three heating rates and two valve settings were investigated with a fixed amount of butene-1 sorbed on charcoal. The results are summarized in Table 4-2. From the data in the table, it is apparent that decreasing the heating rate decreases both the maximum mass spectrometer output and the temperature at which the maximum output is observed. Reducing the pump-out rate increases both the temperature at which the maximum pressure occurs and the mass spectrometer output at the peak. The most important effect of variation is these parameters is on the electrometer output which can be changed by a factor of four. The maximum shift in the temperature of maximum desorption is approximately 50°C which is smaller than the temperature range over which desorption takes place.

An experiment was performed to determine whether the heating rate would affect the temperature range over which desorption occurred. The peak width for this purpose is defined as the difference in temperature between the points on the ascending and descending portions of the desorption curve at which the signal is one half the maximum observed signal. Since this width is dependent on the peak height, sample sizes for this test were adjusted to give the same peak height for the different heating rates. The results in Table 4-3 show that the heating rate has no significant effect on the temperature range over which desorption takes place.

The effect of heating rate and pump-out rate on the separation of contaminants was studied with a mixture of benzene, toluene, xylene, and dioxane. The benzene-toluene separation did not change appreciably with heating rate or pump-out rate over the range of these variables investigated which is the same as that described above. Conditions for analysis of contaminants were therefore chosen to give the fastest analysis time and the maximum sensitivity. A heating rate of 7°C/minute and the maximum opening of the micrometer needle valve were chosen for determination of sensitivity for the selected contaminants.

4.3 QUANTITATIVE ANALYSIS

The mixtures described in Section 3 were used for the quantitative analysis. For each mixture, preliminary sorption tests were performed to establish the sorbent to be used for the individual components of the mixture and the approximate temperature of desorption for each component. The concentrated mixtures were used for these preliminary tests.

TABLE 4-2

Maximum Electrometer Output and Temperature at Maximum Electrometer Output

I. EFFECT OF HEATING RATE

Cell: 1/4" x 4" (290 mg Charcoal) Sample: 76.4 $\mu\ell$ (STP) Butene-1
Valve Setting: 8

HEATING RATE °C/minute	ELECTROMETER OUTPUT (div)	TEMPERATURE AT SIGNAL MAXIMUM (°C)
7.2	410	180
7.0	360	195
7.0	355	185
3.6	144	164
1.8	114	140

Cell: 3/8" x 2" (720 mg Charcoal) Sample: 76.4 $\mu\ell$ (STP) Butene-1
Valve Setting: 8

HEATING RATE °C/minute	ELECTROMETER OUTPUT (div)	TEMPERATURE AT SIGNAL MAXIMUM (°C)
7.0	465	207
7.0	440	195
3.6	200	170
1.8	180	145

II. EFFECT OF PUMP-OUT RATE

Cell: 1/4" x 4" (290 mg Charcoal) Sample: 76.4 $\mu\ell$ (STP) Butene-1
Heating Rate: (1.8°C/minute)

VALVE SETTING	ELECTROMETER OUTPUT (div)	TEMPERATURE AT SIGNAL MAXIMUM (°C)
4	228	150
8	114	140

Heating Rate: (3.6°C/minute)

VALVE SETTING	ELECTROMETER OUTPUT (div)	TEMPERATURE AT SIGNAL MAXIMUM (°C)
4	440	173
8	144	164

TABLE 4-3

Effect of Heating Rate on Desorption Temperature Range

Cell: 1/4" x 4" (290 mg Charcoal) Contaminant: Butene-1
Metering Valve Setting: 8

SAMPLE SORBED (μl-STP)	HEATING RATE (°C/minute)	ELECTROMETER OUTPUT AT MAXIMUM (divisions)	PEAK TEMPERATURE (°C)	PEAK WIDTH AT ONE HALF PEAK MAXIMUM (°C)
229	1.8	340	133	63
114	3.6	345	154	68
76.4	7.0	378	187	68

Dilute samples were prepared from the concentrated mixtures by mixing them with air in the gas proportioner unit. Approximately three liter samples were passed through the sorbent cell at a total flow rate of approximately 750 ml/minute. The sorbed components were desorbed under fixed conditions. Air was precut from the accumulator cell by opening the valve directly to the vacuum system (with inlet to the gold leak valved off) for 15 seconds. (A longer precut time (30-60/sec) was frequently required to reduce the pressure to acceptable values when wet air was used with the charcoal cell.) The cell valve was closed and the cell heated to 50°C for the start of programmed temperature desorption. The inlet system valves were opened and the direct line to the vacuum pump closed to permit the desorbed components to flow past the gold leak through the micrometer valve to the cold trap and the vacuum pump. The valve was set at 8, the most open position, for these tests. The temperature programmer was started and the cell valve opened as soon as the heating cycle of the program started. An immediate scan of the emerging gases was taken; scans were repeated at approximately 20°C intervals. Time, temperature, and pressure (indicated on the thermocouple gauge) were recorded at the start of each scan. A portion of two typical scans is shown in Figure 2-5.

The maximum electrometer output was determined for each contaminant at several different concentrations. Sensitivity values (in terms of divisions/μl sorbed) were calculated from the slope of the curves for these data. These curves are shown in Figures 4-5 through 4-24. Detectability limits were calculated on the basis of a three liter sample, assuming a ten division signal was required.

The temperature at which the maximum electrometer output occurred was obtained either directly from the peak reading or from the intersection of the extrapolated slopes of the rising and descending signal, if it appeared that the top of the thermal peak was intermediate between two nearly equal electrometer signals. The characteristic temperature was taken as the temperature at which the maximum occurred for the lowest concentration tested. This temperature shifts to lower values for higher concentrations or larger amounts of contaminants sorbed. Shifts of approximately 20°C are observed over the concentration range investigated. Typical desorption curves are shown for the test mixtures in Figures 4-25 through 4-39.

A limited amount of data was obtained for the effect of water on determination of the test contaminants. In most instances one or two determinations were carried out using wet air (~90% relative humidity) as diluent. In general, the peak height and peak temperature were not significantly different from those obtained with samples diluted with air taken directly from a cylinder.

Results obtained for the individual contaminants listed in Table 2-1 are described in the following paragraphs. Test gas mixtures are referred to by number as listed in Table 3-1.

4.3.1 ACETONE (FIGURES 4-5, 4-6, 4-25 and 4-26)

The quantitative data obtained for acetone on charcoal show a reasonably linear relationship between the amount of acetone sorbed and the electrometer output at the peak maximum. Figure 4-5 shows that acetone is one of the compounds more strongly retained on charcoal. A sensitivity of 4.8 divisions/$\mu\ell$ is calculated for the m/e 43 peak of acetone on charcoal as shown in Figure 4-6.

On Porapak Q, acetone is one of the least tightly sorbed contaminants. The scatter of the data points for larger amounts sorbed suggest that a significant loss of acetone occurs from Porapak Q when larger amounts are sorbed, corresponding to conditions nearer to saturation of this sorbent. A sensitivity of 5.8 divisions/$\mu\ell$ are calculated for this compound on Porapak Q.

Concentrations of 100 ppm, the required sensitivity, can be determined on charcoal. However, if such concentrations were expected routinely, it might be advisable to decrease the sample size. These higher concentrations are in the saturation range for Porapak Q, when three liter samples are used.

4.3.2 ACETALDEHYDE (FIGURES 4-7 and 4-27)

Data for acetaldehyde sorbed on charcoal show a sensitivity of 2.8 divisions/$\mu\ell$ for the m/e 27 peak, and a sensitivity of 1 division/$\mu\ell$ for the m/e 45 peak. It is well separated on charcoal from other contaminants in Table 2-1 having similar mass spectra. However, the major mass numbers in the spectra are all common to a number of compounds and it may be necessary to use more than one peak to identify this compound in the presence of other similar compounds not included in the list in Table 2-1.

When wet air is used as diluent, the peak appears somewhat broader, but the electrometer output at the peak is not changed nor is the temperature at which this peak occurs.

4.3.3 ALLYL ALCOHOL (FIGURES 4-8 and 4-28)

Porapak Q is a suitable sorbent for this contaminant. The data show a sensitivity of 1.6 divisions/$\mu\ell$ for the m/e 57 peak and 1 division/$\mu\ell$ for the m/e 31 peak. Allyl alcohol desorption partially overlaps that of ethyl acetate which is present in the same mixture, so that mass numbers common to both compounds peak at a point intermediate between the two main peaks in the desorption

curve. The effect of water is uncertain. The two points obtained using wet air as a diluent define a line with a slope about 50% less than the line defined by the dry air. With the limited data available, the significance of the difference cannot be evaluated.

The mass spectra for allyl alcohol determined in these experiments shows a significantly higher fraction of m/e 31 (62%) than reported in the literature (32%). This observation suggests that some other alcohol (possibly ethyl) may be present in the sample in unknown concentrations but the mass spectrometer should be calibrated with pure allyl alcohol to resolve this discrepancy.

Assuming a peak of ten divisions is required for detection, allyl alcohol could be detected at concentrations of approximately 2 ppm; this is higher by a factor of ten than the required sensitivity of 0.2 ppm.

4.3.4 AMMONIA

This compound was not commercially available in analyzed mixture. Tests to determine a suitable sorbent were carried out by bubbling air through a solution of ammonia in propanol. Ammonia was retained on Molecular Sieve 5A but its desorption temperature was too close to that of water to permit detection of this compound at low concentration in air containing water. Charcoal did not appear to be satisfactory sorbent at the relatively high concentrations of ammonia used in these tests but this sorbent should be reinvestigated with ammonia at lower concentrations.

4.3.5 BENZENE (FIGURES 4-9 and 4-32)

Porapak Q is a suitable sorbent for benzene. Its desorption temperature is relatively close to that of dioxane, which has a non-interfering mass spectra, and that of carbon disulfide from which interference due to the $C^{12}S^{32}S^{34}$ isotopic species can be expected. This interference could make it difficult to determine trace amounts of benzene in the presence of large concentrations of carbon disulfide. Benzene is well separated from xylene in desorption temperature; consequently contribution to the benzene 78 peak from xylene is negligible for the mixtures of these two contaminants.

The sensitivity for benzene is calculated to be 12.7 divisions/$\mu\ell$ on the basis of analyses of mixtures #4 and #5 at Perkin-Elmer Aerospace Systems. This value appears to fit the data best for small amounts of benzene sorbed. If the analysis reported by the vendor for mixture #5 is used, results for the two mixtures are inconsistent. Agreement between our analysis and that of the vendor for benzene in mixture #4 (390 vs 418 ppm) is good and the difference in results for mixture #5 probably result from sampling errors. A concentration of 2.5 ppm (required sensitivity) is readily detectable.

4.3.6 BUTENE-1 (FIGURES 4-10, 4-29 and 4-30)

Butene-1 is determined on charcoal; it is not retained satisfactorily on Porapak Q through the air precut. A sensitivity of 5.6 divisions/$\mu\ell$ is calculated for this compound based on m/e 41. The available data indicated a

detectability limit of 2 ppm based on extrapolation of the data points. There is an apparent loss of about 5$\mu\ell$ of butene-1 in the system. The cause for this apparent loss is not presently understood. More data in the low concentration range would be useful in investigating this phenomena. Water does not interfere with determination of this compound.

4.3.7 CARBON DIOXIDE (FIGURE 4-31)

Carbon dioxide is retained on Molecular Sieve 5A but quantitative data obtained are inconsistent. For the purchased gas mixture #12, one determination indicates a sensitivity of 5.6 divisions/$\mu\ell$. For carbon dioxide in air (compressed air with an assumed carbon dioxide content of 330 ppm), the average sensitivity is 2.7 divisions/$\mu\ell$ but individual values range from 1.7 to 5.8 divisions/$\mu\ell$. With the relatively large air samples used, saturation and loss of carbon dioxide in the air precut may result in low values. Additional experimental effort is required to obtain accurate data for determination of sensitivity for carbon dioxide.

4.3.8 CARBON DISULFIDE (FIGURES 4-11 and 4-33)

Carbon disulfide is retained and determined on Porapak Q. The sensitivity is 10.6 divisions/$\mu\ell$. The mass spectrometer is particularly sensitive to this compound and concentrations of the order of 2 ppm are easily detectable. The m/e 76 peak used for determination is free from interferences except for a very small contribution from benzene which is not separated from carbon disulfide or Porapak Q. Water has no effect on determination of this compound.

4.3.9 CARBON MONOXIDE (FIGURES 4-12, 4-34 and 4-35)

A number of sorbents were tested for retention of this compound at room temperature. These include Molecular Sieve 4A and 5A, charcoal, silica gel (Davissons 08 grade), Porapak Q, and an oil suspension of iron phthalocyanine on Porasil and on Porapak Q. These were all ineffective. A special sorbent of palladium coated charcoal was prepared by dissolving 1 g of $PdCl_2$ in water, heating to boiling and adding approximately on ml of a mixture of $HC\ell$ and HNO_3 to clear the solution. Ten grams of charcoal were added and after a few minutes the colored solution completely decolorized. Reduction of the palladium chloride to metallic palladium was indicated by the appearance of the charcoal. The charcoal was filtered, washed with distilled water and dried in air under an infrared lamp. A 1.4 gram sample of this material was used to prepare a 4" x 3/8" x .065" cell.

Desorption of carbon monoxide from this cell starts at about 100°C and reaches a maximum at 185°C under the standard operating procedure. Air alone gives a small signal at m/e 28 with a maximum at about 230°C and the sorbent without air also has a background of about 10 divisions of 28 which slowly increases to 22 divisions at temperatures above 200°C. Part of the blank is probably due to a small leak known to be present in the system when these samples were analyzed. The increase in the blank at high temperature is not due to carbon dioxide.

The possibility that the observed desorption peak for m/e 28 was due to reaction of water with the filament was ruled out on the basis of the air blank and from the fact that the mass spectrometer is equipped with a rhenium filament, which reduces the sample distortion frequently encountered with carbonized tungsten filaments. Figure 4-35 shows desorption of water from the palladium-charcoal sorbent during the analysis of carbon monoxide shown in Figure 4-34.

This sorbent is not the most desirable from the point of view of its reactivity to and possible inactivation by other possible contaminants. These facets of its use have not been explored. Also the reproducibility of preparing the sorbent needs to be studied. In view of the toxicity of carbon monoxide, some further effort to investigate this and similar type sorbents seem indicated.

4.3.10 1,4-DIOXANE (FIGURES 4-13 and 4-32)

Dioxane is sorbed on Porapak Q and can be quantitatively determined on this sorbent. The major mass numbers are m/e 28, 58 and 88. At m/e 28, a sensitivity of 9.7 divisions/$\mu\ell$ is calculated on the basis of analysis of mixtures #4 and #5 in our laboratory. As in the case of benzene, use of the vendor's analysis yields inconsistent results for the two mixtures.

Desorption temperatures for ethyl acetate and dioxane are fairly close; however, dioxane can be differentiated from ethyl acetate by the m/e 58 peak which is absent from the ethyl acetate spectra. The required sensitivity of 10 ppm is detectable using m/e 28, 58 or 88. Analysis of a mixture of acetone, allyl alcohol, ethyl acetate and dioxane would however present difficulty unless an accurate knowledge of the spectra and sensitivity are available for the mass spectrometer employed.

4.3.11 ETHYL ACETATE (FIGURES 4-14 and 4-28)

Porapak Q is a suitable sorbent for ethyl acetate. A sensitivity of 6 divisions/$\mu\ell$ is calculated for m/e 43, the major mass peak, and 0.7 divisions/$\mu\ell$ for m/e 61. The required sensitivity of 40 ppm is detectable with either mass number. Possible interference with dioxane was discussed previously; mass number 61, present in the ethyl acetate and not the dioxane spectrum, should be useful in interpreting results from analysis of mixtures of ethyl acetate and dioxane.

Extrapolation of the test data indicates an apparent blank value of about 40 divisions for m/e 43; the reason for this blank is not understood at present. Based on one experiment, water has no effect on the analysis of this compound.

4.3.12 ETHYLENE DICHLORIDE (FIGURES 4-15, 4-25 and 4-26)

This compound can be determined on Porapak Q. Two mixtures containing this compound give sensitivity values of 1.4 and 1.1 divisions/$\mu\ell$ based on m/e 62. This difference of about 20% is probably representative of the accuracy of

the vendor's analysis. Extrapolation of the data points indicate that concentrations less than 2 ppm are not detectable. Loss of approximately 6$\mu\ell$ indicates that the compound may be adsorbed in the inlet system, possibly in the teflon coating on the walls. Concentrations of 10 ppm should be readily detectable.

4.3.13 FORMALDEHYDE

Vendors refused to quote on preparation of test gas mixtures containing this compound. A dilute solution of formaldehyde in water was prepared and a gas sample was obtained by bubbling air through this solution. Charcoal was tested as a sorbent but the results obtained were inconclusive. It appeared that formaldehyde was not sorbed or was lost in the precut. Comparison with acetaldehyde suggests that formaldehyde should be desorbed at relatively low temperature ($< 135°C$) from charcoal and that Molecular Sieve 5A might be a more suitable sorbent. The main difficulty in detecting this compound lies in the fact that the major mass numbers are coincident with fragment peaks from a number of other organic compounds. Therefore, a good separation of this compound from others is required for its detection.

4.3.14 FREON-11 (FIGURES 4-16 and 4-39)

This compound can be determined on either charcoal or Porapak Q. A sensitivity of 2.6 divisions/$\mu\ell$ is calculated for determination on charcoal, based on m/e 101. This compound is not detectable at concentrations below 3 ppm and, as in the case of ethylene dichloride, irreversible sorption in the Teflon coating on the walls of the inlet system is suspected. Detection level is currently set at 7 ppm.

4.3.15 HYDROGEN CHLORIDE

Hydrogen chloride could not be detected in the Laboratory Contaminant Sensor. Sorption on charcoal and Molecular Sieve 5A was tested but hydrogen chloride was not detected during desorption from either sorbent. This result is not too surprising for Molecular Sieve 5A which probably reacts with hydrogen chloride irreversibly, but was rather unexpected for charcoal. At present, it is not certain whether hydrogen chloride was not sorbed on charcoal or whether it was retained so tightly that it did not desorb at temperatures below 250°C. A third possibility is that the hydrogen chloride reacted with exposed metal surfaces in the gas proportioner and that a true sample was not obtained for test purposes. Since it was possible to detect hydrogen chloride in the test gas mixture #7 by direct analysis, reaction in the inlet system is probably not involved, and by analogy, it seems unlikely that reaction in the gas proportioner is the difficulty because the materials to which the test gas mixtures is exposed are similar to those in the inlet system. Additional tests with other sorbents are required to develop analytical capability for this compound.

4.3.16. HYDROGEN SULFIDE

Hydrogen sulfide was tested on Porapak Q and charcoal but did not appear to be retained on either sorbent. (Carbon disulfide which is also present in

test gas mixture #10, is retained on both sorbents.) The reactivity of this compound is similar to that of hydrogen chloride. However, attempts to analyze mixture #10 directly for hydrogen sulfide gave widely scattered results which could have been the result of reaction of hydrogen sulfide in the inlet system. For this compound, also, tests with other sorbents are necessary and, in addition, the inlet system and the sampling system should be re-examined and exposed metal parts coated or eliminated.

4.3.17 METHANE

Methane was not retained on any of the sorbents tested - Porapak Q, charcoal or Molecular Sieve 4A or 5A. It would probably be retained on the Molecular Sieves at subambient temperatures ($< 25°C$) but the restrictions of space flight do not permit cooling the accumulator cell. Under these conditions, it is anticipated that it will not be possible to detect methane. Fortunately low concentrations of methane are not particularly hazardous. The toxicity of methane is a result of simple asphyxiation - displacement or dilution of the oxygen content of the atmosphere - and relatively high concentrations (greater than one percent) can be tolerated. The flammability limits are also relatively high. Methane can be determined directly by other instruments proposed for use on spacecraft at concentrations well below those which are hazardous and it is concluded, therefore, that additional efforts to determine methane with the Laboratory Contaminant Sensor are not warranted.

4.3.18 METHYL ALCOHOL (FIGURES 4-17 and 4-25)

Methyl alcohol is determined on charcoal; a sensitivity of 2.3 divisions/$\mu\ell$ is calculated for this compound. Extrapolation of the data points indicates a loss of about 16$\mu\ell$ of this compound in the system. This corresponds to a limit of detection at 5 ppm. Additional data in the low concentration range is required to verify the extrapolation. However, no difficulty is anticipated in detecting 20 ppm, the required sensitivity. No interference from other compounds listed in Table 2-1 exists for this compound.

4.3.19 METHYLENE CHLORIDE (FIGURES 4-18, 4-25 and 4-26)

Methylene chloride is determined on charcoal with a sensitivity of 3.7 divisions/$\mu\ell$ for m/e 44 the major mass peak. Extrapolation of the data indicates a blank of about 50 divisions at m/e 49. Since there is no background in the instrument at this mass number under the conditions used for analysis, the cause of this blank in not known.

No difficulty is anticipated in determining 50 ppm, the required sensitivity for methylene chloride. On charcoal it is well separated from all compounds listed in Table 2-1 which might cause interference.

4.3.20 NITRIC OXIDE (FIGURES 4-19, 4-31 and 4-36)

Nitric oxide is retained on Molecular Sieve 5A and on charcoal to a limited extent. On both sorbents the desorption curve is very broad, extending over

the entire temperature range. This behavior is not understood at present but it may be due to an effect of water on the sorbents. The data for charcoal shown in Figure 4-20 suggests that saturation of the sorbent occurs at relatively low concentrations. A tentative value of 2.4 divisions/$\mu\ell$ is estimated from the initial slope of this curve.

More experimental work is required to develop a good analytical capability for this compound.

4.3.21 NITROUS OXIDE (FIGURES 4-20 and 4-37)

Nitrous oxide can be determined on Molecular Sieve 5A; a sensitivity of 0.66 divisions/$\mu\ell$ is calculated for m/e 30. The major mass number m/e 44 cannot be used for analysis because of interference from carbon dioxide. The maximum in the desorption curve occurs at a temperature of 125°C. The broad desorption of nitric oxide (major mass number m/e 30) from Molecular Sieve 5A could cause inaccuracy in determination of nitrous oxide although nitric oxide does not reach its maximum desorption at temperatures below 230°C.

At present, the detectability limit for nitrous oxide is set at 5 ppm assuming no interference from nitric oxide. To obtain the required sensitivity of 1 ppm, changes in the mass spectrometer operating conditions would be required.

4.3.22 PHENOL

Vendors declined to bid on the preparation of phenol - air or nitrogen mixtures. Qualitative experiments with a mixture prepared in our laboratory indicate that phenol is tightly retained on Porapak Q and does not desorb below 230°C. While this may result from interaction of phenol with system components other than the sorbent, it is expected that some less retentive sorbent will be required for the analysis of high boiling compounds such as phenol.

4.3.23 SULFUR DIOXIDE (FIGURES 4-21 and 4-38)

Sulfur dioxide is retained satisfactorily on charcoal. Quantitative results indicate a sensitivity of 2.8 divisions/$\mu\ell$. The data extrapolate to zero at an amount of sulfur dioxide corresponding to a concentration of 2ppm. More data in the low concentration range are required to establish this limit. Because of this, the lower limit for detection is currently set at 3 ppm; it is believed that additional data would permit re-evaluation of this value to a number nearer the required sensitivity of 0.5 ppm.

4.3.24 TOLUENE (FIGURES 4-22 and 4-32)

Toluene is determined on Porapak Q; a sensitivity of 11.6 divisions/$\mu\ell$ is calculated for m/e 91 based on the vendor's analysis. The sensitivity calculated from our analysis is lower by about 35% (7.3 divisions/$\mu\ell$). The data show a rather large scatter and at present, no choice can be made on the basis of consistency of results between the two values. However, even at the lower sensitivity figure, there is no difficulty in obtaining the required sensitivity of 20 ppm.

Xylene and toluene desorb at temperatures which are close enough to each other that difficulty may be experienced in detecting small amounts of toluene in the presence of large quantities of xylene on the basis of m/e 91; however, the m/e 92 peak is ten times more intense in the toluene spectra than in the xylene spectra and careful calibration in conjunction with the degree of separation which does exist should permit detection of toluene under these conditions.

4.3.25 VINYL CHLORIDE (FIGURES 4-23 and 4-39)

Vinyl chloride is determined on charcoal. Sensitivity for m/e 62 and 27 are nearly identical, 3.8 and 3.5 divisions/$\mu\ell$ respectively. The required sensitivity of 50 ppm can be readily detected. No interference from other compounds in Table 2-1 is expected for vinyl chloride.

4.3.26 m-XYLENE (FIGURES 4-24 and 4-32)

m-Xylene is determined on Porapak Q. The data obtained with mixture #5 are not consistent with that obtained from mixture #4 on the basis of either the vendor's analysis or our analysis. Response to the compound appears to be less sensitive at lower concentration on the basis of our analysis. This could result from the upward shift of the maximum desorption temperature at small amounts of compound sorbed. This would result in measuring the response on the shoulder of the desorption curve instead of at the peak since the peak temperature is at or above the maximum permissible temperature for Porapak Q. Sensitivity for this compound is adequate to detect the compound at 10 ppm concentration, but until the problem of the discrepancy in the results from different mixtures is resolved, the lower limit for detection cannot be established.

4.4 LOW VOLTAGE DATA

An ionization potential control is incorporated in the mass spectrometer design allowing the energy of the ionizing electron beam to be varied from 6 to 22 volts, in addition to the normal fixed energy of 70 volts. Using low energy electrons for ionization generally results in simpler mass spectra; many of the fragment peaks are eliminated or reduced in intensity, but this mode of operation also leads to an appreciable reduction in sensitivity. The effect of electron energy on the sensitivity was measured for several permanent gases in the initial phase of the program, and comparative data at 70 and 12 volts electron energy were obtained for contaminants during later desorption experiments. Data for argon, helium, and carbon dioxide are shown in Figures 4-40, 4-41 and 4-42. The ratio, m/e 28/44, for carbon dioxide is shown as a function of electron energy in Figure 4-43.

Inspection of Figures 4-40 through 4-42 reveals that there is a measurable ion current below the ionization potential; this is attributed to the high energy tail of the Boltzman distribution for the molecules. That the ratio of m/e 28 to 44 does not go to zero with decreasing electron energy is not surprising since the strength of the C - O bond in carbon dioxide is less than one half the ionization potential (5.56 ev vs. 13.8 ev for ionization potential).

Data for the contaminants are shown in Figures 4-44, 4-45, 4-46 and 4-47. These data were obtained in several ways; alternate mass scans were taken at 12 ev and 70 ev in some instances or a single scan at 12 ev was run at the peak of the desorption curve. For data on mixture #5 (benzene, dioxane, toluene and xylene) and mixture #14 (vinyl chloride and Freon-11), separate desorption experiments were monitored at 12 ev and 70 ev.

The most striking reduction in fragmentation resulted for the aromatics and is shown in Figure 4-44. The fragment ions due to benzene at masses 49 - 53 and at mass 39 were almost completely eliminated; the mass 63 group of fragment ions from toluene are also eliminated, as are the doubly ionized peaks at and near mass 45. Dioxane still fragments appreciably.

Figure 4-45 shows high and low voltage data for mixture #9 (acetone, methanol, methylene and ethylene chloride). The spectra shown were taken at a point in the desorption program where the main components in the vapor phase are acetone and methylene chloride, with a small amount of ethylene chloride. Comparison of the high and low voltage experiments shows the loss in sensitivity, which is about a factor of 2.5 for m/e 43 (acetone fragment) and 49 (methylene chloride). The intensity of the acetone m/e 58 parent ion increases relative to that of the fragment ion (m/e 43) at low voltage. The reverse is observed for the chlorinated compounds; fragmentation is apparently more efficient at 12 ev for these compounds. The intensity ratio of m/e 62 - 98 (CH_2ClCH_2Cl - HCl) increases from 4 to 10 and that of m/e 49 - 84 (CH_2Cl_2 - HCl) increases from 2.5 to 3.5. A similar effect is observed for vinyl chloride; the ratio of 62 (CH_2 = CHCl) to 27 (CH_2 = CH-Cl - HCl) in unchanged at 12 ev compared to 70 ev. In contrast, loss of a second chlorine atom from Freon-11 (to give m/e 66) appears to be completely eliminated; the molecular ion (m/e 136) is not observed at either high or low voltage in our experiments.

The simplification of spectra is best judged by comparison of the low voltage, high concentrations spectrum with the high voltage, low concentration spectrum, shown in Figure 4-46. Many fragment ion peaks are discernible in the spectrum of the low concentration sample but at nearly comparable intensity of the major peaks many of these are eliminated in the low voltage spectra.

Allyl alcohol and ethyl acetate spectra at low voltage show effects similar to those described for acetone. Complete fragmentation is not eliminated but many of the less intense fragments are eliminated and the intensities of the higher molecular weight ions are increased relative to those of the lower molecular weight fragments.

For butene-1, the intensity of the molecular ion peak at m/e 56 increases by a factor of two relative to the most intense peak (m/e 41) with low voltage ionization. The intensity of the fragment ion at m/e 28 increases only slightly. Major fragments at m/e 27 and 39 are reduced by a factor of five in intensity. Many of the less intense fragments are eliminated. The sensitivity at the major peak, m/e 41, is reduced by about a factor of three.

In summary, the use of low voltage ionization results in reduced fragmentation for most compounds and reduced sensitivity. The sensitivity is reduced by

about a factor of three for most compounds tested. The reduction in fragmentation is most striking for aromatic compounds. For butene-1, the only hydrocarbon tested, as well as for the oxygen containing compounds, many of the less intense fragment ions are eliminated, but major fragment ions are still present although their intensity is generally reduced relative to the parent ion. In contrast, fragment ions which result from loss of hydrogen chloride from halogenated compounds are observed to be relatively more intense under low ionization voltage.

There appears to be a certain advantage in using low ionization voltage for the analysis of mixtures. By elimination of many of the less intense fragment ion peaks, the spectra are simplified and it appears that the probability of concident mass numbers for different compounds should be reduced. Complete elimination of all fragment ions is not necessary or desirable. For example, if only molecular ion peaks appear in the spectra, it would not be possible to distinguish dioxane from ethyl acetate (both mass 88). The major disadvantages associated with this mode of operation are the loss in sensitivity and the lack of a large compilation of reference spectra, such as is available for many compounds with normal (70 ev) ionization. The loss of sensitivity may be overcome by modifications to the instrument electronics. Reference spectra are helpful in identifying unsuspected contaminants. However, for very exact analytical work, it is necessary to calibrate the response of the individual mass spectrometer for the compounds of interest in any event, and this can be done equally well with low ionization voltage. The only limitation anticipated is the stability of the electron beam at low voltage. This factor must be evaluated experimentally.

Continued investigation of low ionization spectra should prove rewarding in developing the ultimate capability of the Laboratory Contaminant Sensor.

4.5 TOTAL SYSTEM TESTING

Routine monitoring of contaminants in a confined atmosphere requires sampling through all three (or four including the palladium-charcoal) sorbents. Some experiments were carried out to determine if the three sorbents cells could be connected in series during sampling to retain the contaminants. In these experiments the Porapak Q cell and the charcoal cell described earlier were connected in series using stainless steel fittings and samples of mixtures containing vinyl chloride and Freon-11, butene-1, or acetone, methylene chloride, ethylene dichloride, and methane were passed through the cells. The concentrated mixtures were used without dilution for these tests. Air was precut from the cells in series, the cells were valved off and separated, and desorption was carried out separately from each cell. In all cases, the contaminants were retained on the Porapak Q cell, the first in line in the sampling train. Even for butene-1 which is not retained well enough on Porapak Q for determination, none passed through to the charcoal cell. If the Porapak Q cell was heated to 70°C during the precut, vinyl chloride was transfered to the charcoal cell. It appears that the small, relatively high concentration samples employed in these experiments, were insufficient to saturate the sorbent, Porapak Q, and hence all the butene-1 was retained. This could be true for the other compounds tested also. But it is

somewhat surprising that the air precut could be carried out without causing some of the butene to be transferred to charcoal. Possibly some butene was lost in the dead volume between the two accumulator cells.

It was concluded from these experiments that serial sorption through separated cells did not result in separation of contaminants on the different sorbents. However, these experiments should be repeated with low concentration, large volume samples comparable to those to be used for routine analysis, before the concept of serial sorption is discarded.

Under these conditions it is expected that a compound which has a small equilibrium constant on the first sorbent will reach saturation on the first sorbent after a relatively small volume of sample (1/10) has passed through the cell; in the second sorbent cell the compound (assuming a large K value) will be completely sorbed in the initial section of the cell and presumably never reach saturation over the full length of the cell. The small amount of contaminant retained on the first sorbent should be negligible compared to the amount retained on the second. Such behavior is predicted on the assumption of linear isotherms, which are concentration independent. If the equilibrium constants are concentration dependent in such a way that the constant is higher at low concentrations, serial sorption may not be effective but under these conditions sorbents which were unsatisfactory for determination of certain contaminants at high concentration may be suitable for very low concentration. The total system operation must be evaluated to establish the instrumental detectability limits and to choose sorbents for contaminants at concentrations which are consistent with these limitations.

It may be necessary to take three separate samples - one for each sorbent cell - to cover the range of contaminants, or to design a cell which would hold three sorbents and permit heating each sorbent separately. This facet of the development program requires more investigation to establish the best analytical techniques for completely unknown mixtures.)

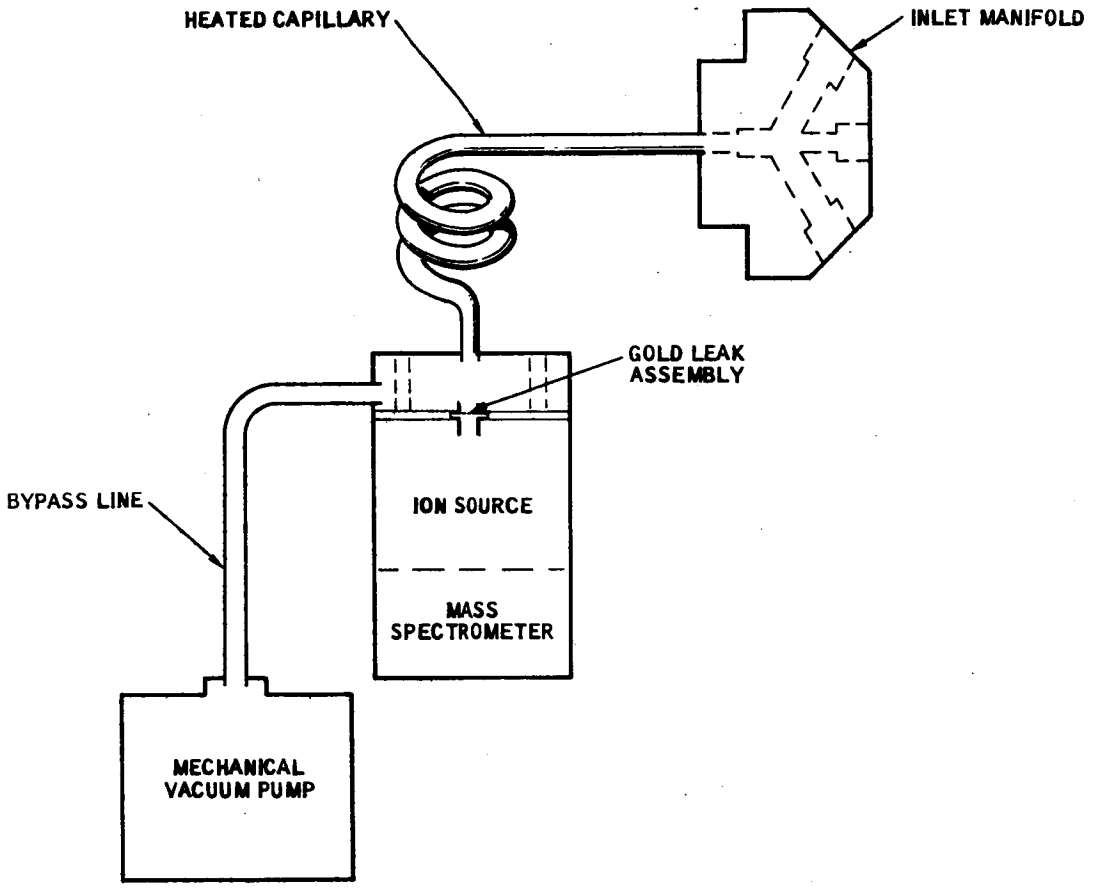


FIGURE 4-1
CAPILLARY INLET SYSTEM

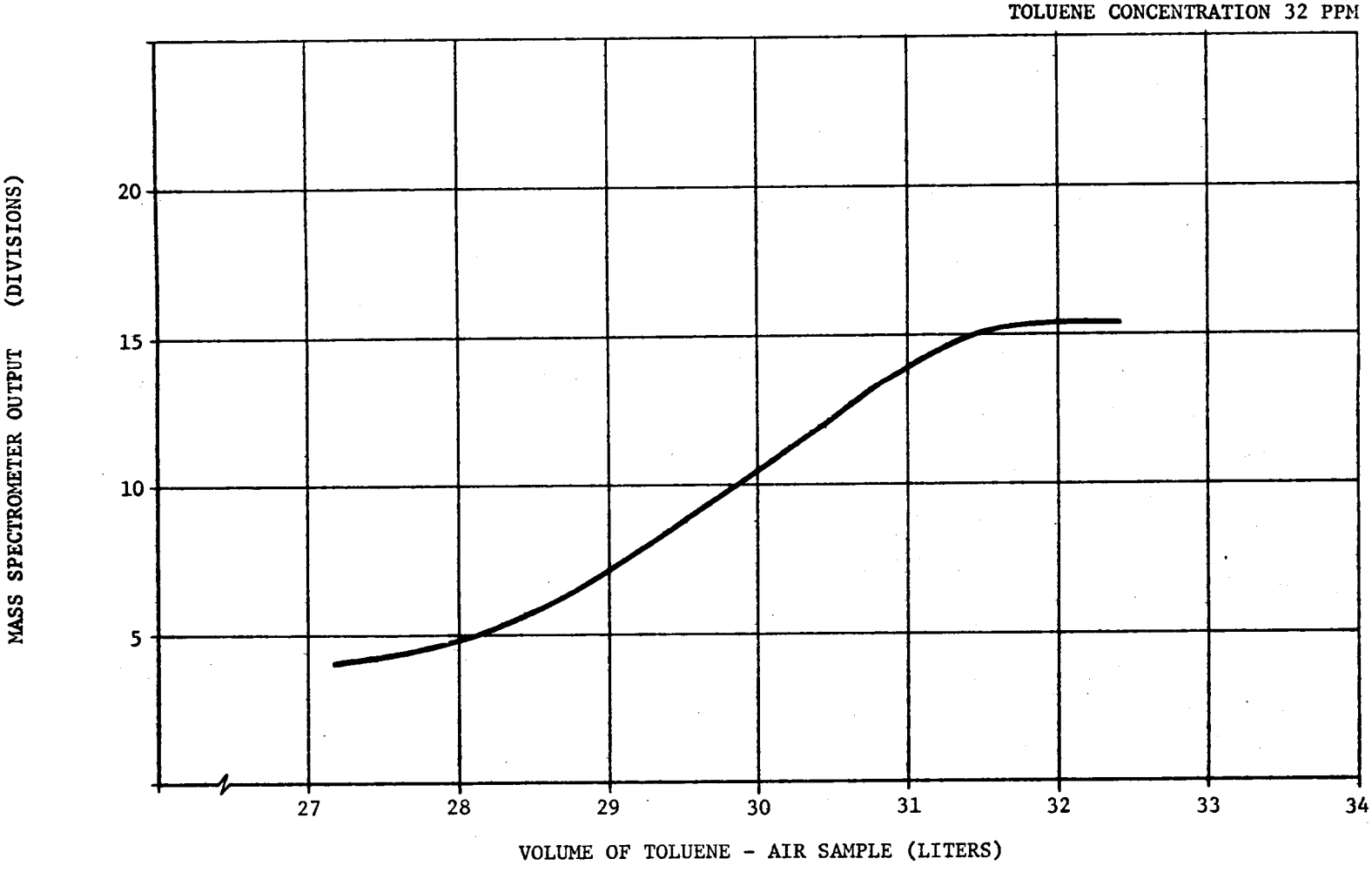


FIGURE 4-2

FRONTAL ANALYSIS OF TOLUENE ON PORAPAK Q

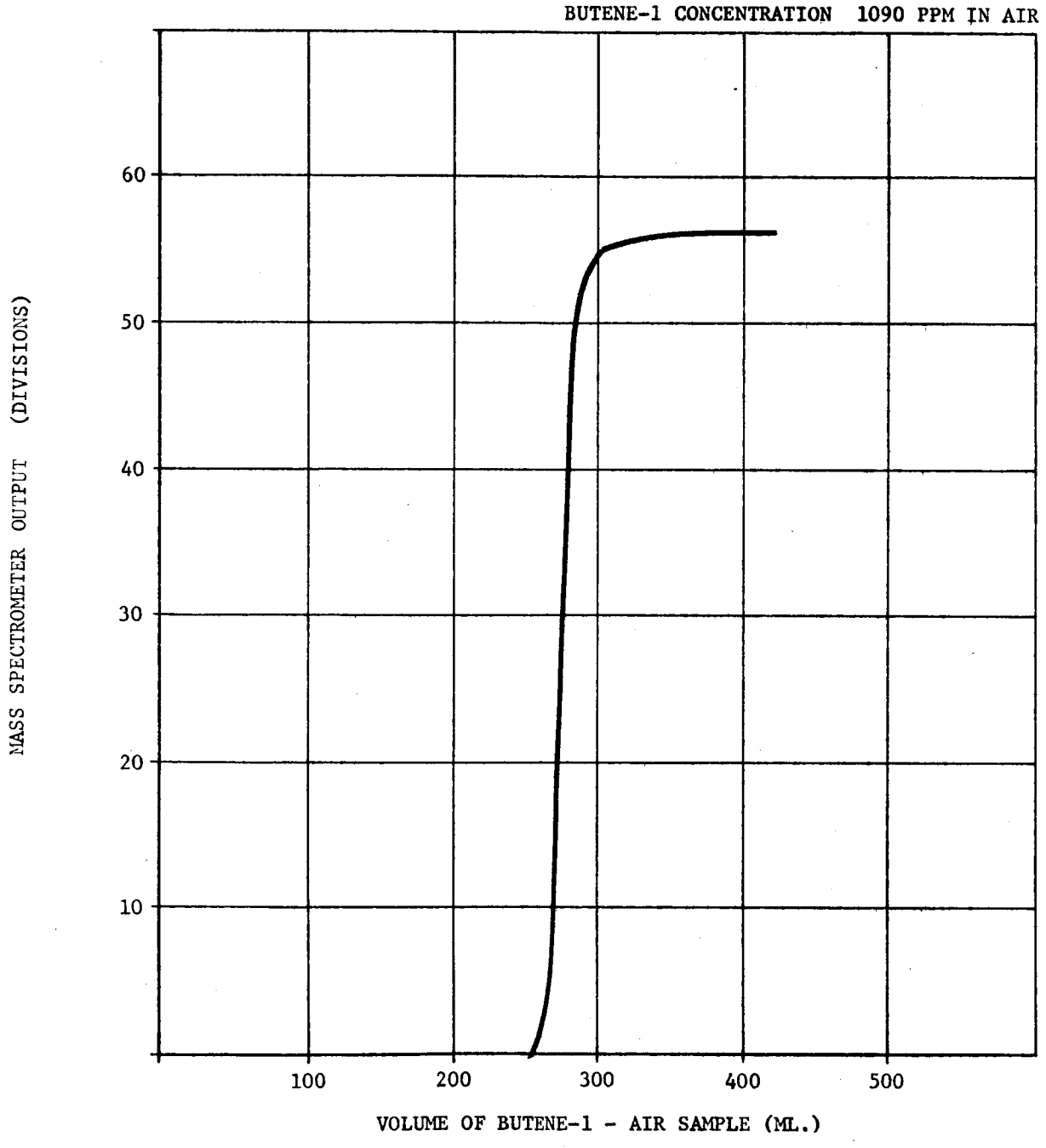


FIGURE 4-3

FRONTAL ANALYSIS OF BUTENE-1 ON PORAPAK Q

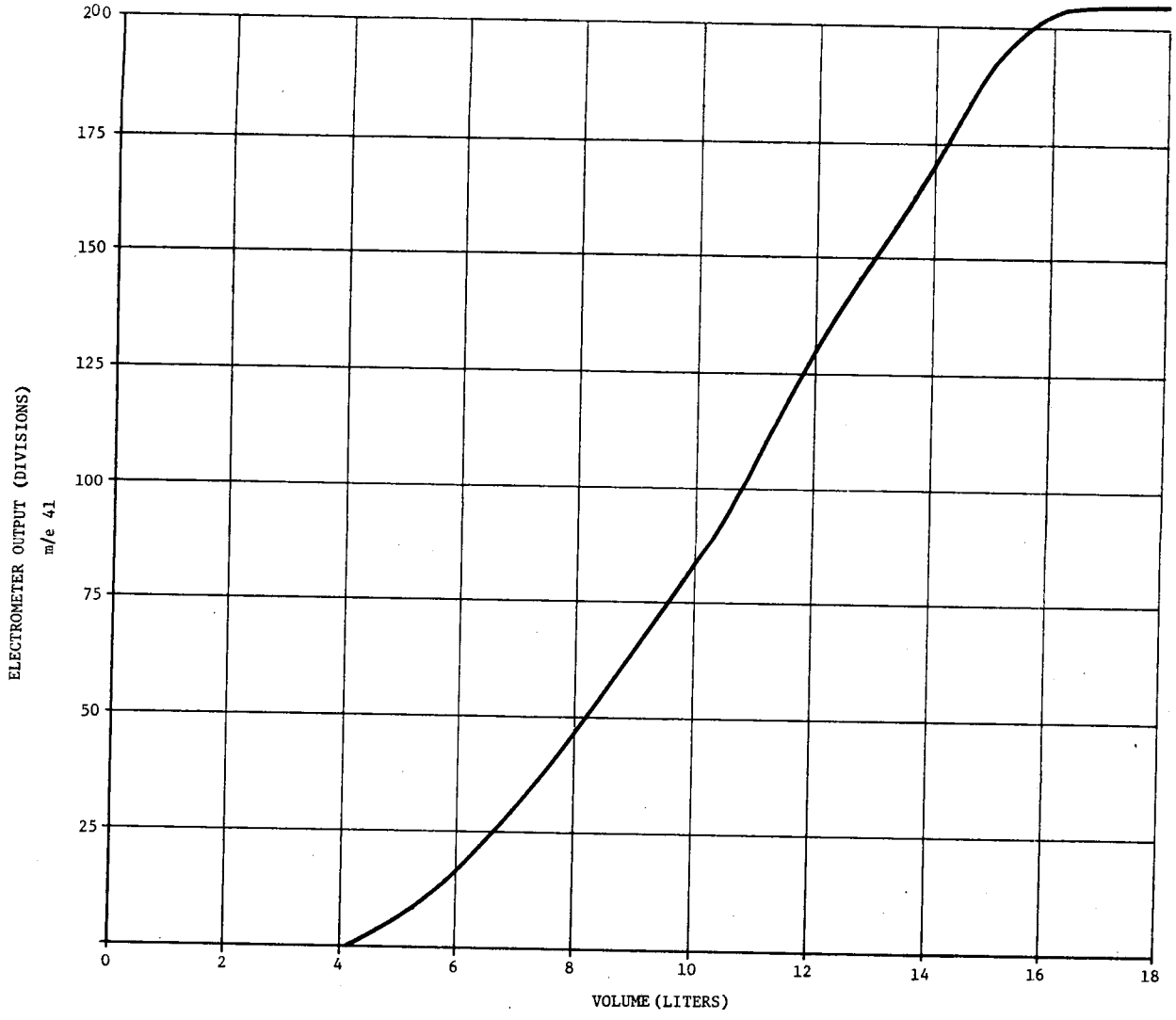


FIGURE 4-4
FRONTAL ANALYSIS BUTENE-1 ON CHARCOAL

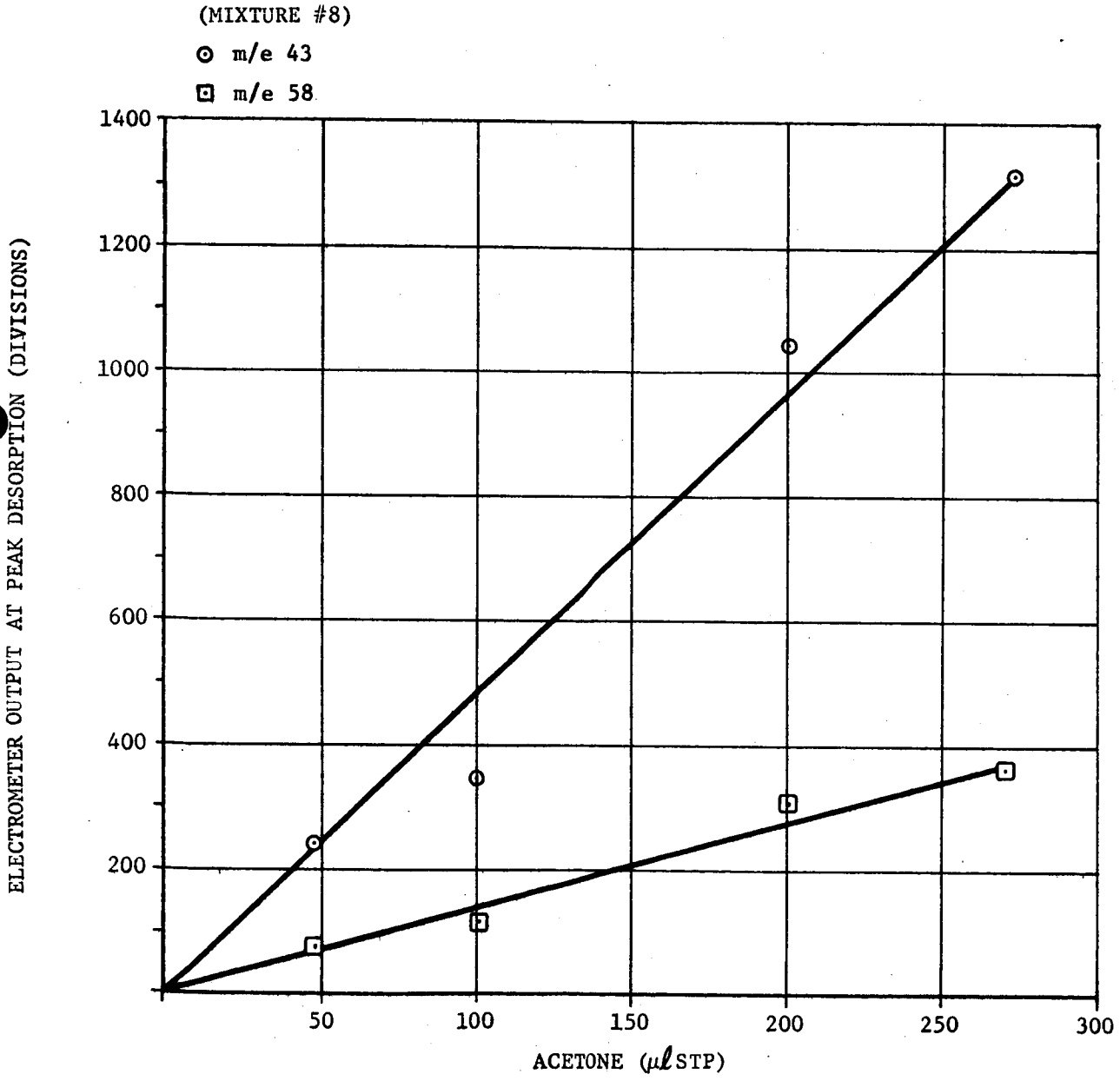


FIGURE 4-5

OUTPUT VS. AMOUNT SORBED
ACETONE ON CHARCOAL

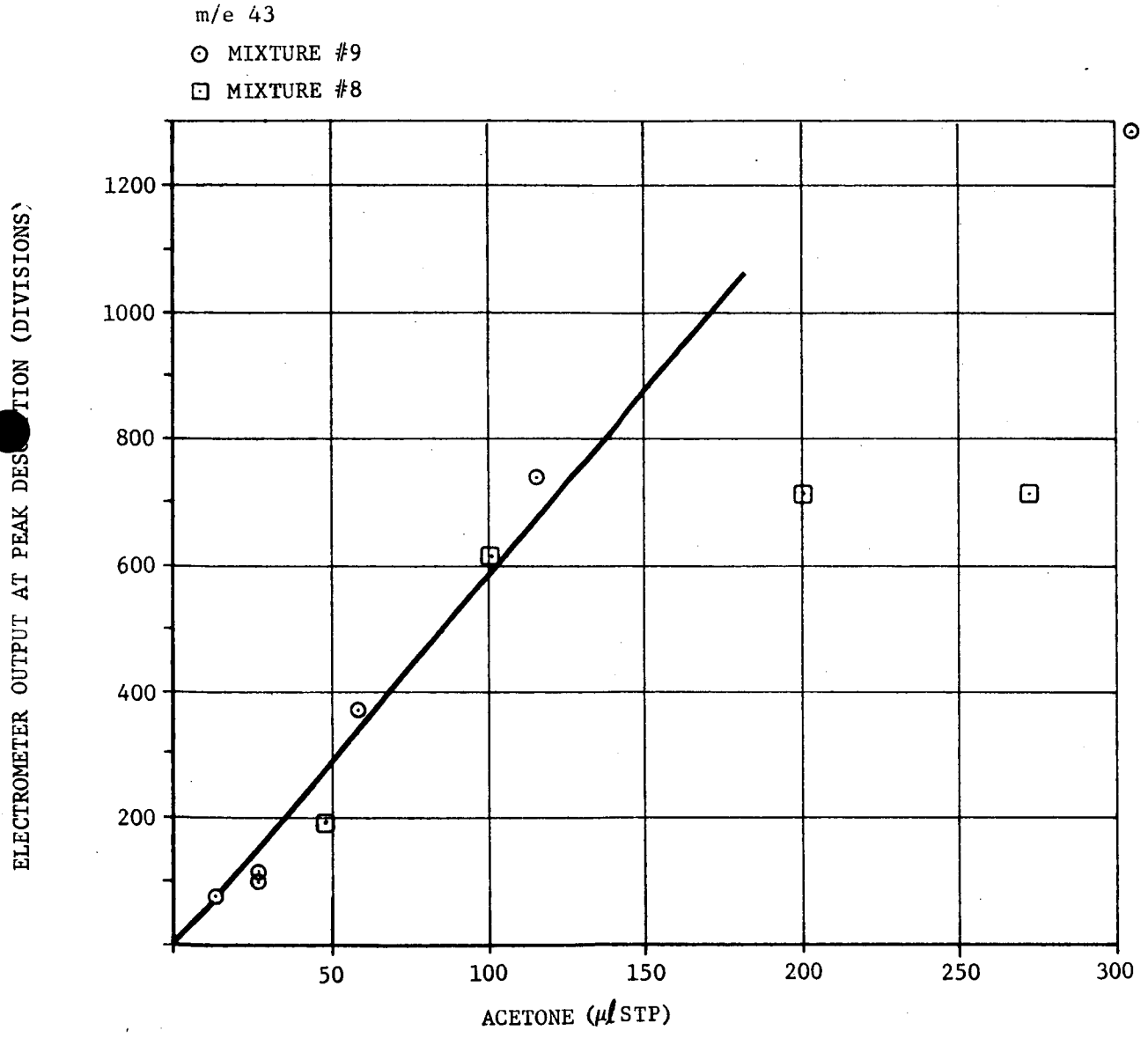


FIGURE 4-6

OUTPUT VS. AMOUNT SORBED

ACETONE ON PORAPAK Q

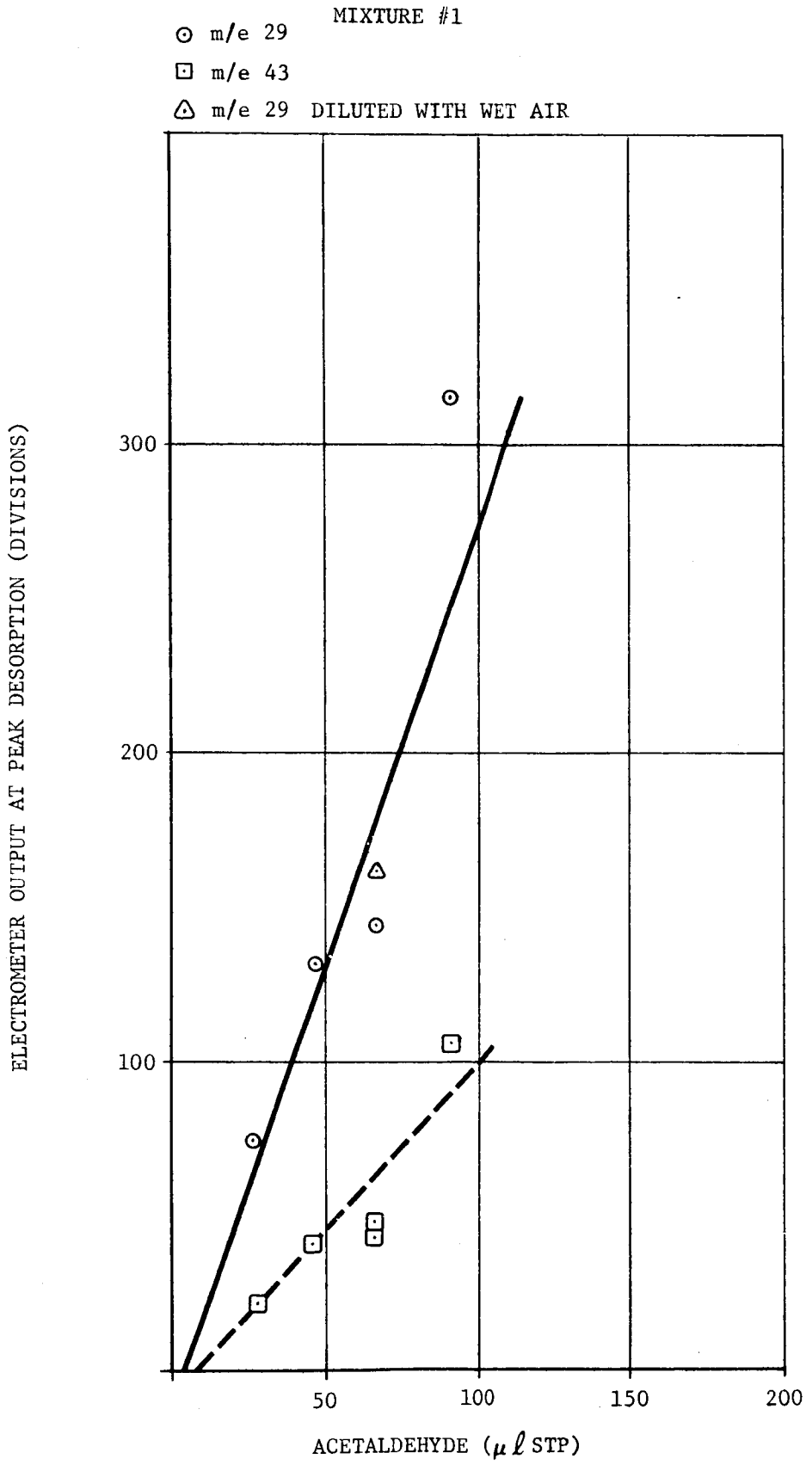


FIGURE 4-7

OUTPUT VS. AMOUNT SORBED
ACETALDEHYDE ON CHARCOAL

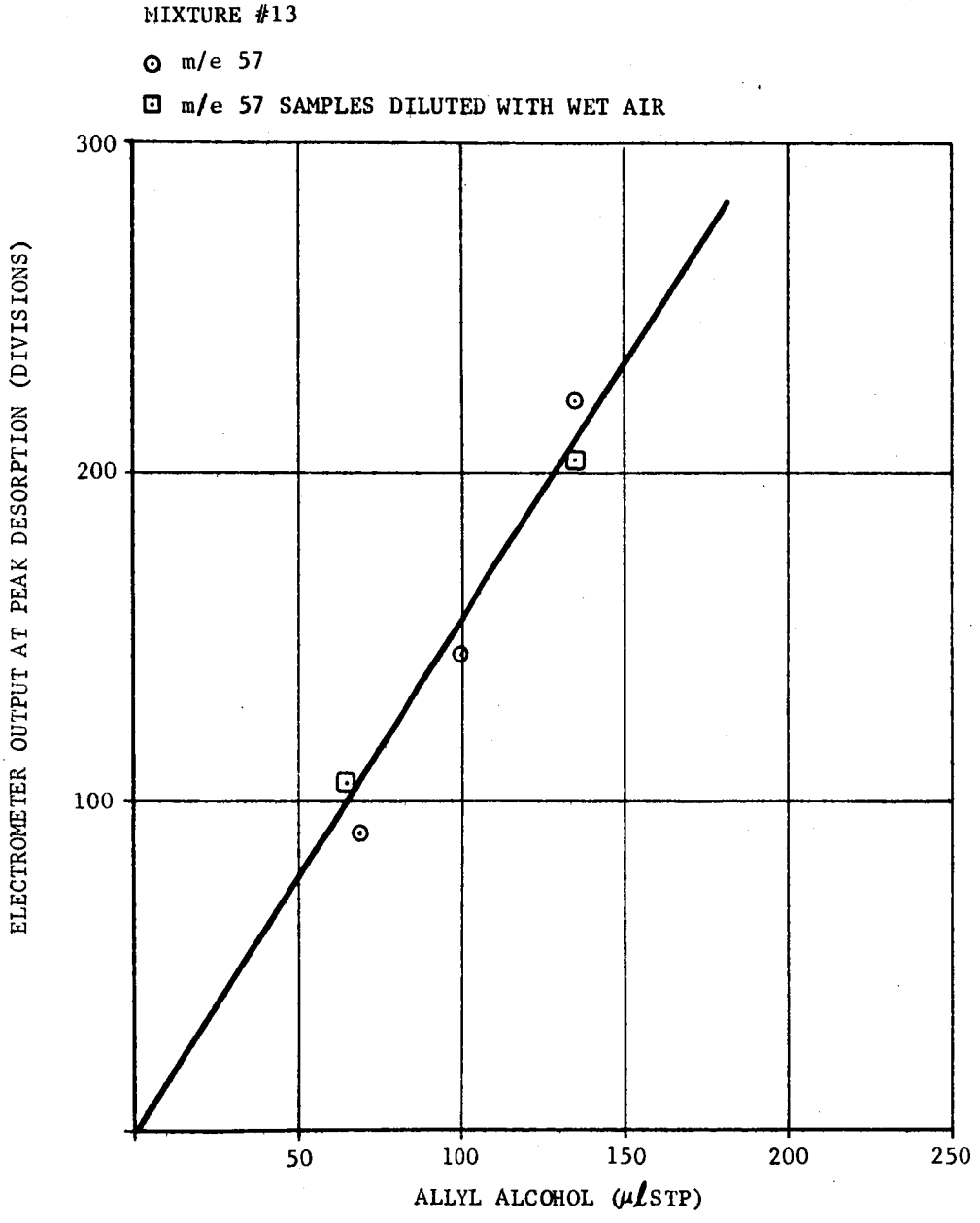


FIGURE 4-8

OUTPUT VS. AMOUNT SORBED
ALLYL ALCOHOL ON PORAPAK Q

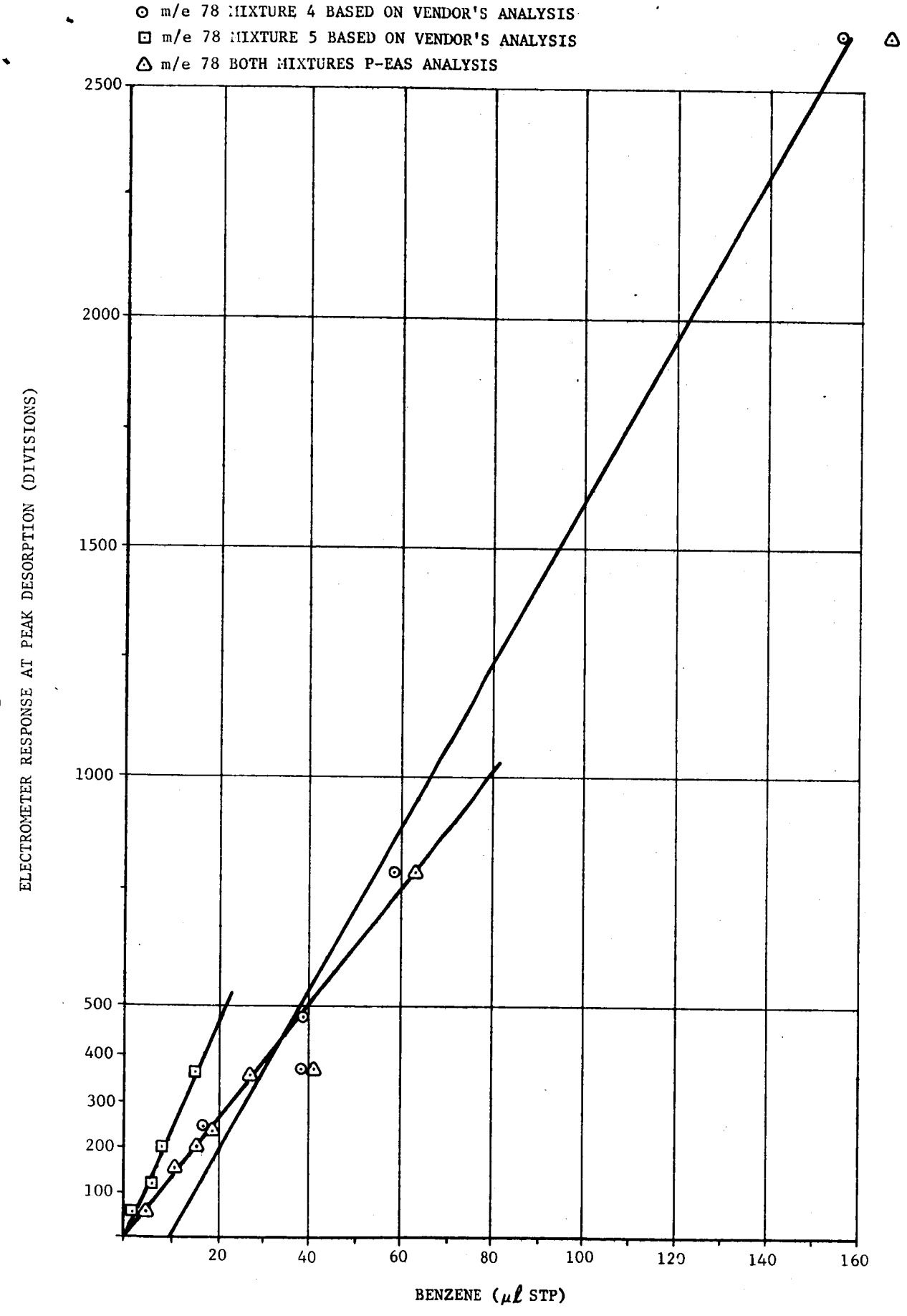


FIGURE 4-9
RESPONSE VS. AMOUNT SORBED
BENZENE ON PORAPAK Q

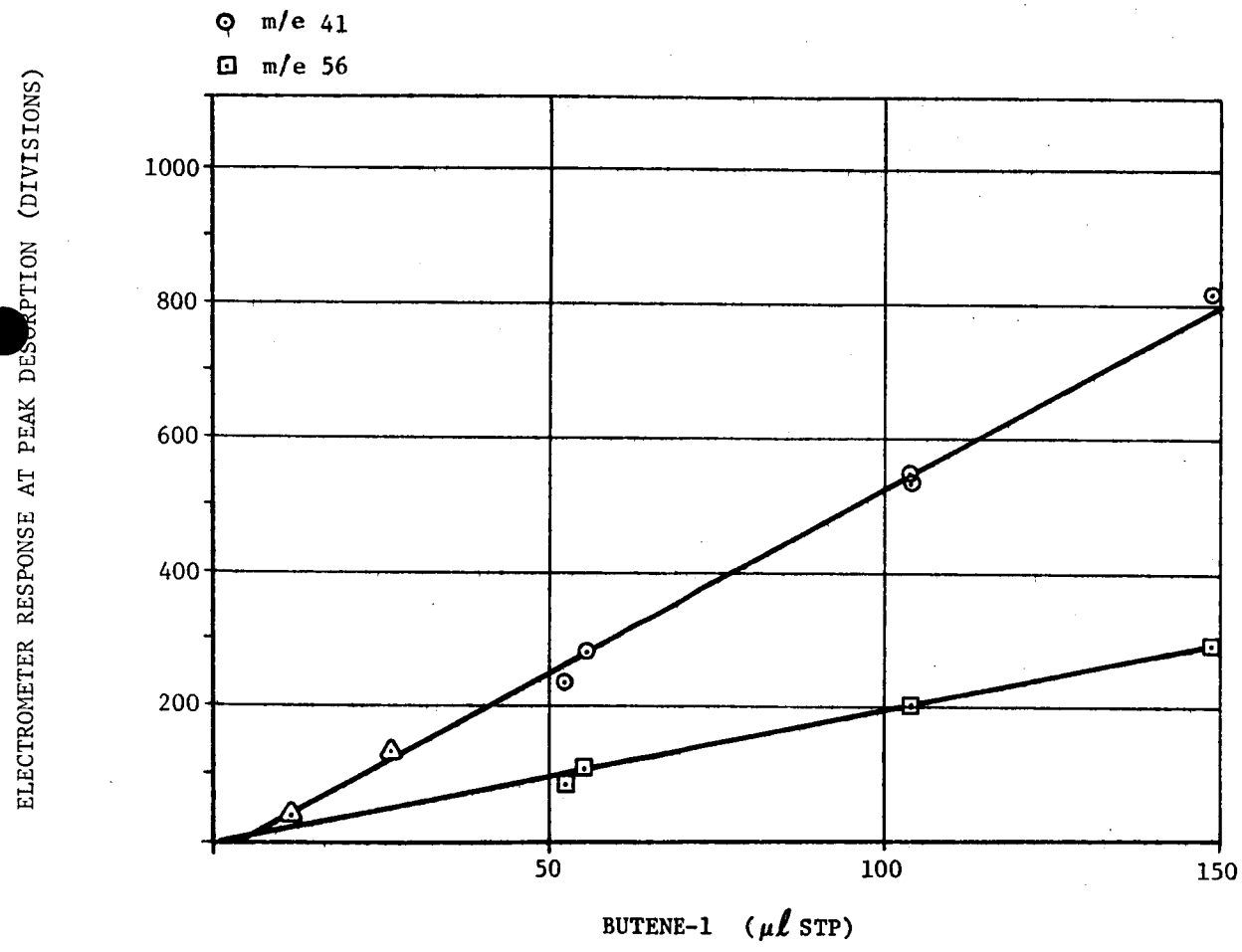


FIGURE 4-10
OUTPUT VS. AMOUNT SORBED
BUTENE-1 ON CHARCOAL

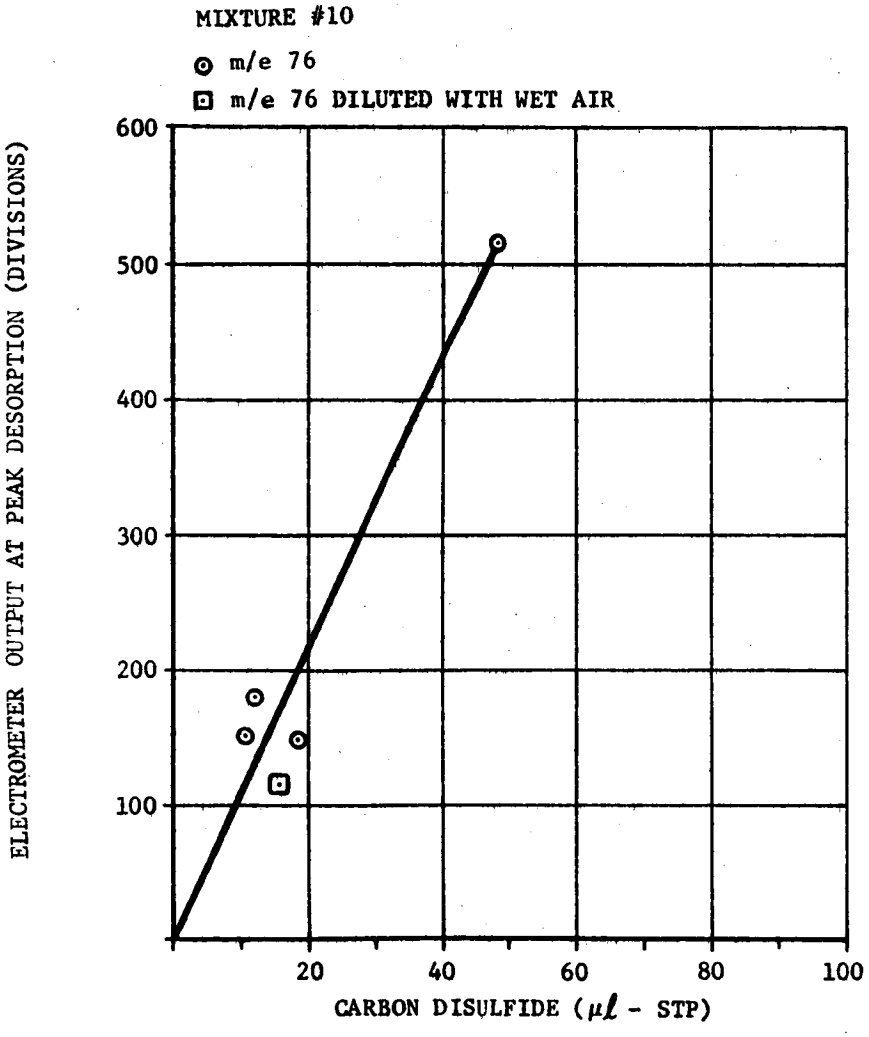


FIGURE 4-11

OUTPUT VS. AMOUNT SORBED

CARBON DISULFIDE ON PORAPAK Q

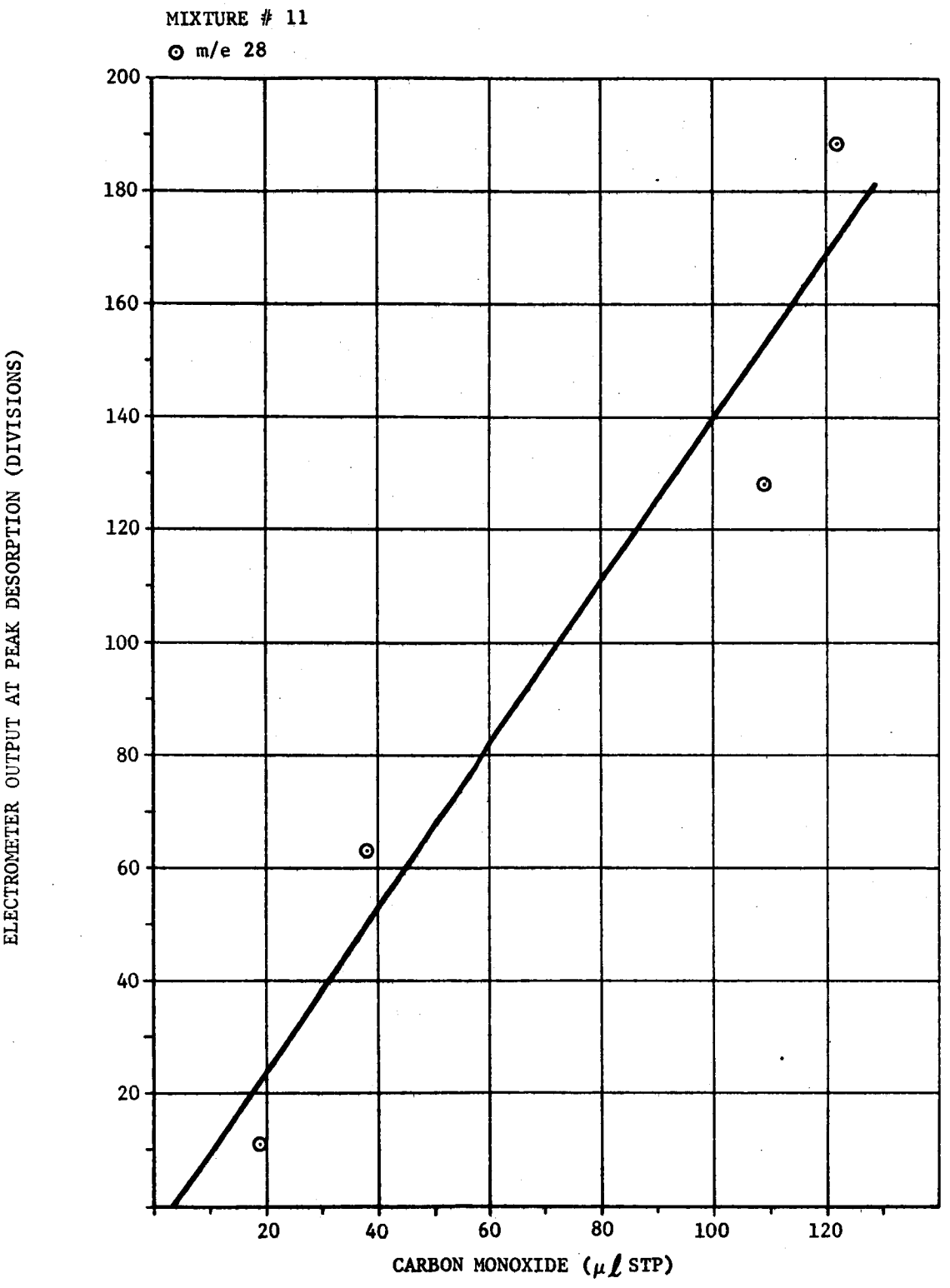


FIGURE 4-12
OUTPUT VS. AMOUNT SORBED
CARBON MONOXIDE ON PALLADIUM CHARCOAL

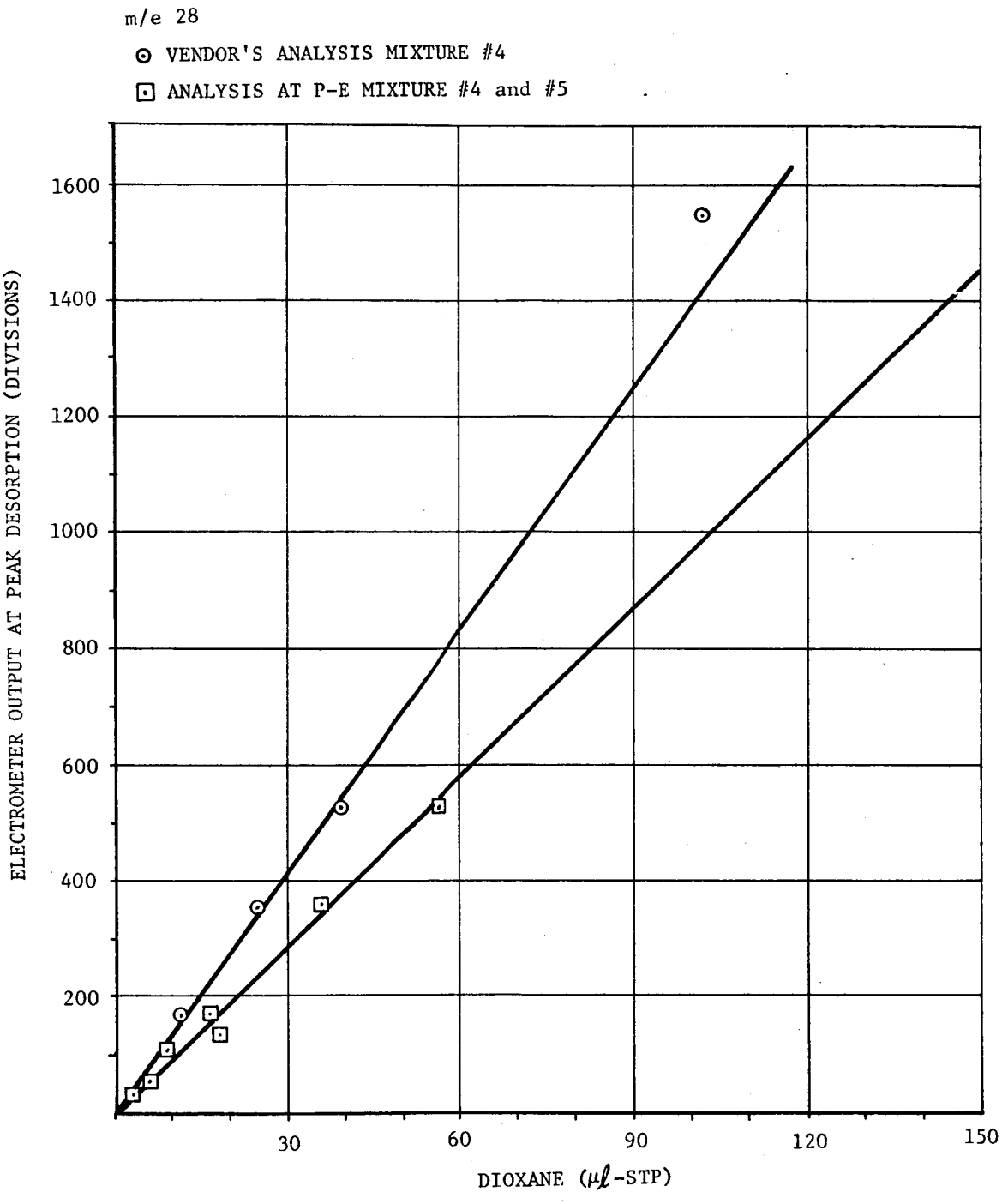


FIGURE 4-13
OUTPUT VS. AMOUNT SORBED
1,4-DIOXANE

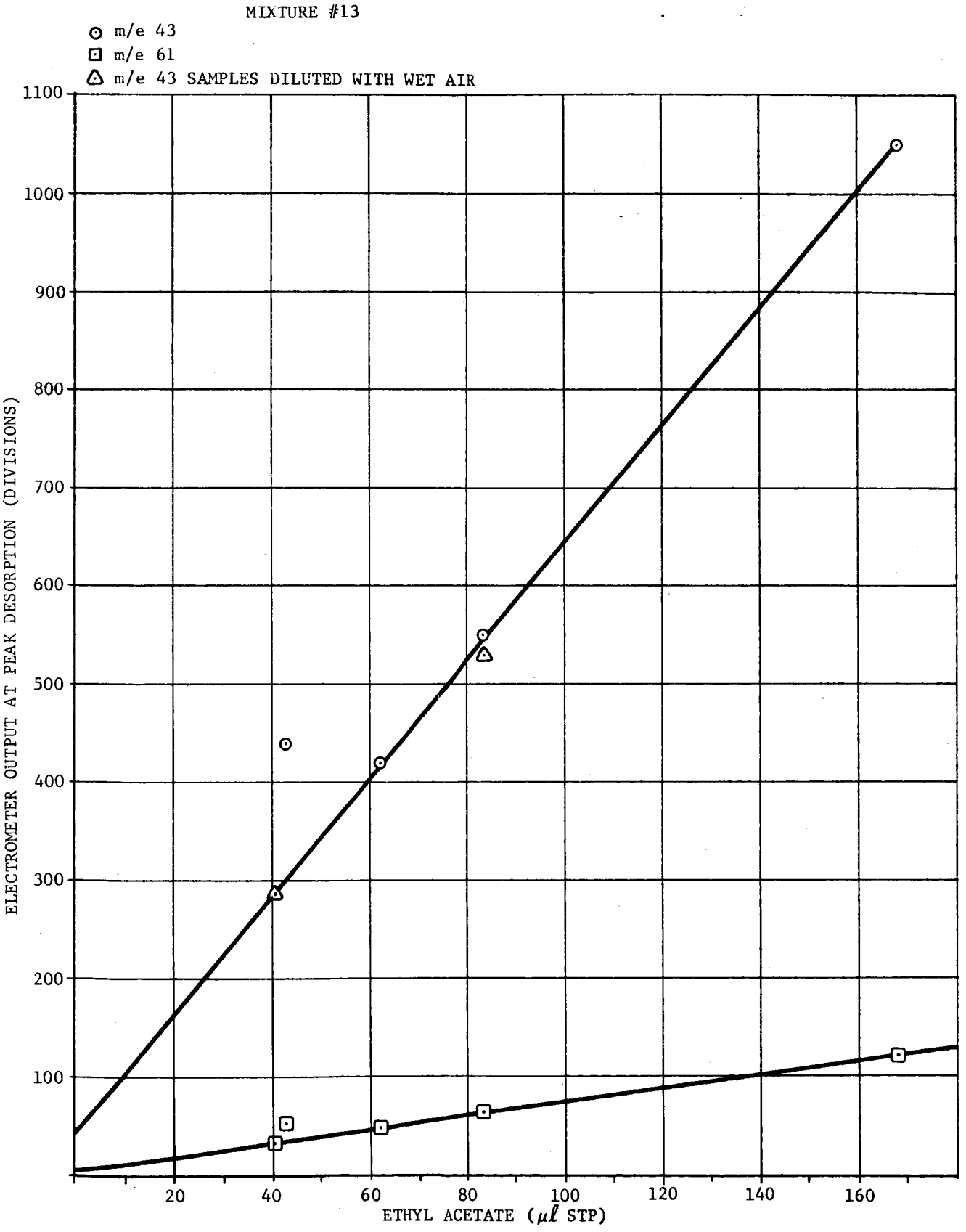


FIGURE 4-14
OUTPUT VS. AMOUNT SORBED
ETHYL ACETATE ON PORAPAK Q

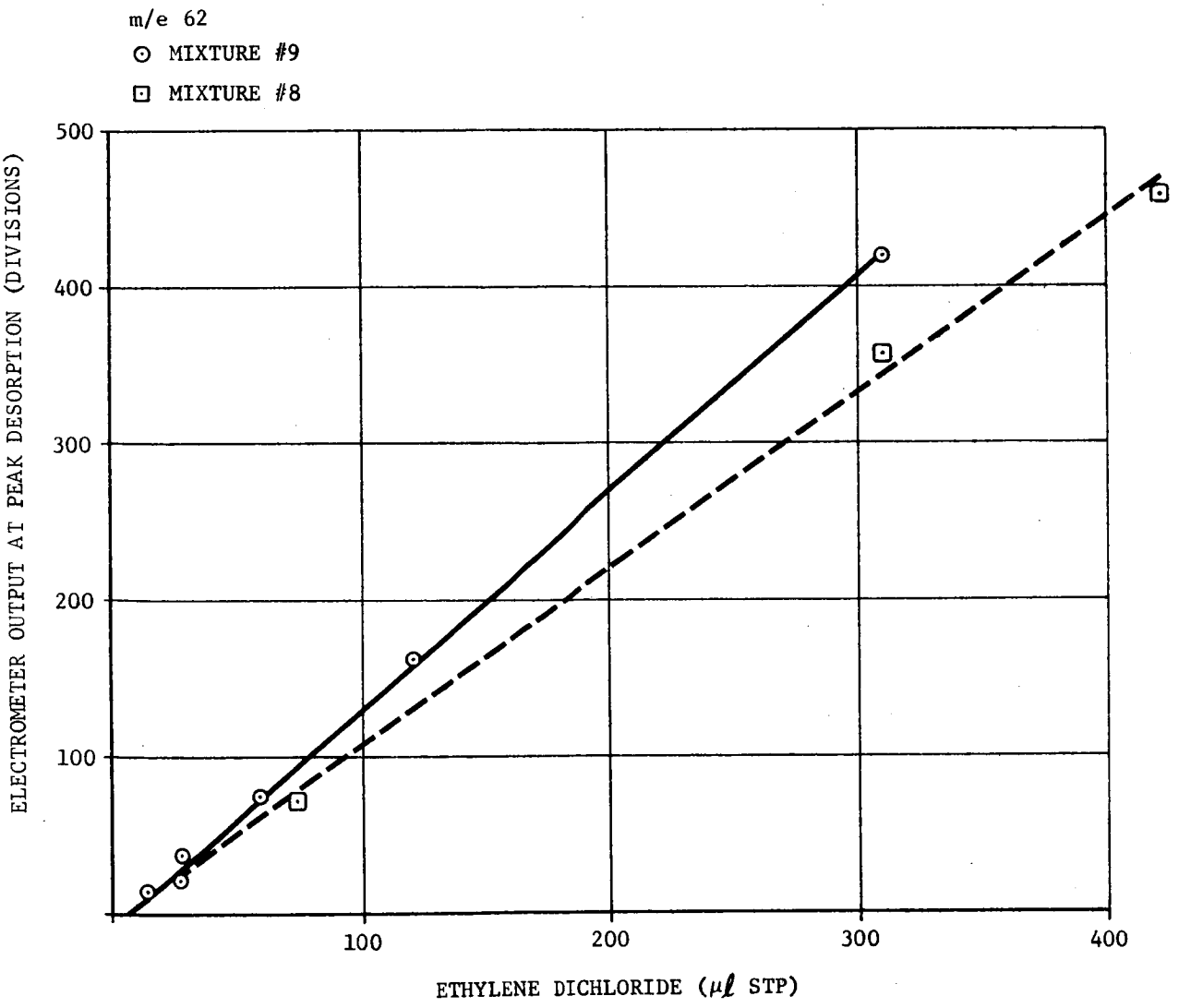


FIGURE 4-15

OUTPUT VS. AMOUNT SORBED
ETHYLENE DICHLORIDE ON PORAPAK Q

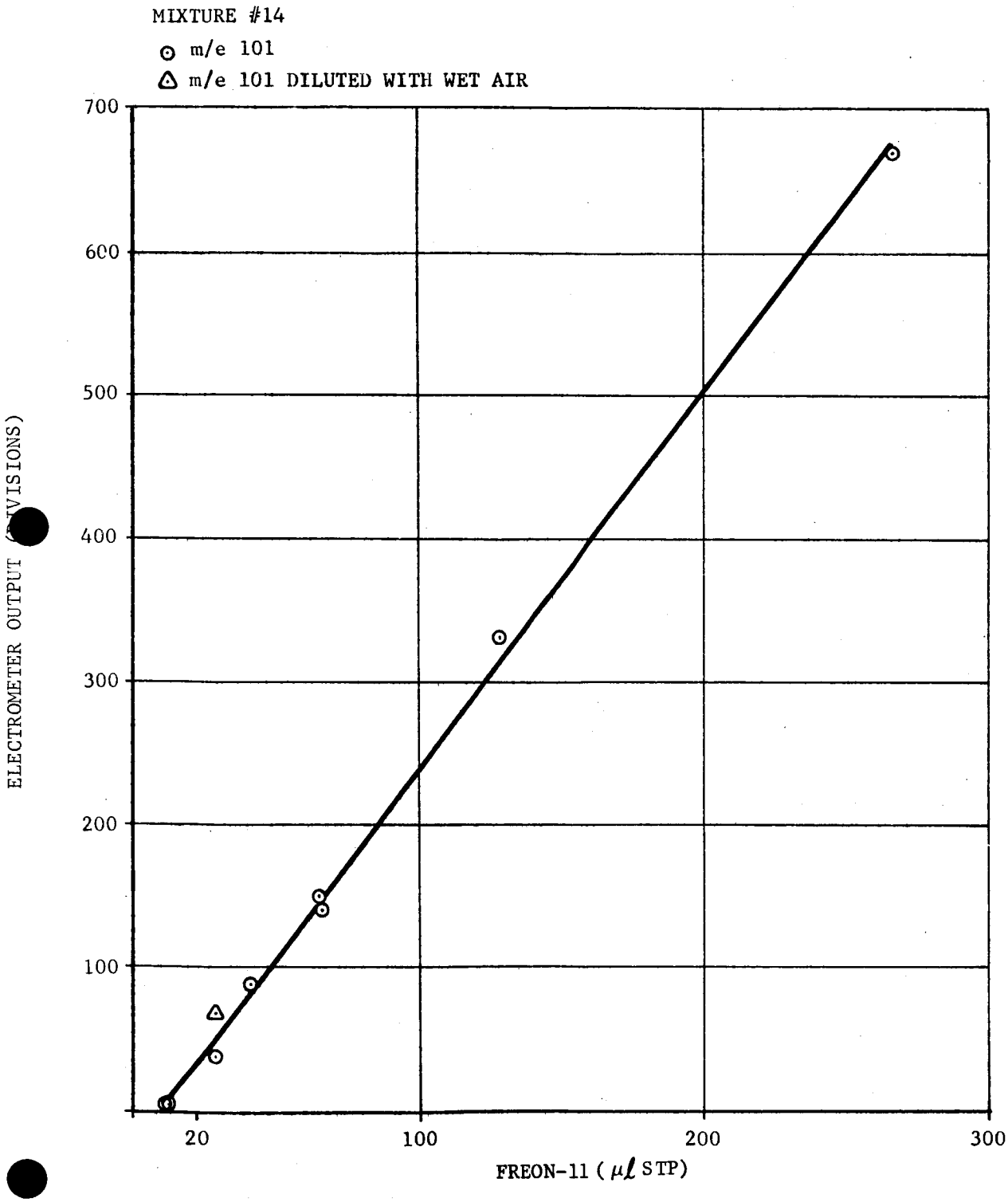


FIGURE 4-16
OUTPUT VS. AMOUNT SORBED
FREON-11 ON CHARCOAL

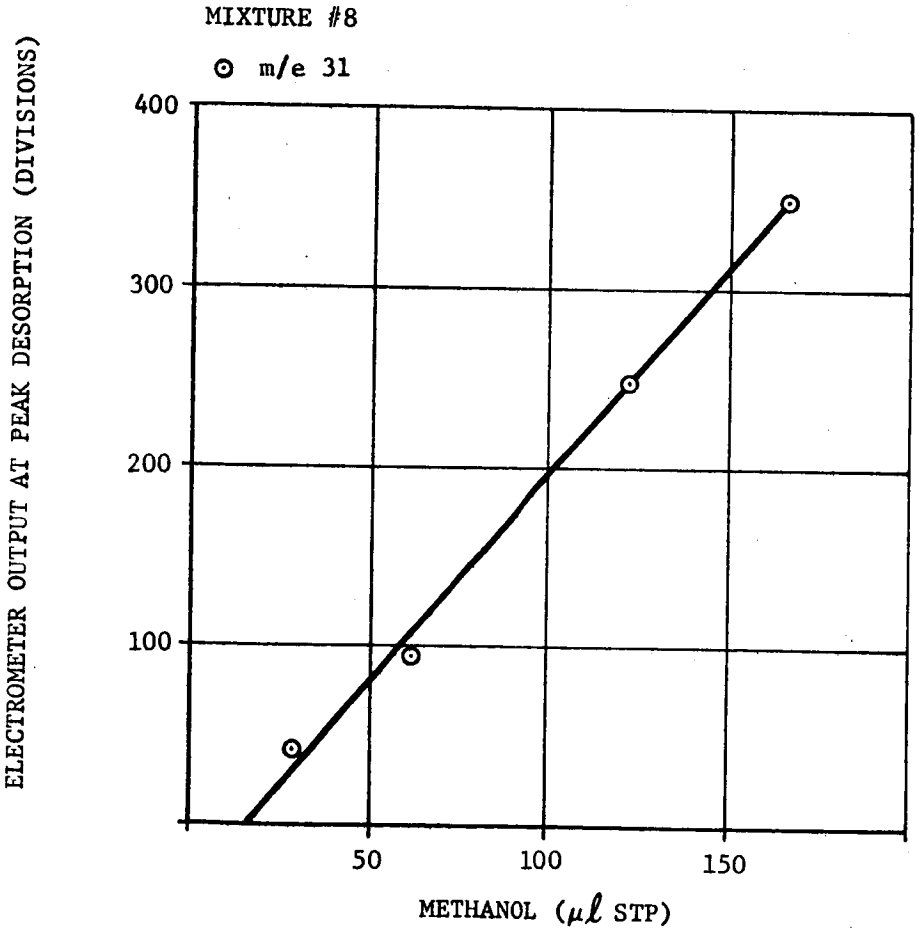


FIGURE 4-17
OUTPUT VS. AMOUNT SORBED
METHANOL ON CHARCOAL

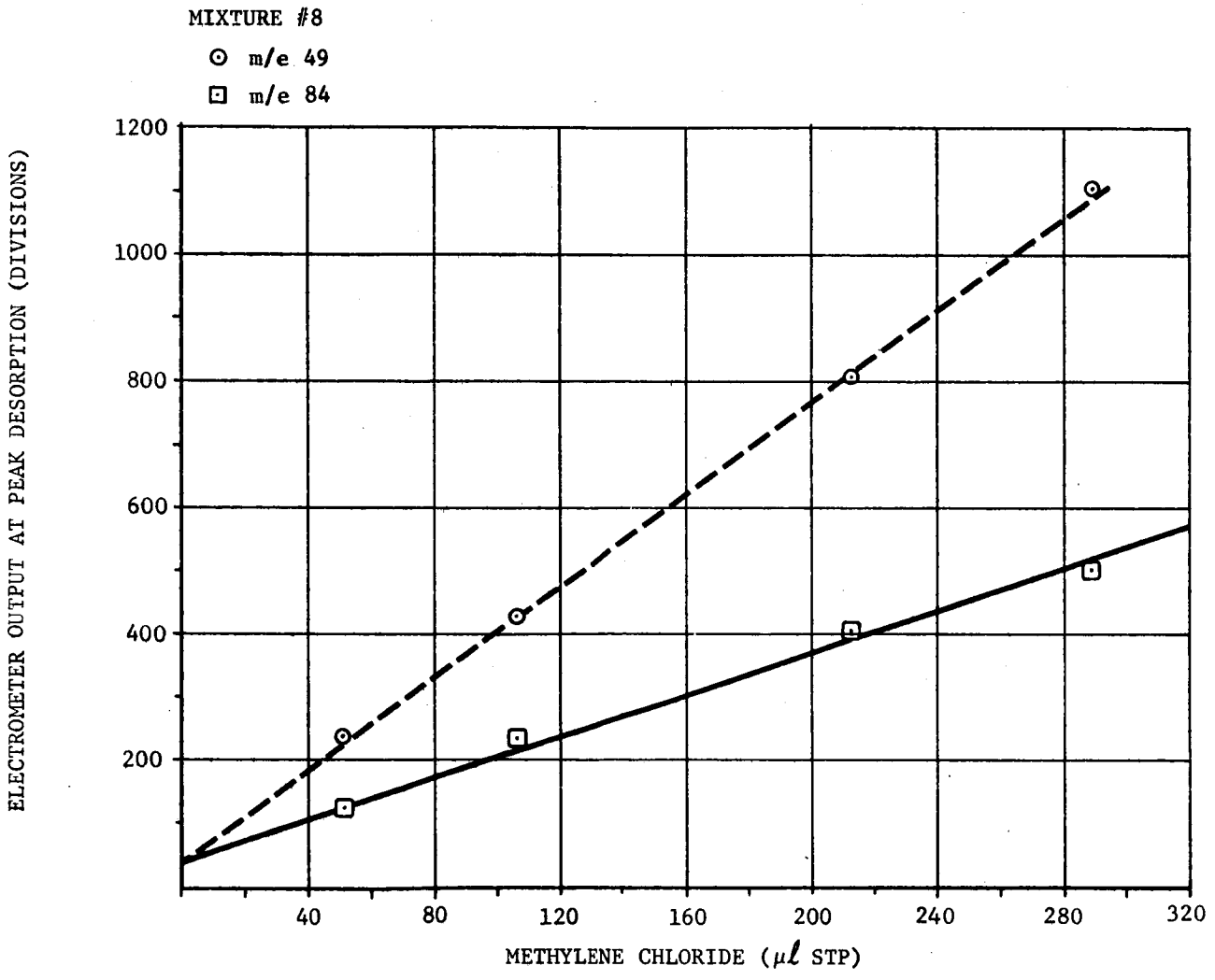


FIGURE 4-18
OUTPUT VS. AMOUNT SORBED
METHYLENE CHLORIDE ON CHARCOAL

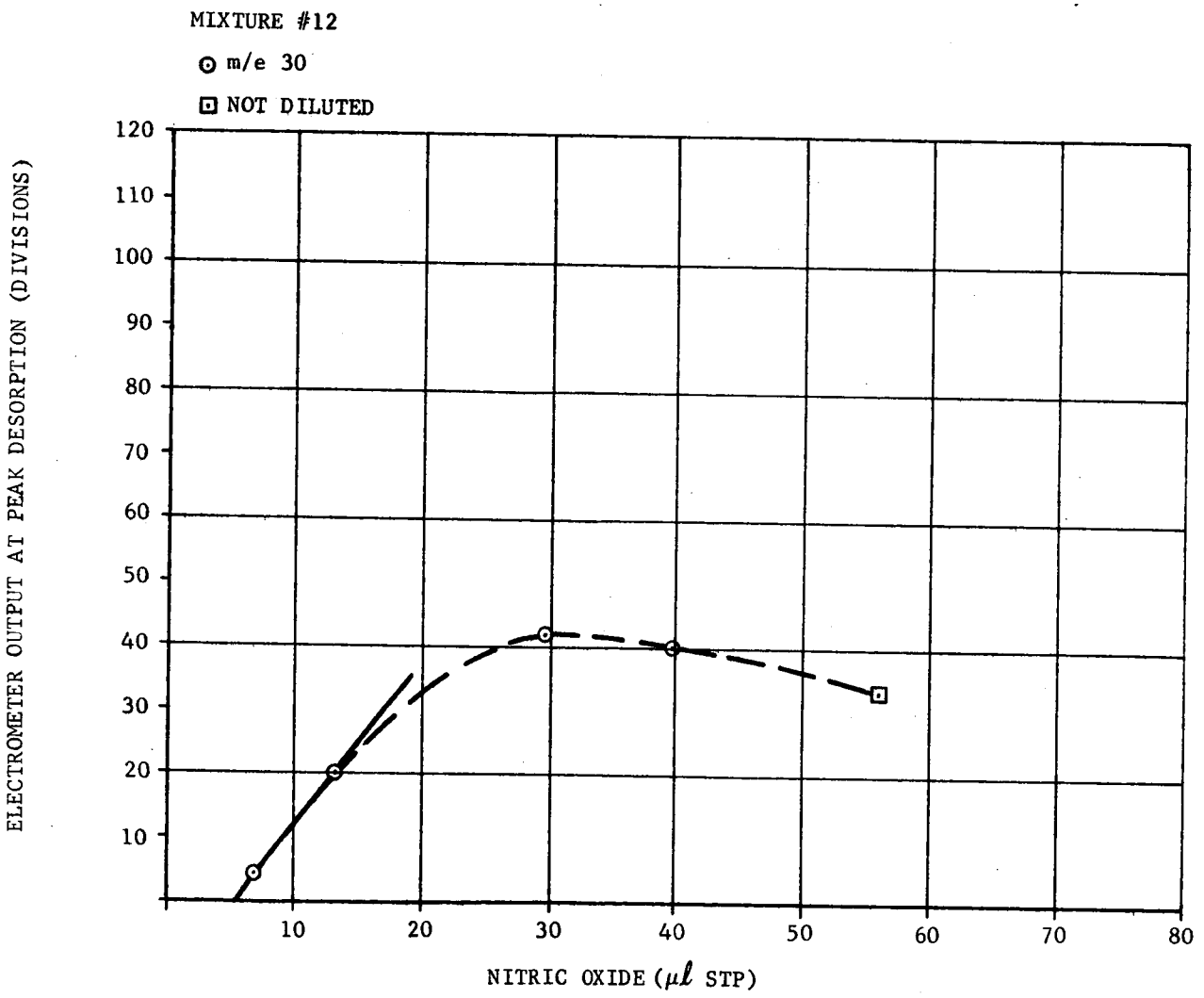


FIGURE 4-19

OUTPUT VS. AMOUNT SORBED
NITRIC OXIDE ON CHARCOAL

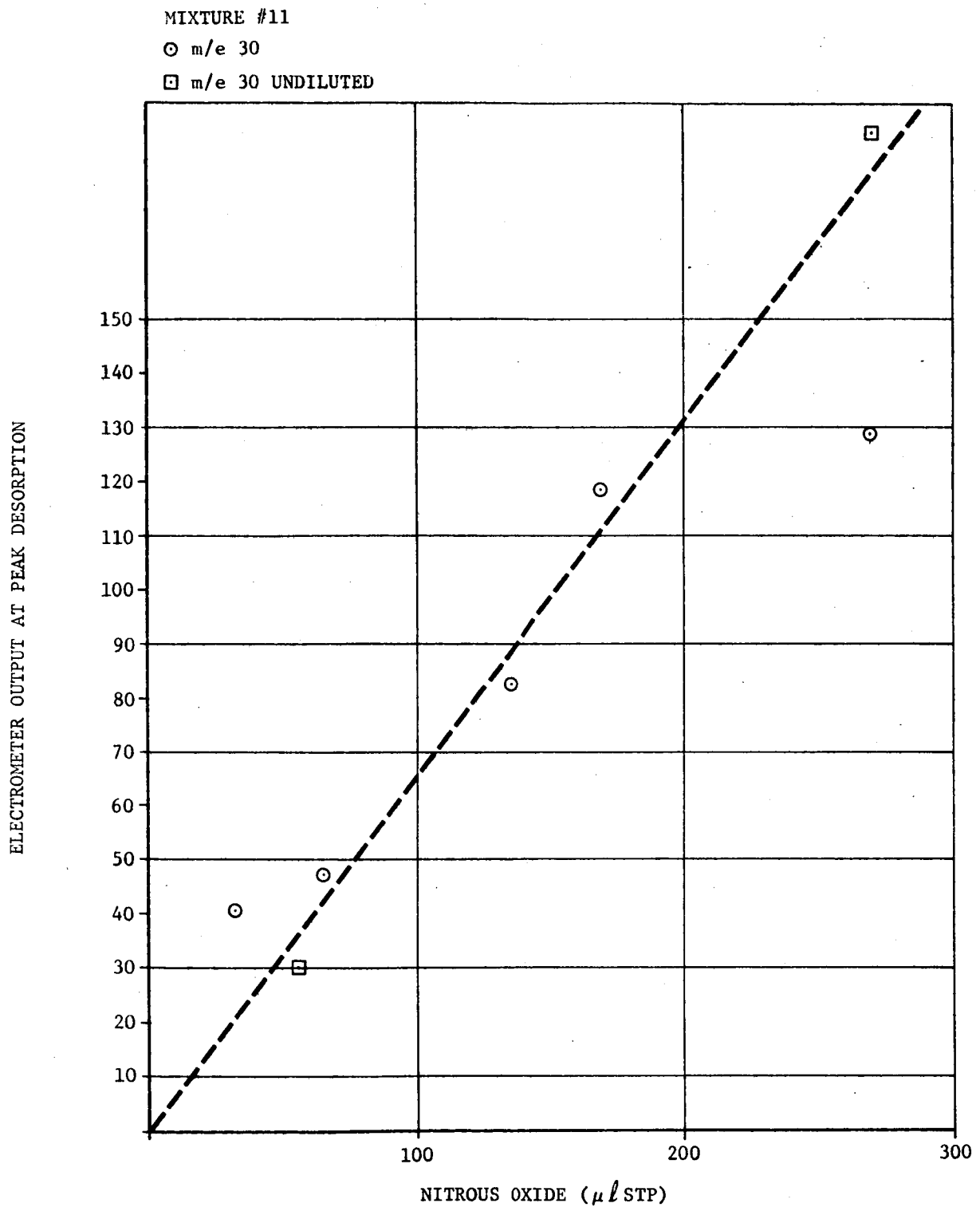


FIGURE 4-20
OUTPUT VS. AMOUNT SORBED
NITROUS OXIDE ON MOLECULAR SIEVE 5A

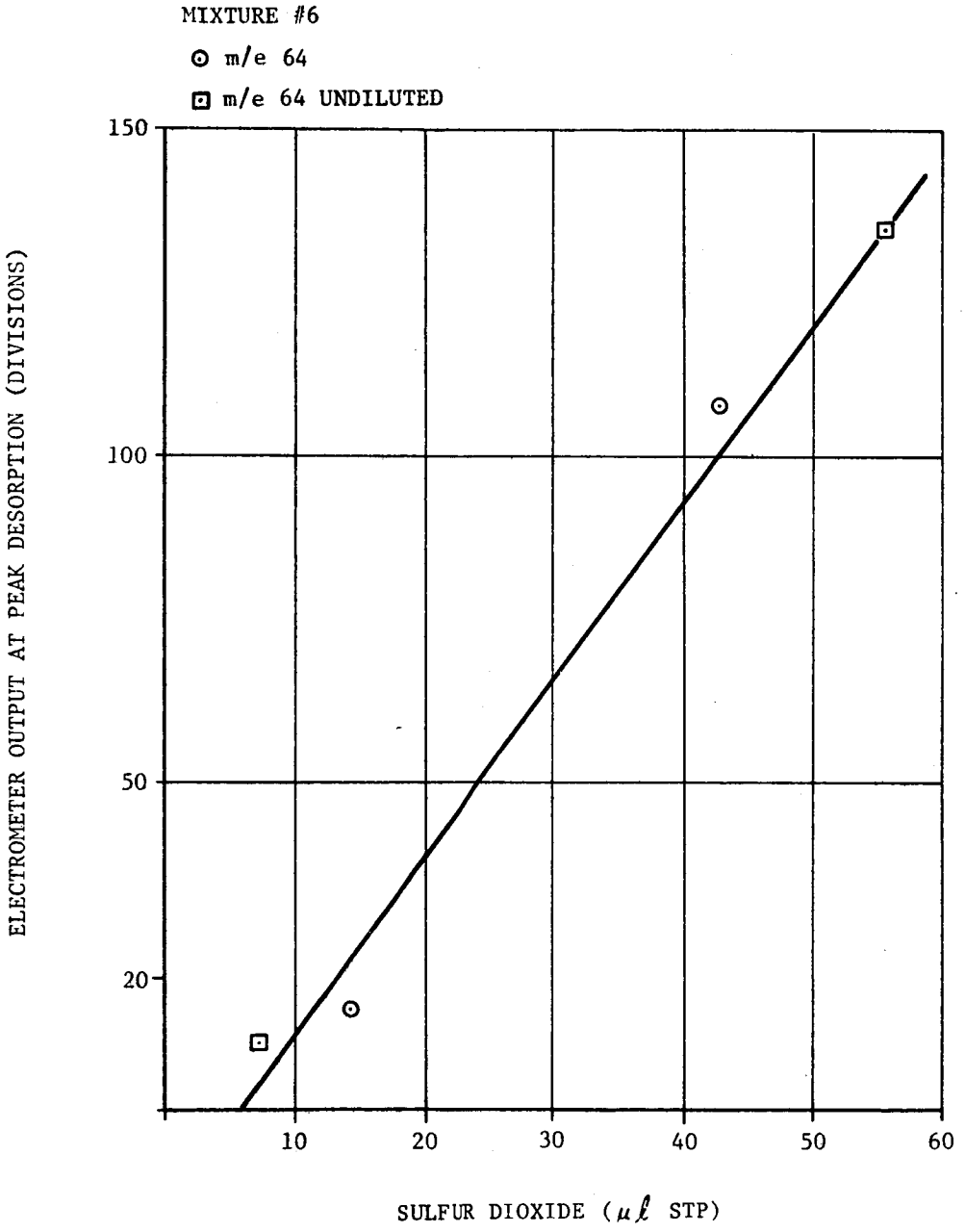


FIGURE 4-21
OUTPUT VS AMOUNT SORBED
SULFUR DIOXIDE ON CHARCOAL

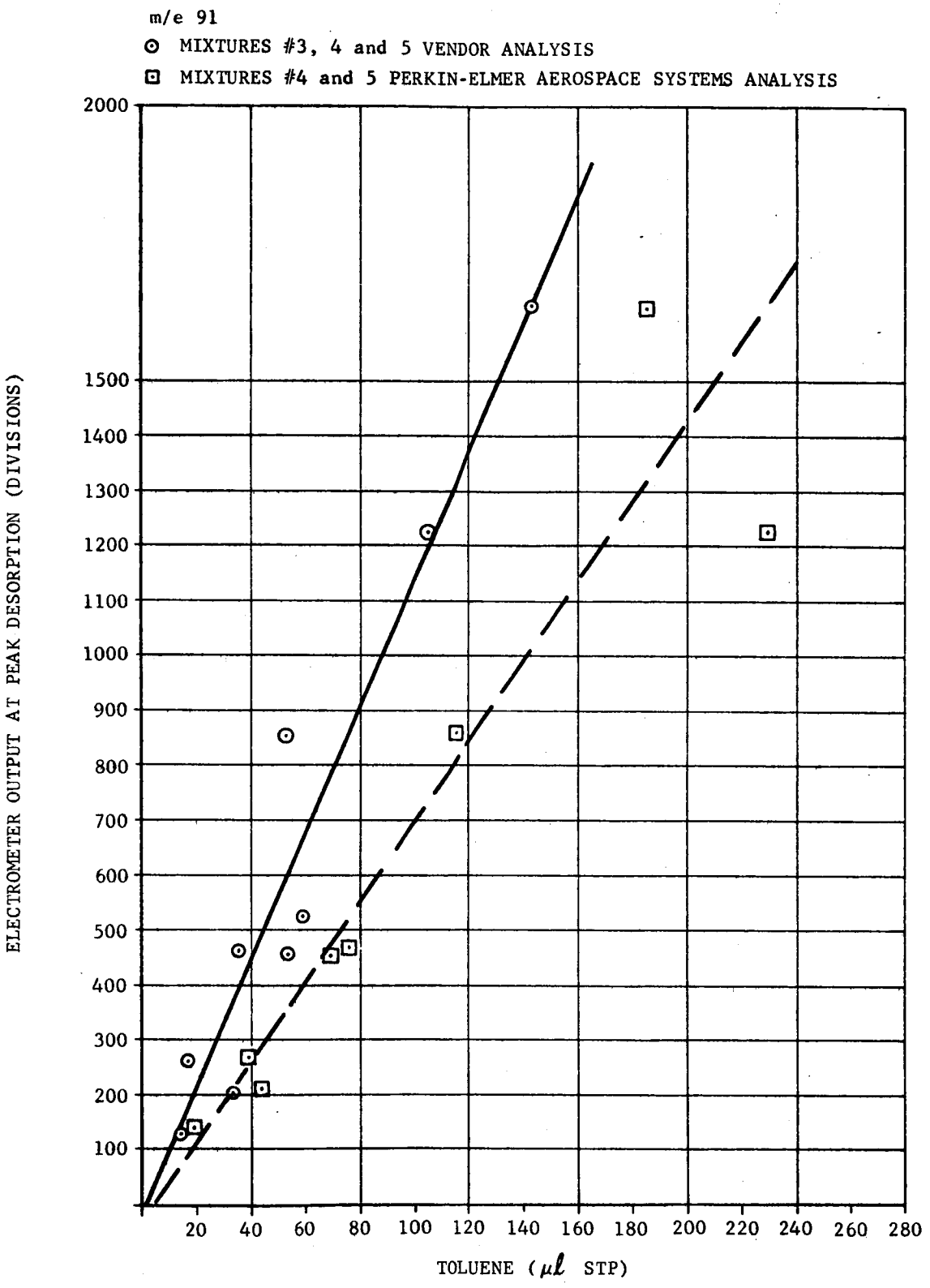


FIGURE 4-22
OUTPUT VS. AMOUNT SORBED
TOLUENE ON PORAPAK Q

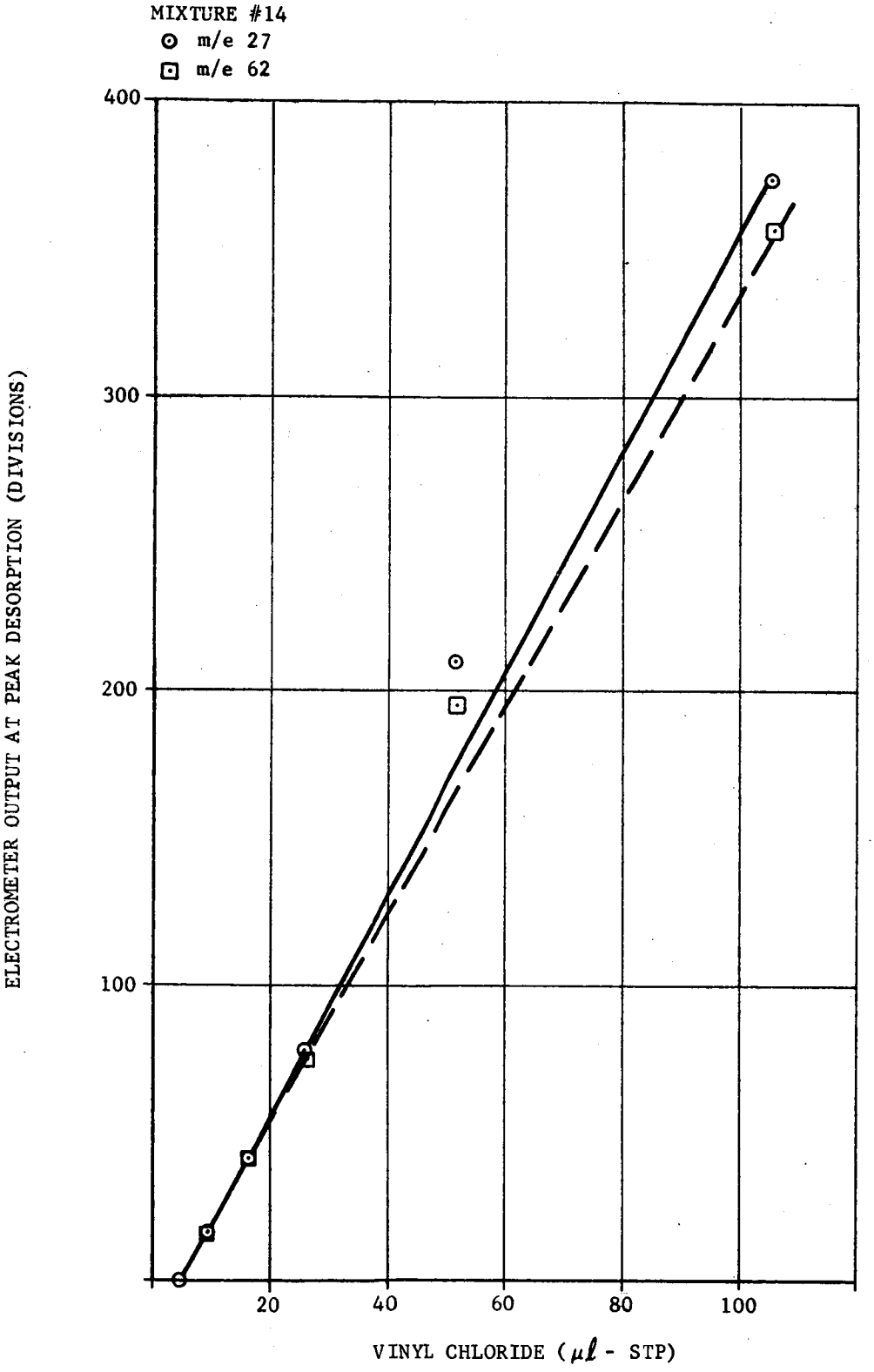


FIGURE 4-23
OUTPUT VS. AMOUNT SORBED
VINYL CHLORIDE ON CHARCOAL

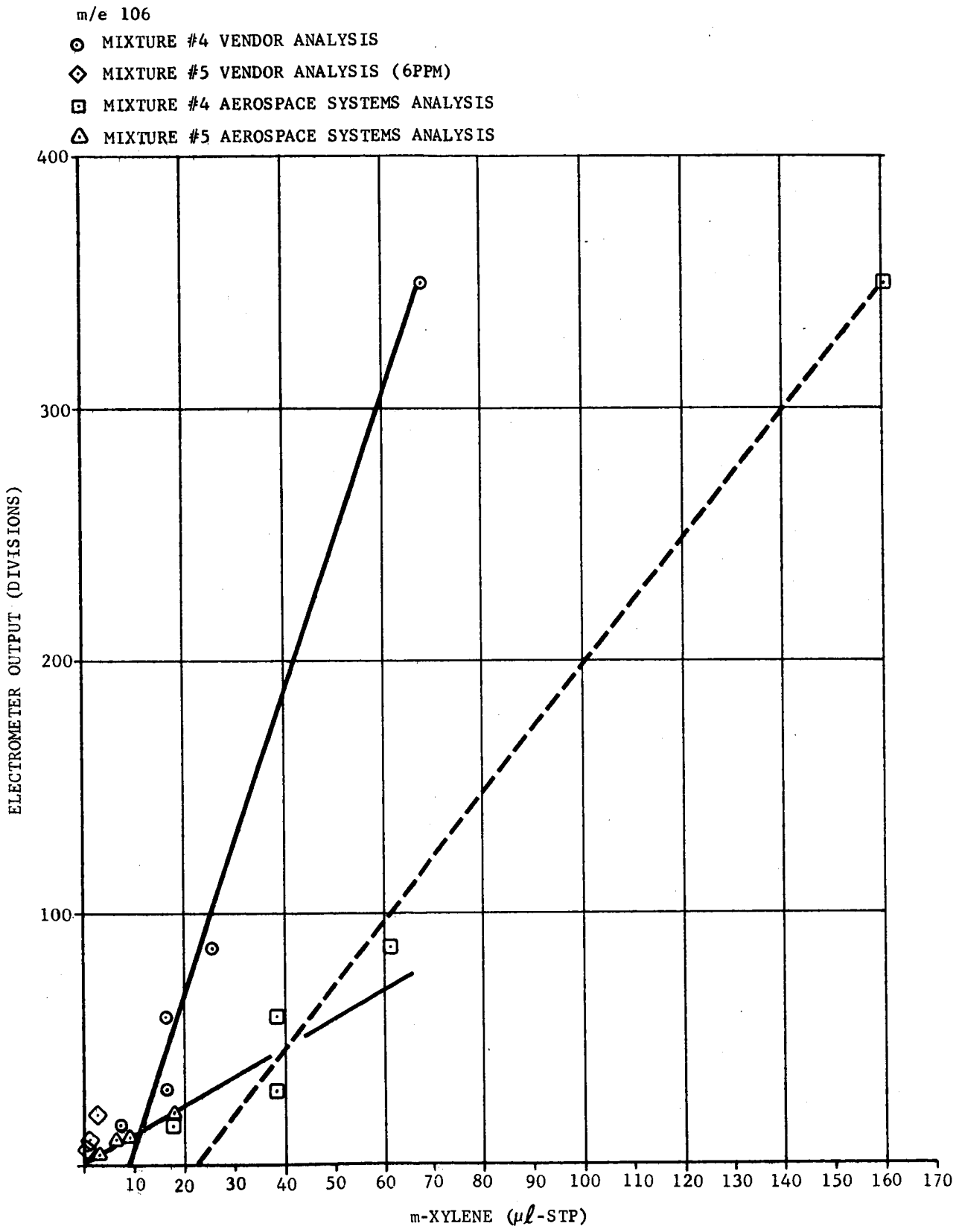


FIGURE 4-24
OUTPUT VS. AMOUNT SORBED
M-XYLENE ON PORAPAK Q

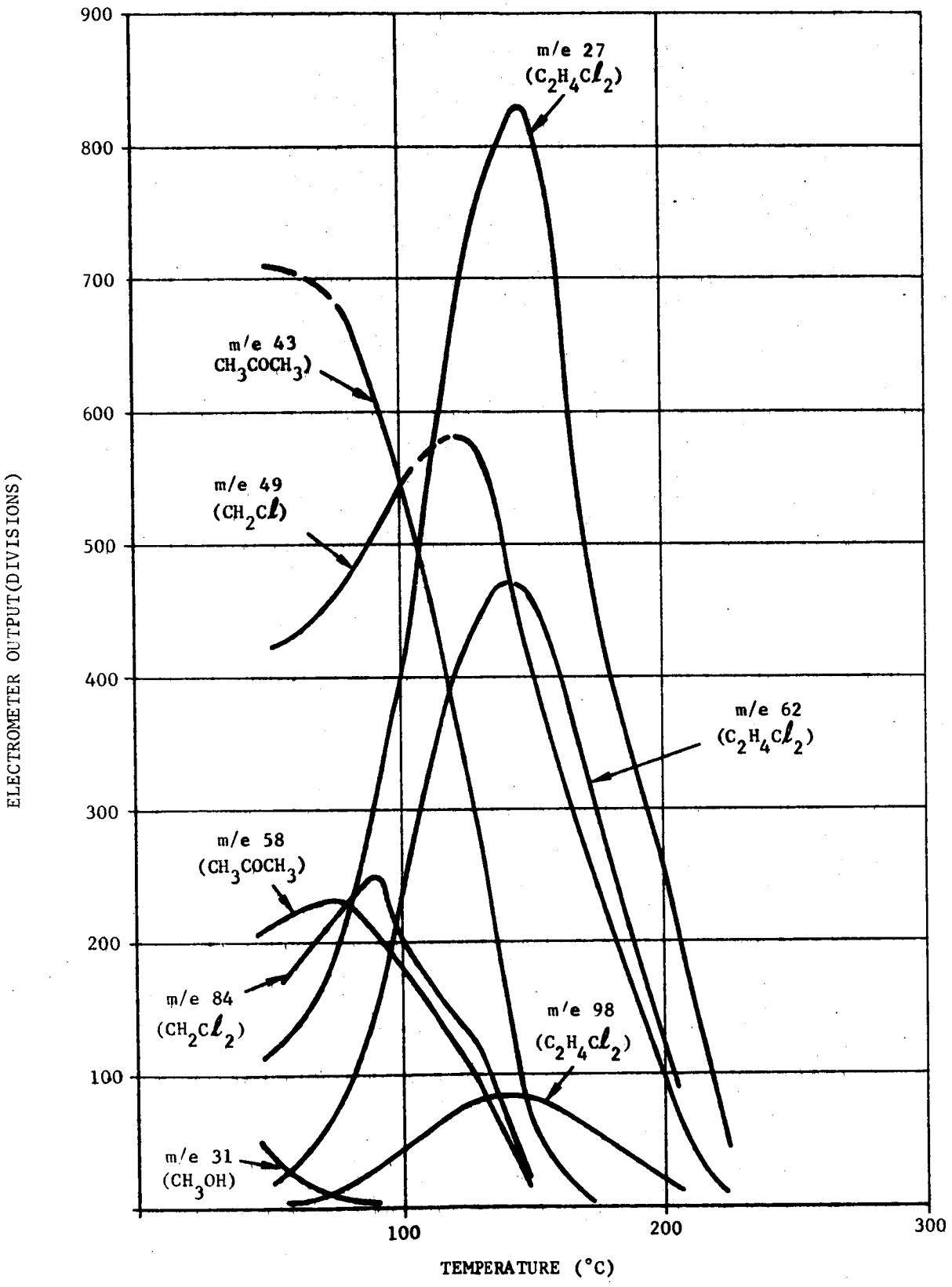


FIGURE 4-25

ACETONE, METHYLENE CHLORIDE, ETHYLENE DICHLORIDE AND METHANOL ON PORAPAK Q

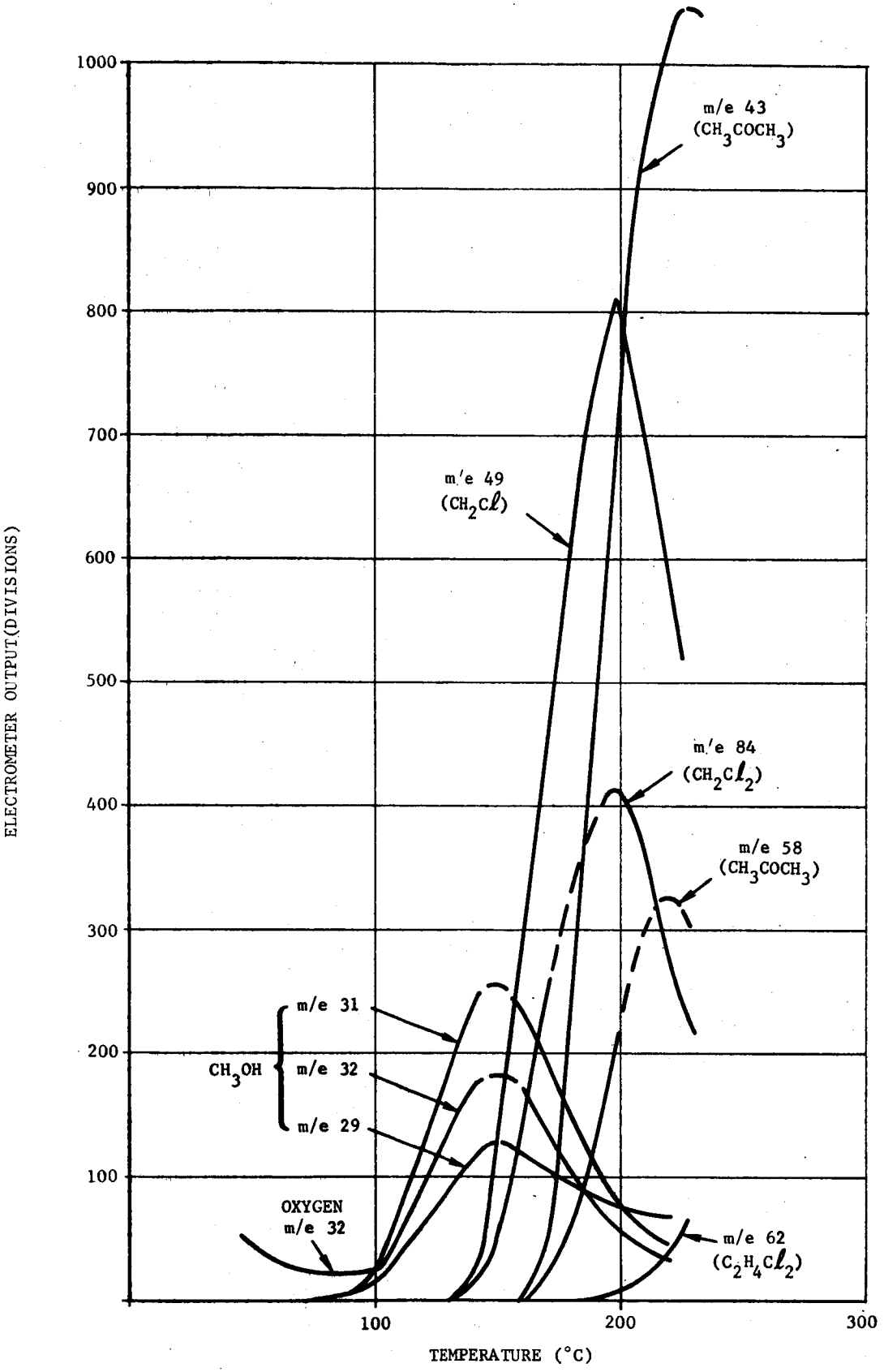


FIGURE 4-26
DESORPTION CURVE
ACETONE (CH_3COCH_3), METHANOL (CH_3OH), METHYLENE CHLORIDE (CH_2Cl_2) AND ETHYLENE DICHLORIDE ($C_2H_4Cl_2$) CHARCOAL

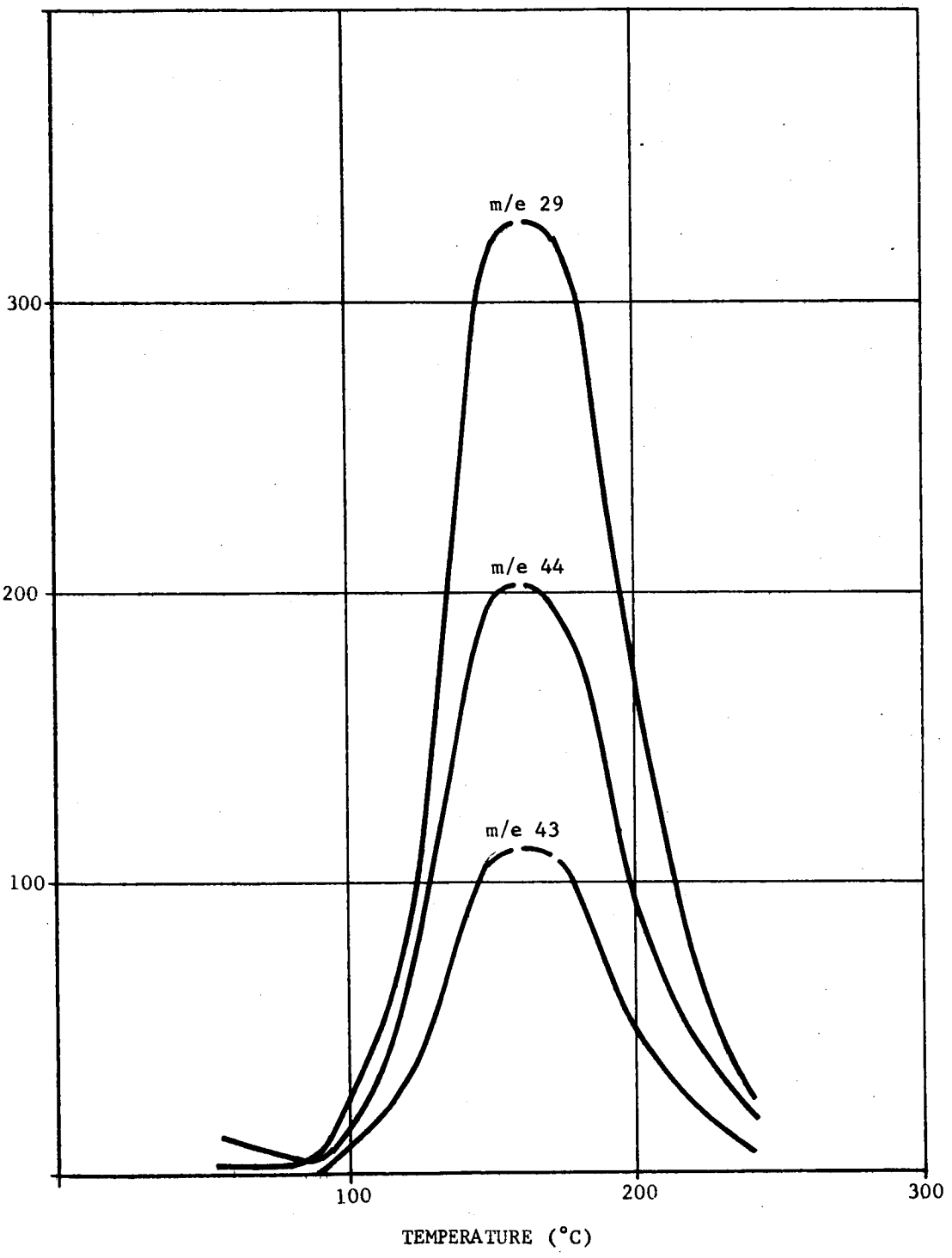


FIGURE 4-27

DESORPTION CURVE
ACETALDEHYDE ON CHARCOAL

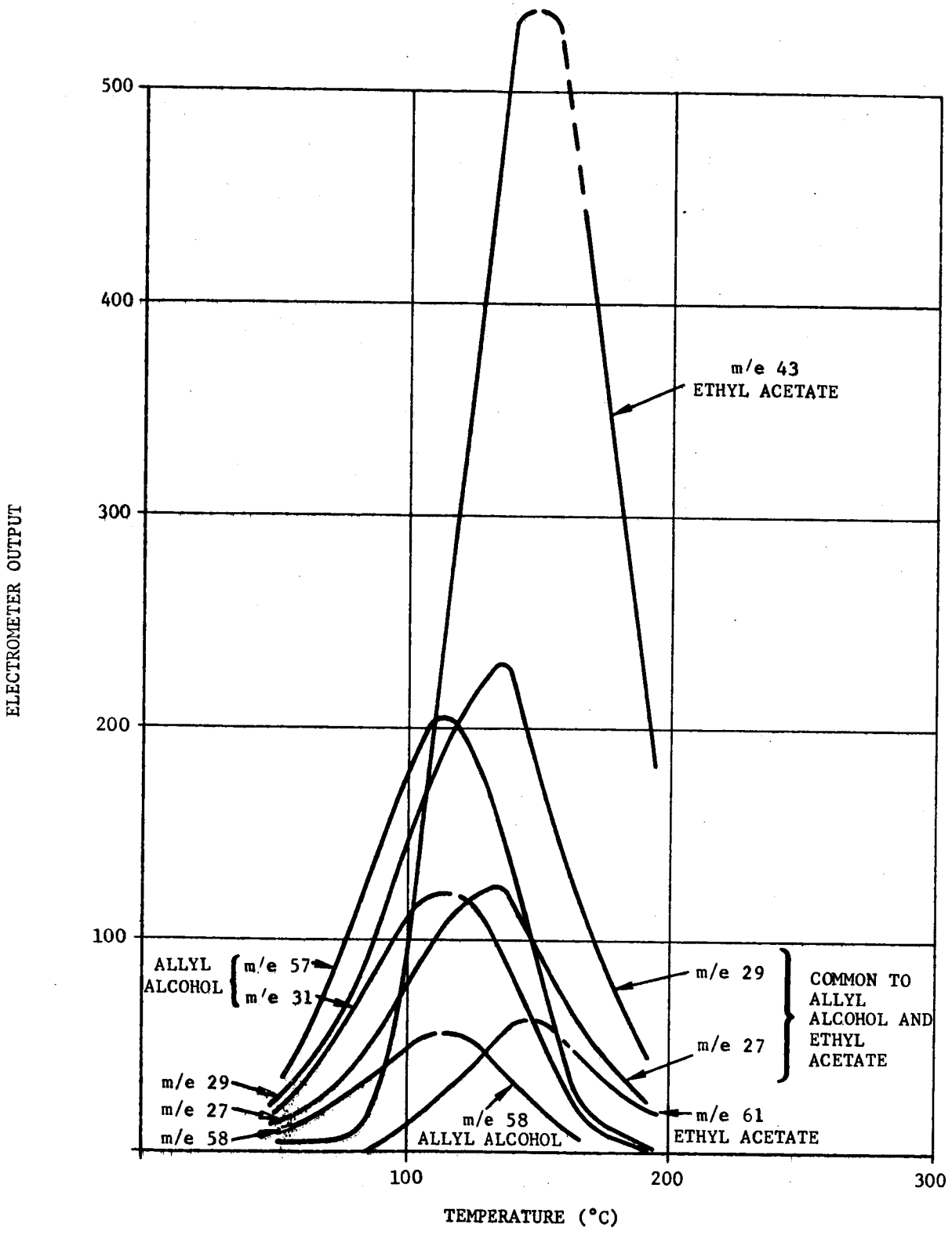


FIGURE 4-28
DESORPTION CURVE
ALLYL ALCOHOL (CH_2=$CHCH_2OH$)
AND ETHYL ACETATE ($C_2H_5O_2CH_3$) PORAPAK Q

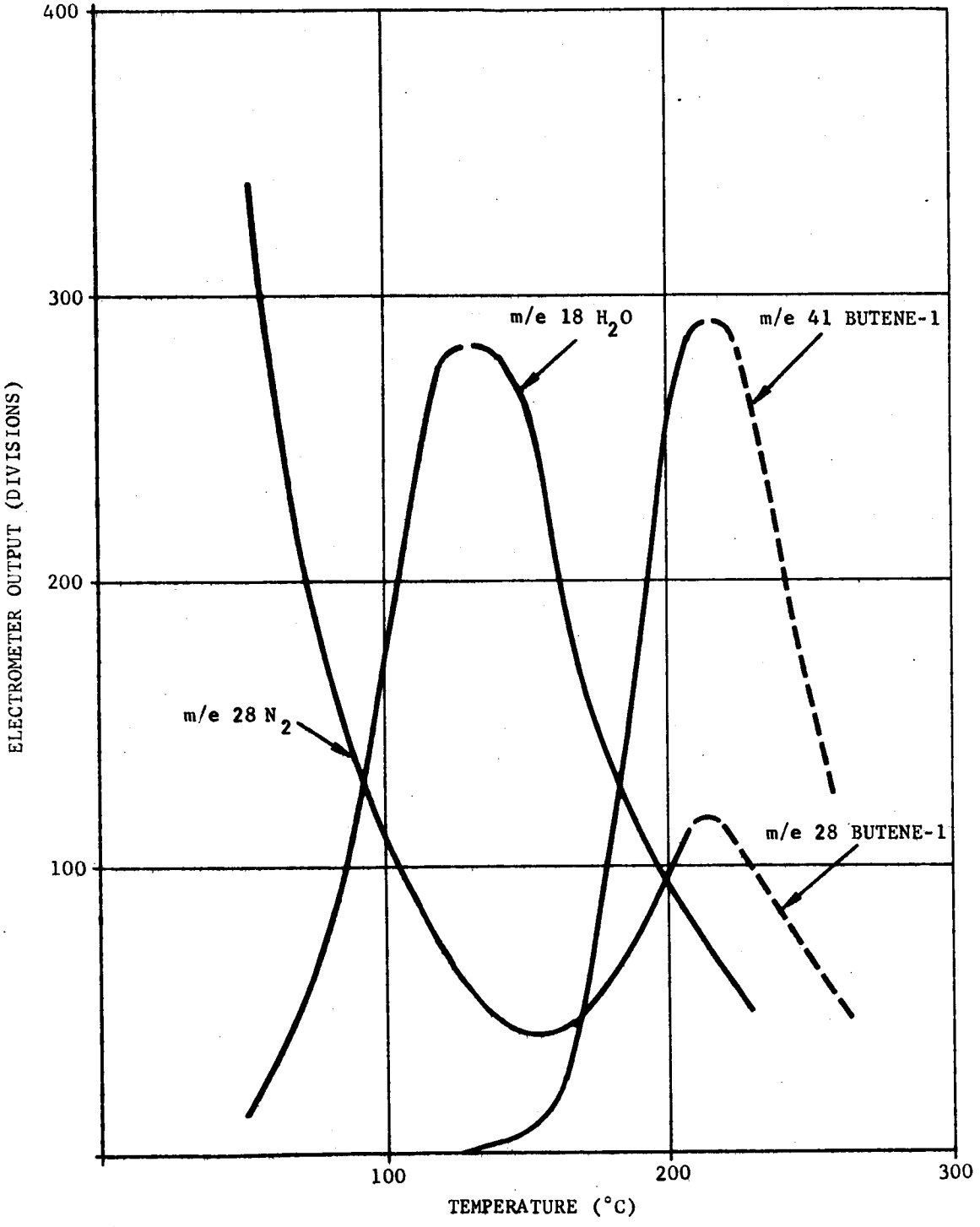


FIGURE 4-29

DESORPTION CURVE
BUTENE-1 DILUTED WITH AIR ON CHARCOAL

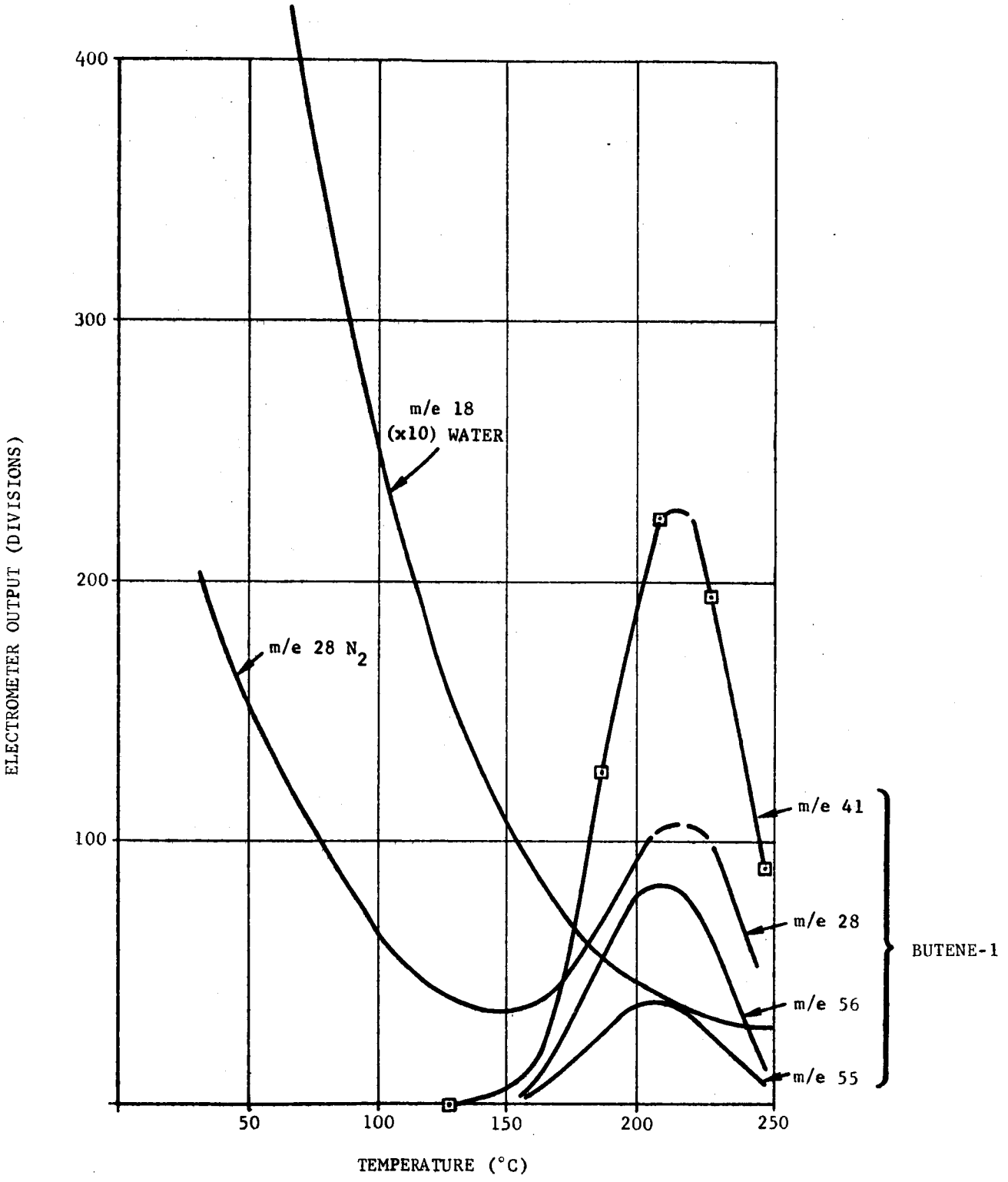


FIGURE 4-30

DESORPTION CURVE
BUTENE-1 DILUTED WITH WET AIR ON CHARCOAL

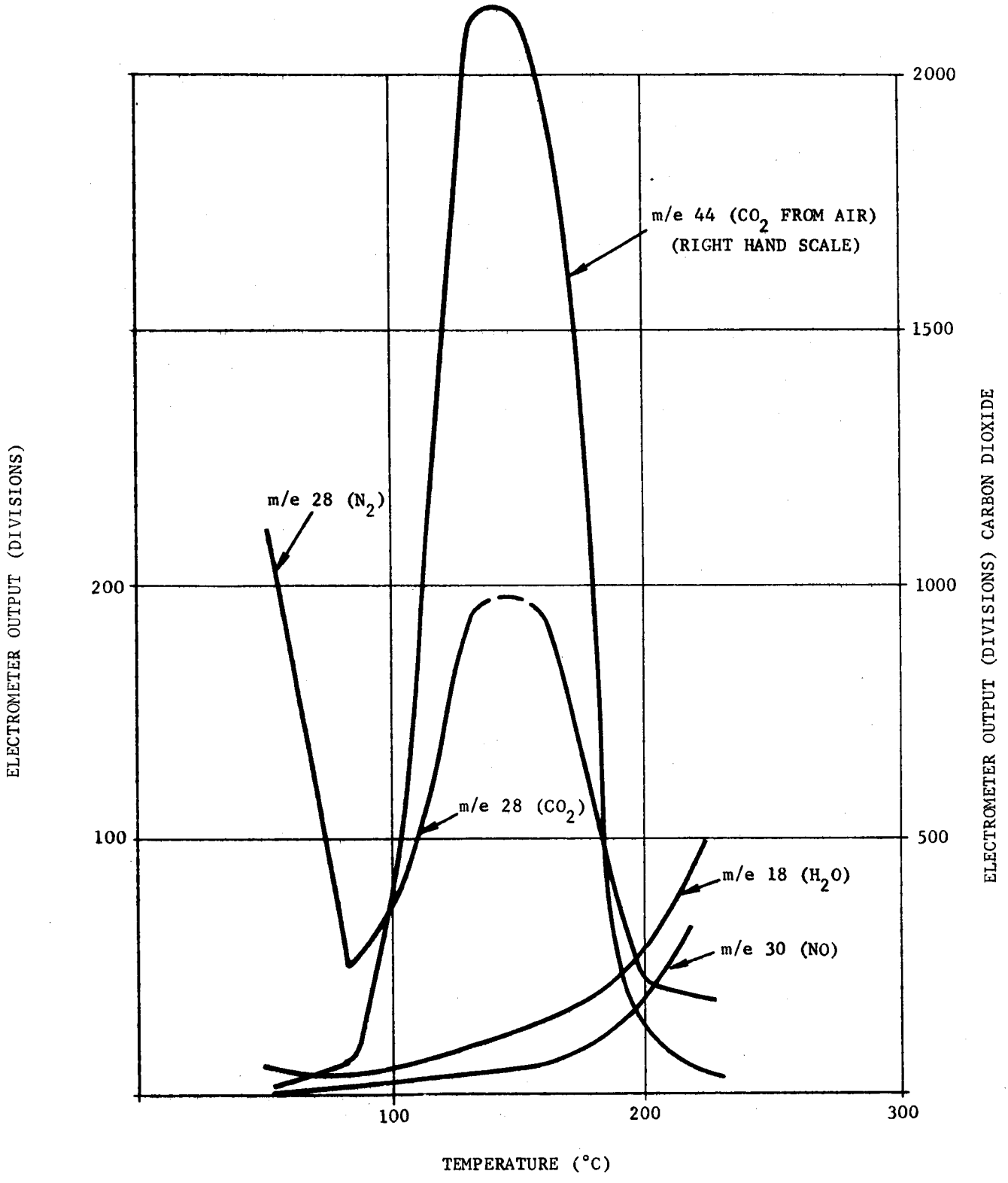


FIGURE 4-31
DESORPTION CURVE
NITRIC OXIDE (NO) CARBON DIOXIDE (CO_2) METHANE IN AIR ON MOLECULAR SIEVE 5A

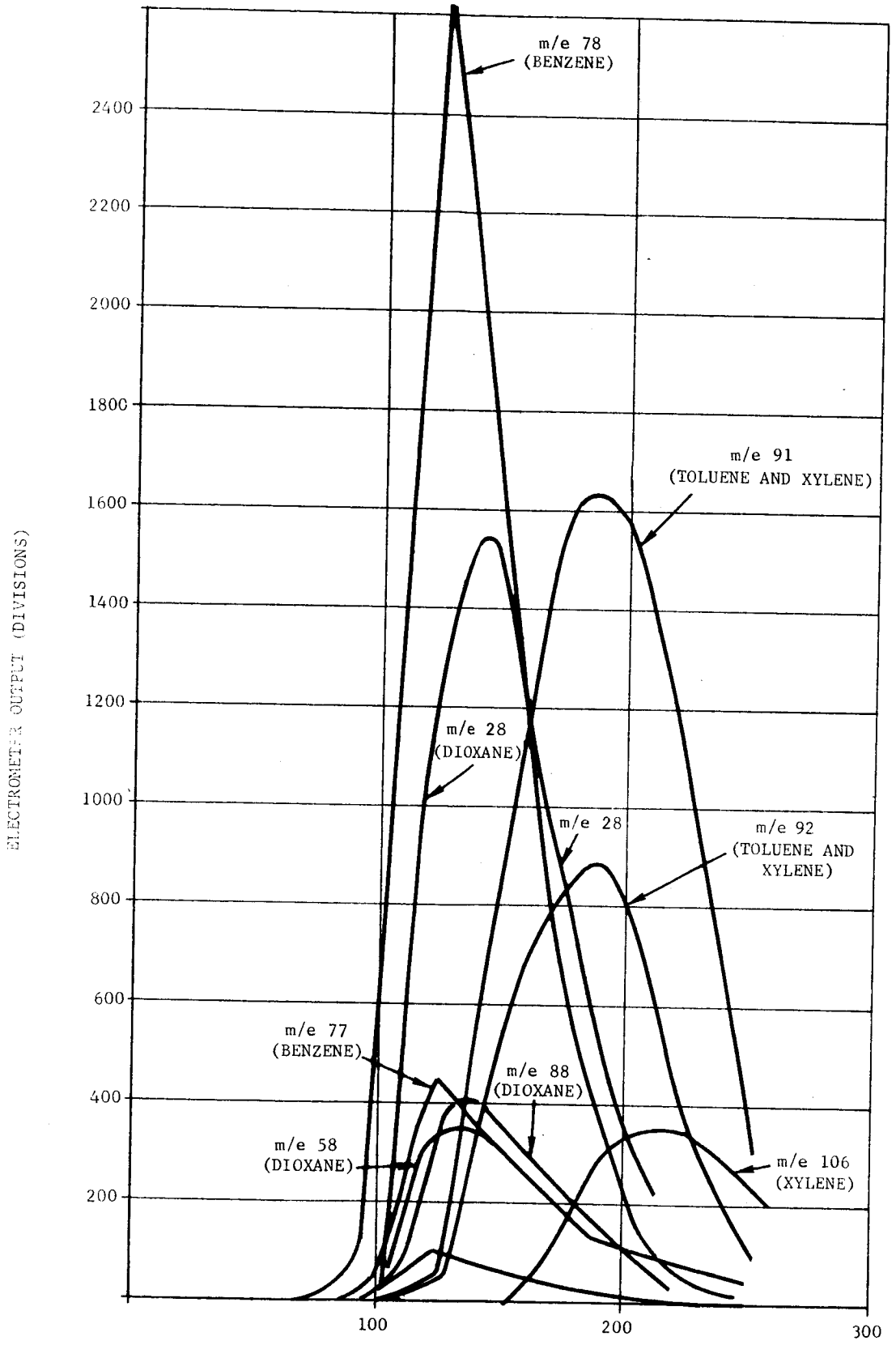


FIGURE 4-32
DESORPTION CURVE
BENZENE, DIOXANE, TOLUENE, M-XYLENE PORAPAK Q

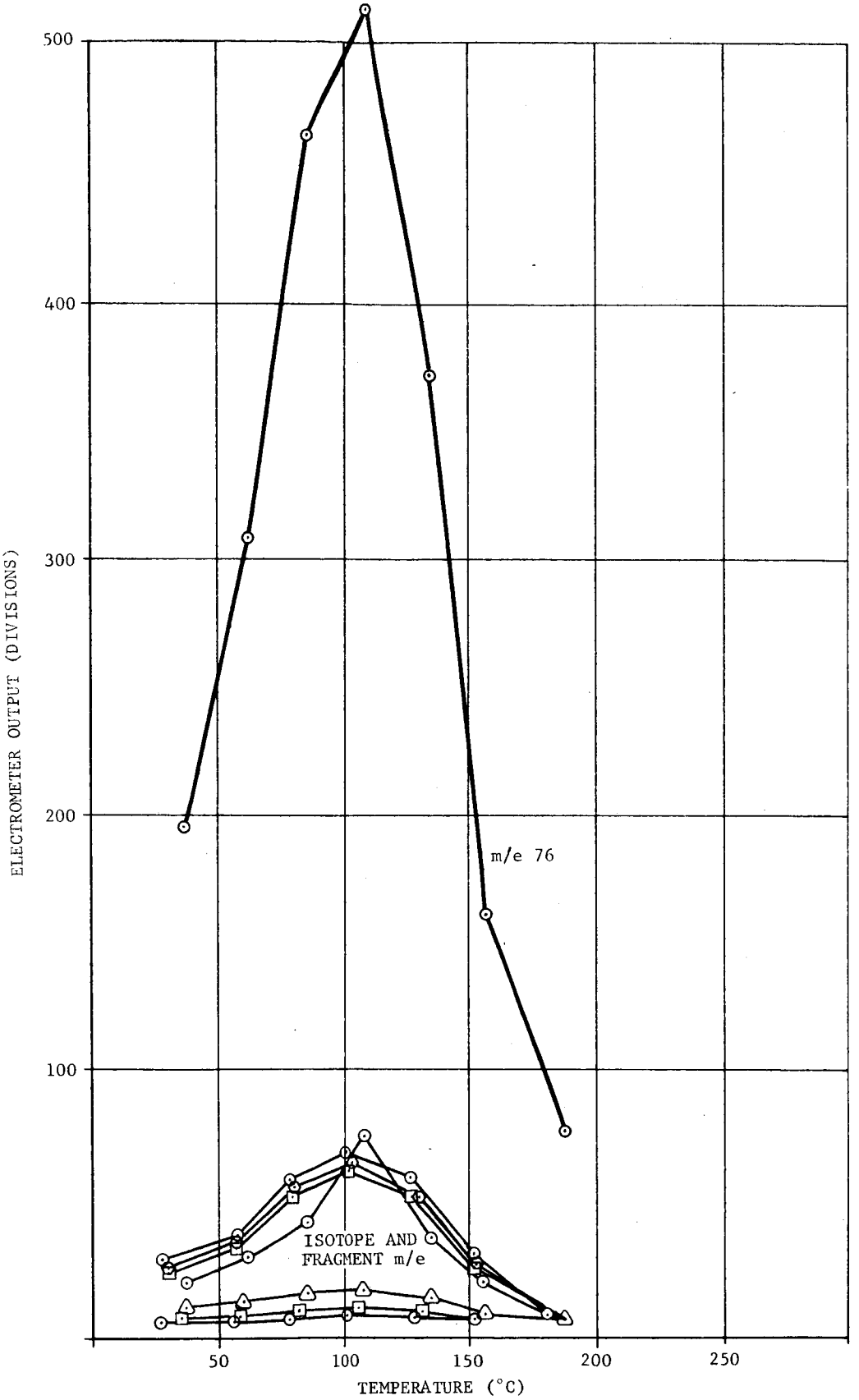


FIGURE 4-33
DESORPTION CURVE
CARBON DISULFIDE PORAPAK Q

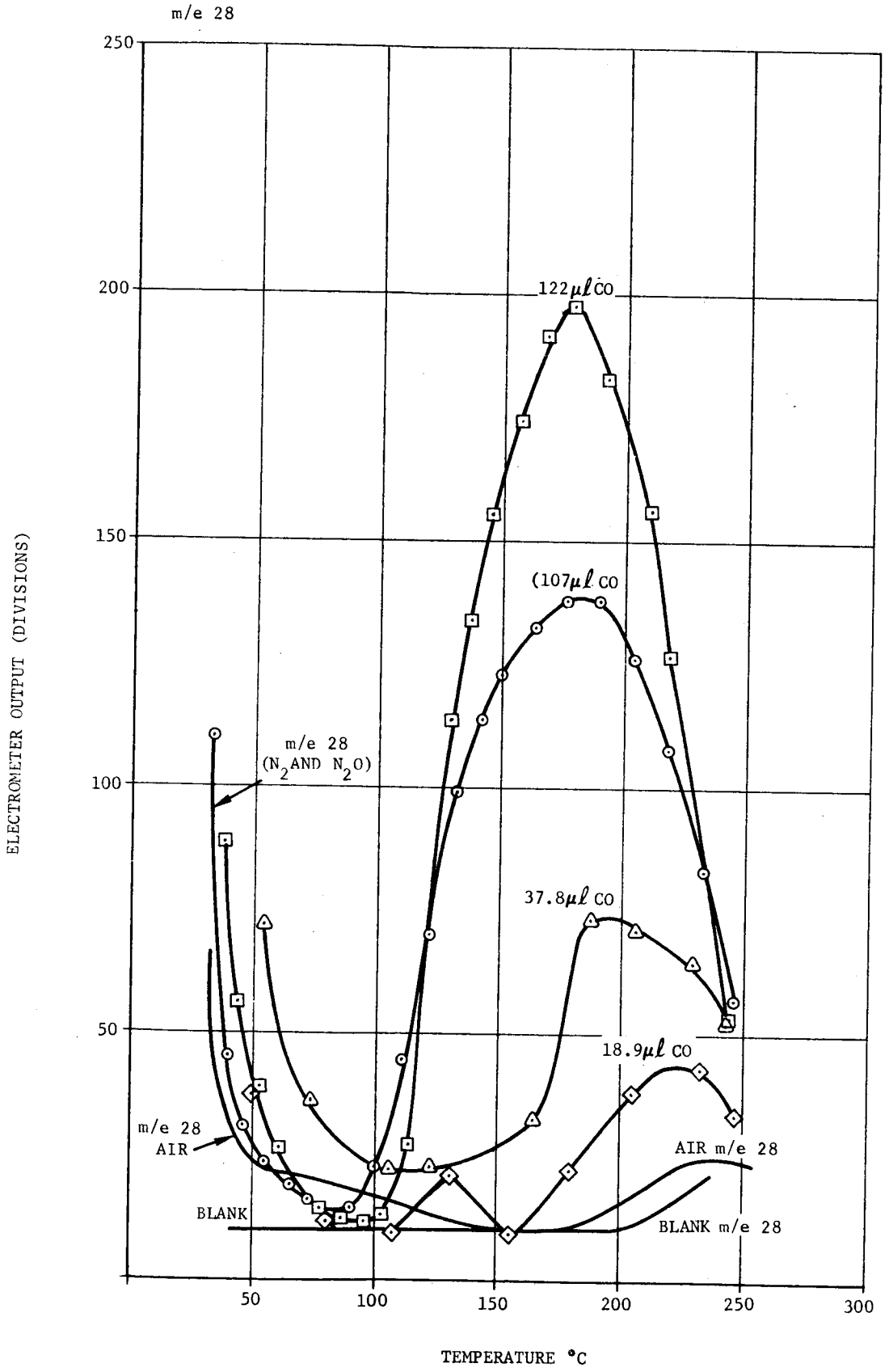


FIGURE 4-34
CARBON MONOXIDE DESORPTION
FROM PALLADIUM-CHARCOAL

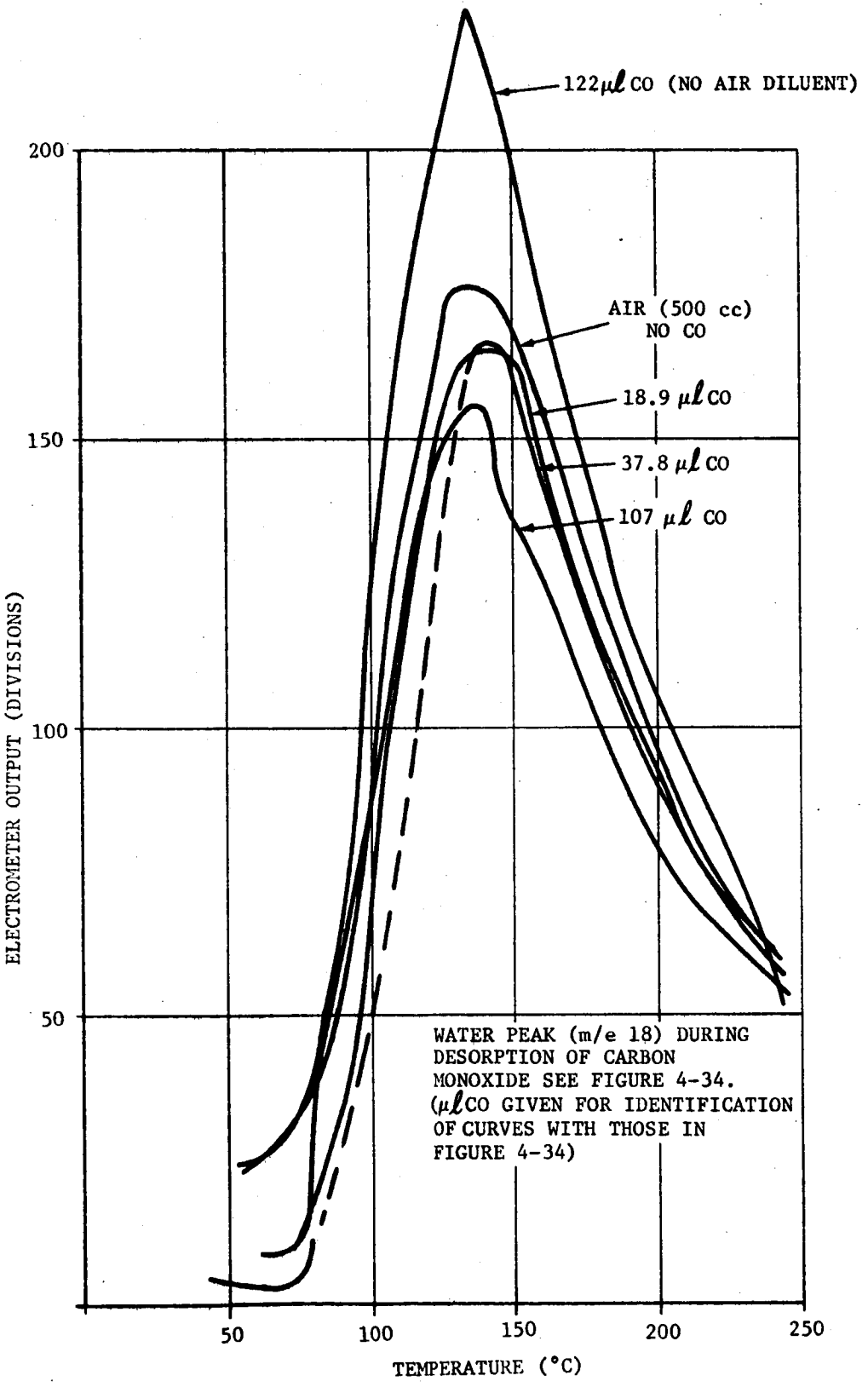


FIGURE 4-35
DESORPTION CURVE
PALLADIUM CHARCOAL

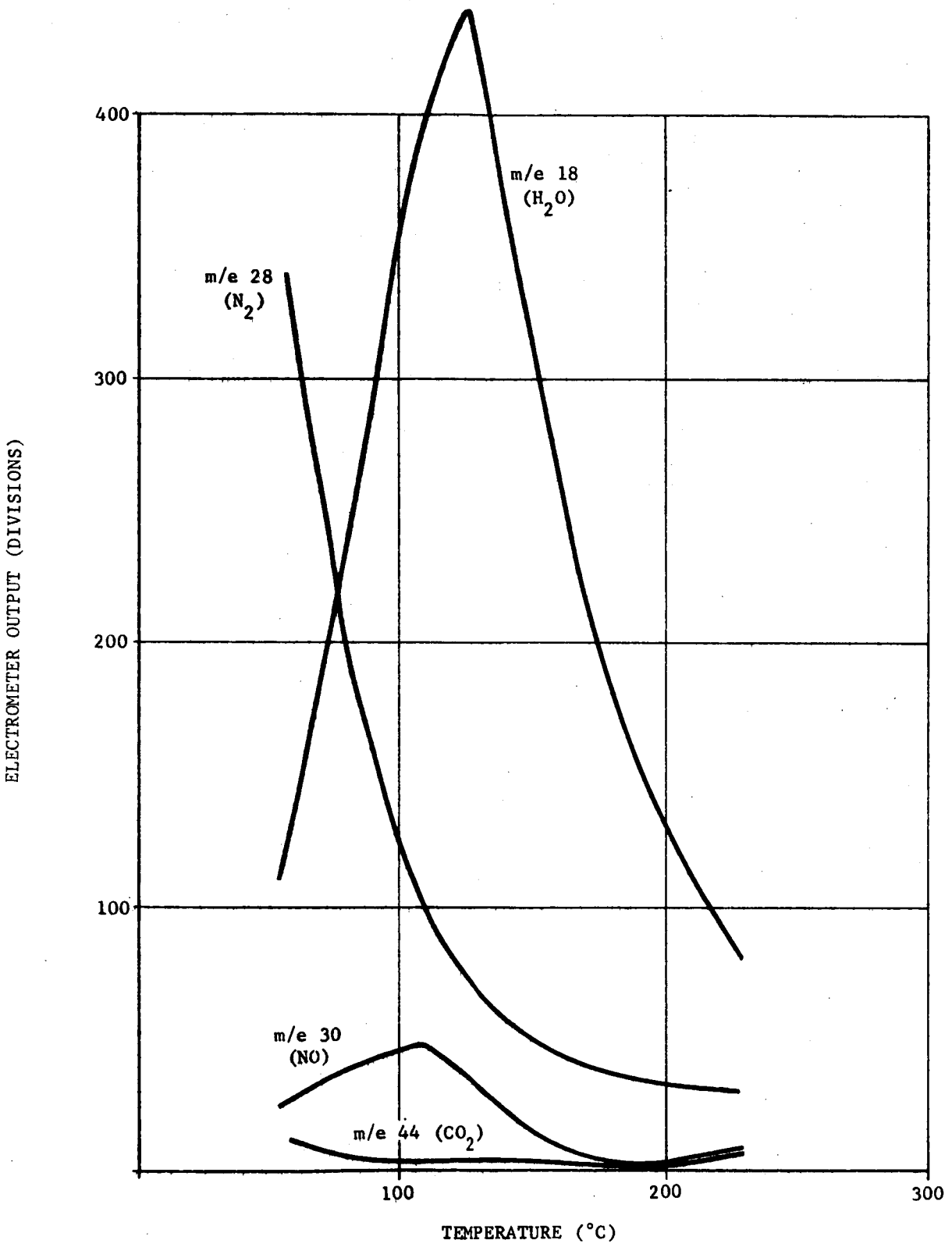


FIGURE 4-36
DESORPTION CURVE
NITRIC OXIDE (NO) CARBON DIOXIDE (CO_2) METHANE IN AIR CHARCOAL

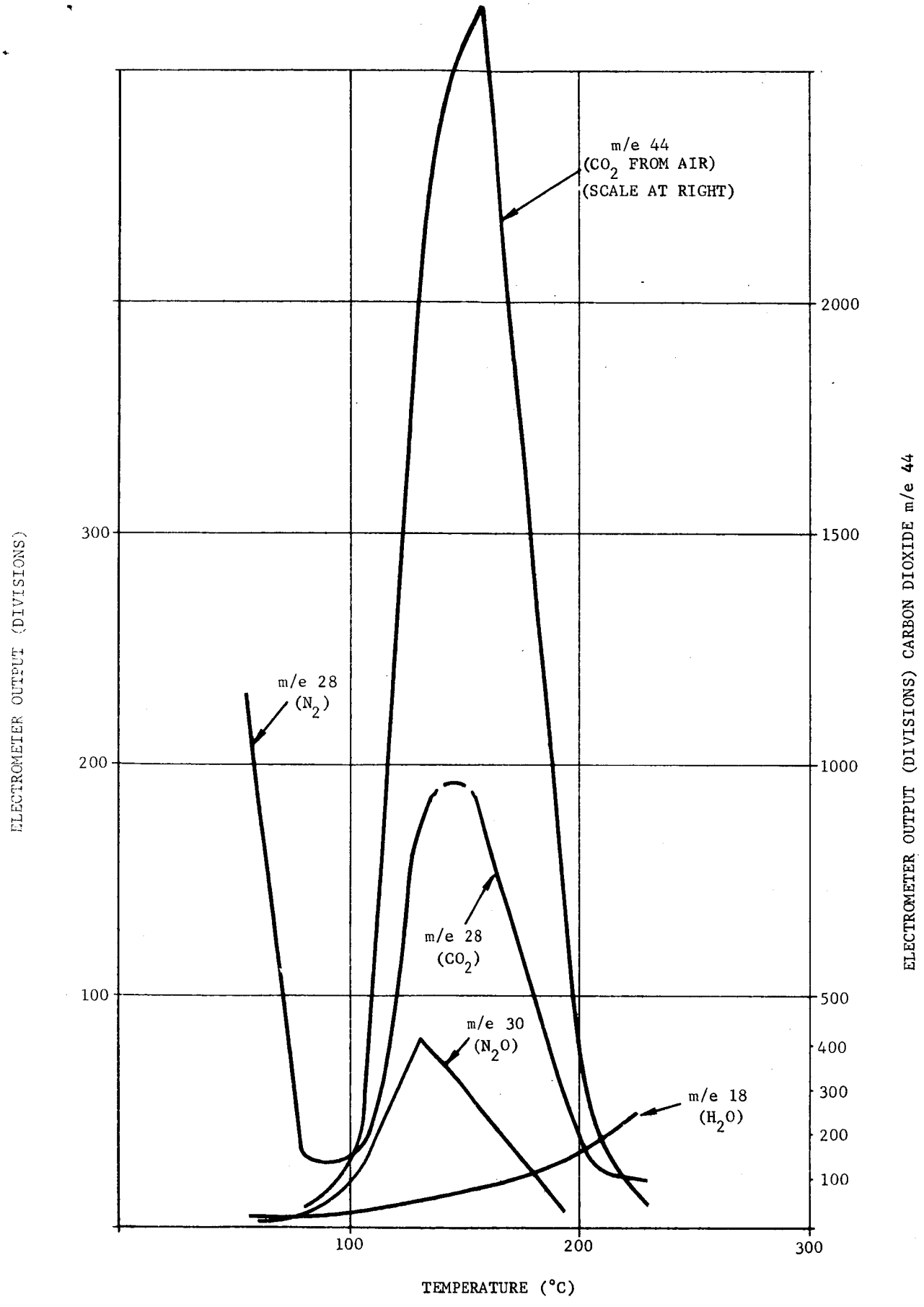


FIGURE 4-37
DESORPTION CURVE
NITROUS OXIDE (N_2O) CARBON MONOXIDE (CO) IN AIR MOLECULAR SIEVE 5A

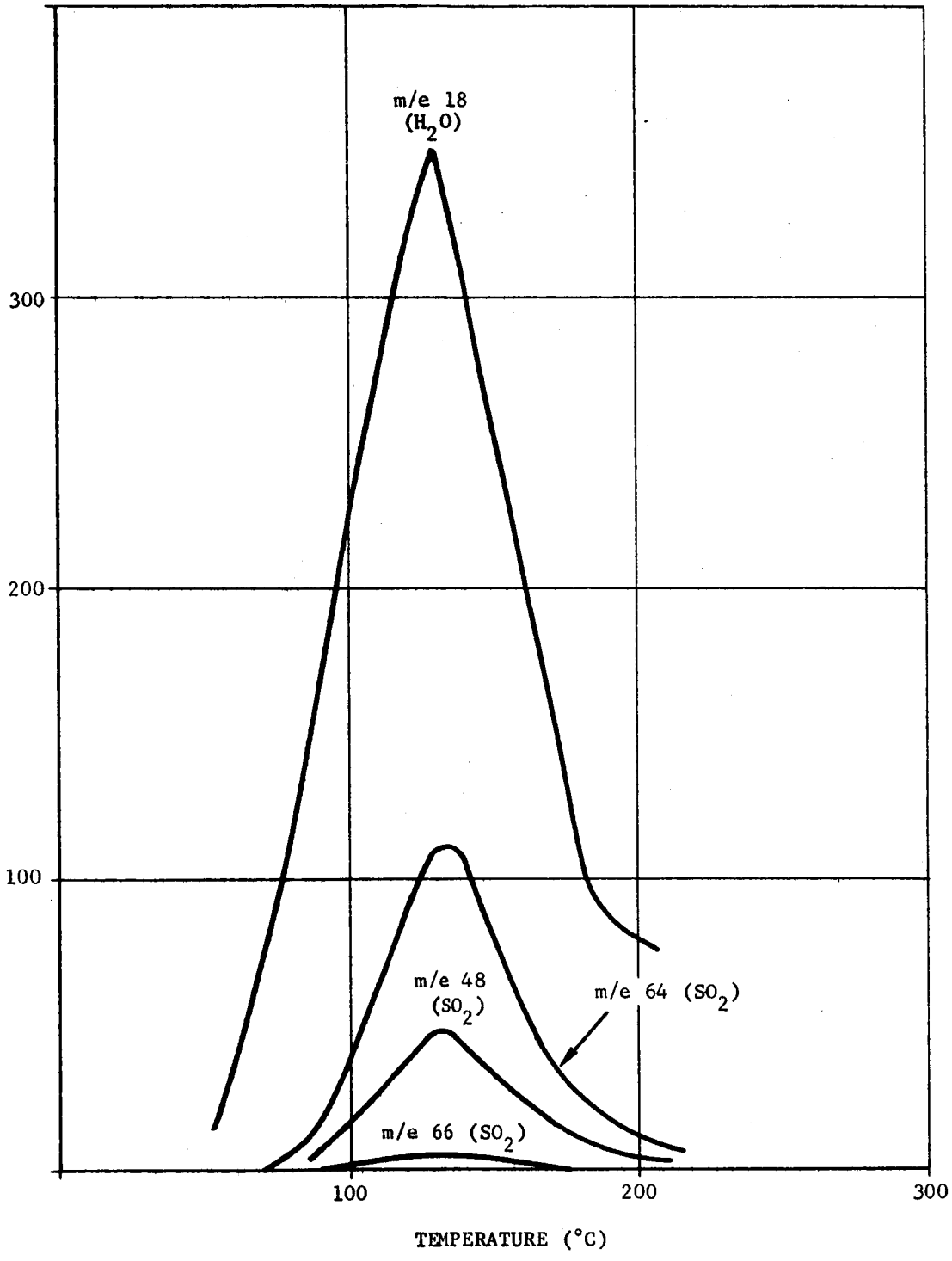


FIGURE 4-38
DESORPTION CURVE
SULFUR DIOXIDE (SO_2) CHARCOAL

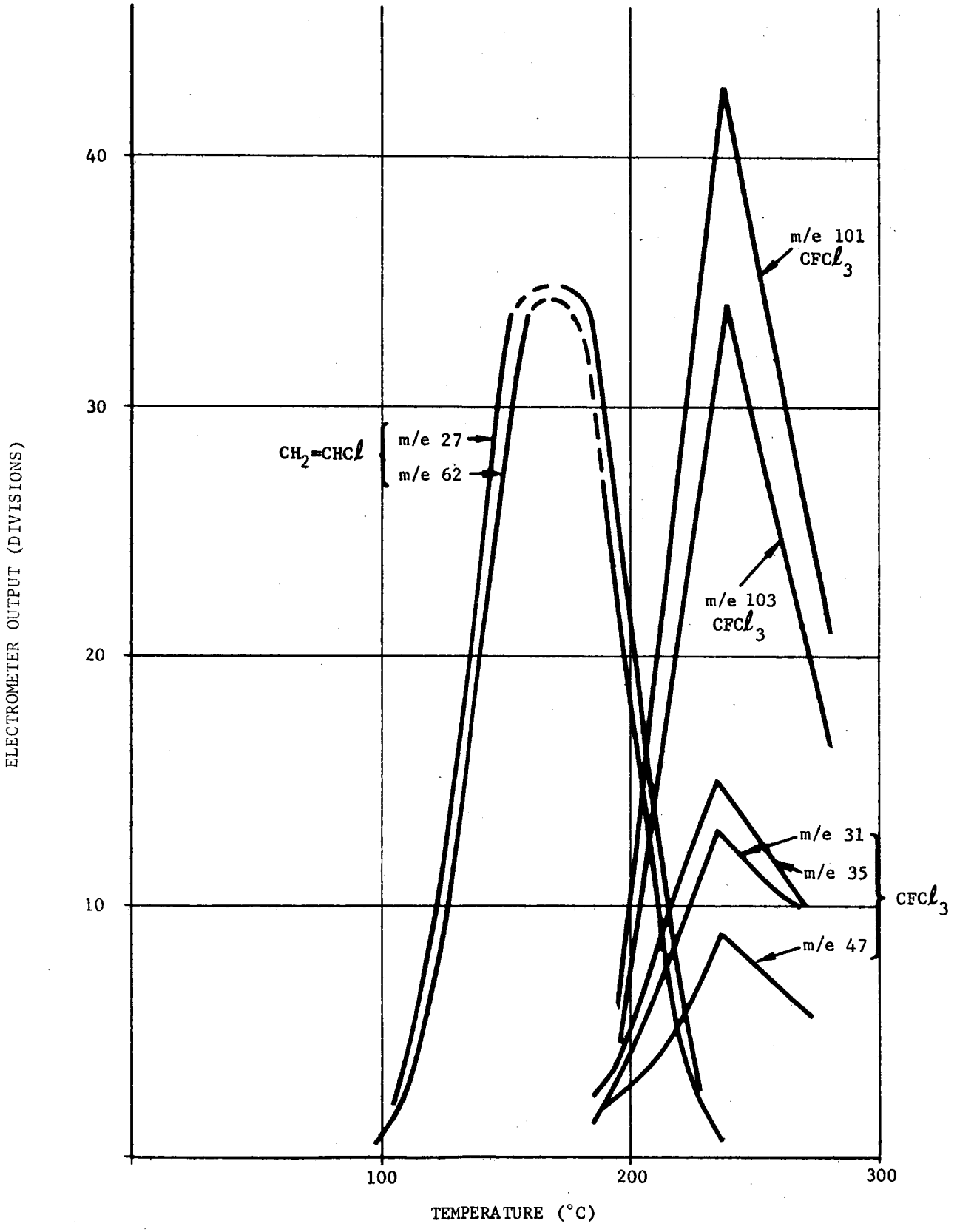


FIGURE 4-39
DESORPTION CURVE
VINYL CHLORIDE (CH_2=CHCℓ) AND FREON-11 ($CFCℓ_3$) CHARCOAL

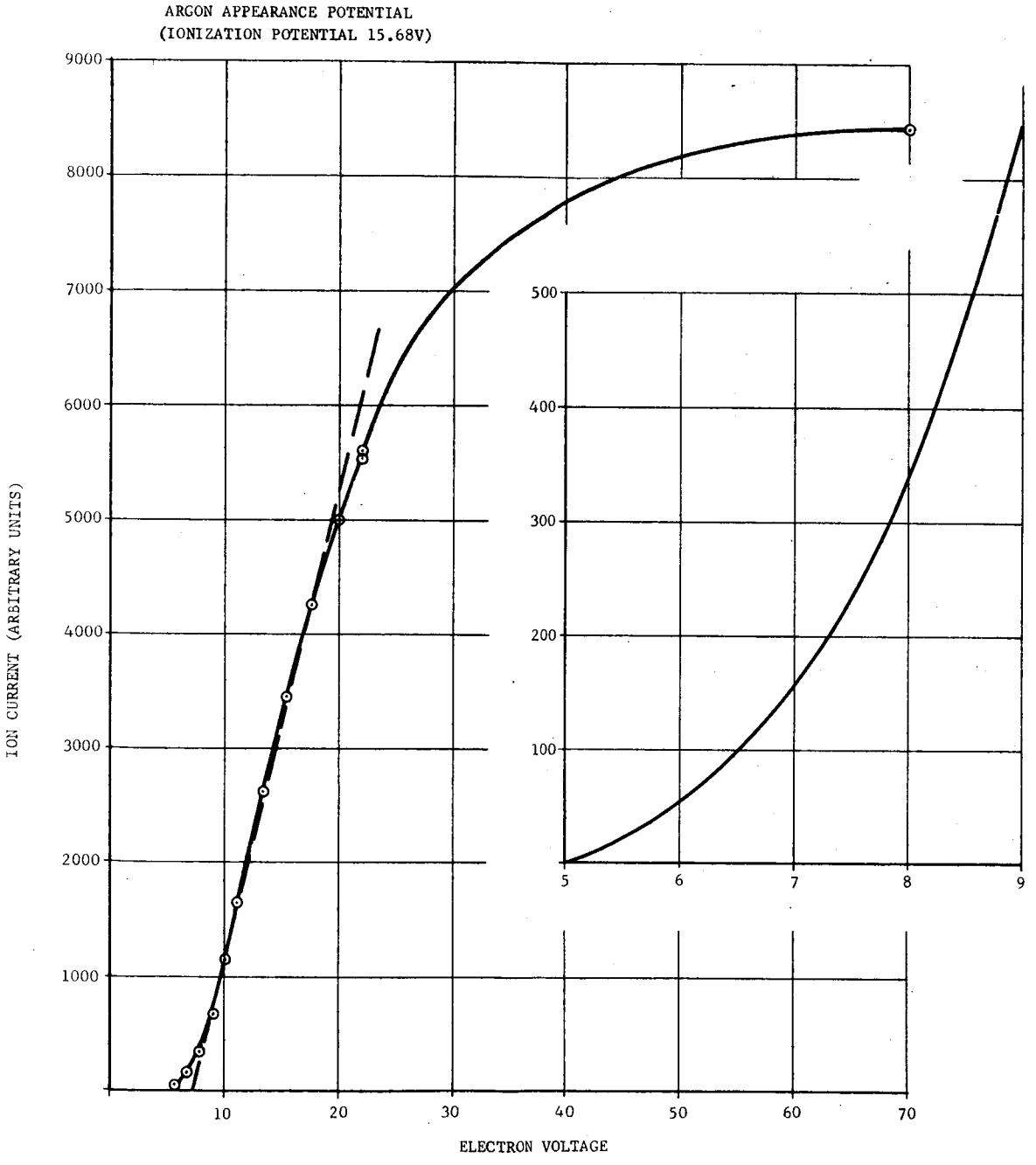


FIGURE 4-40
IONIZATION OF ARGON AS A FUNCTION OF ELECTRON ENERGY

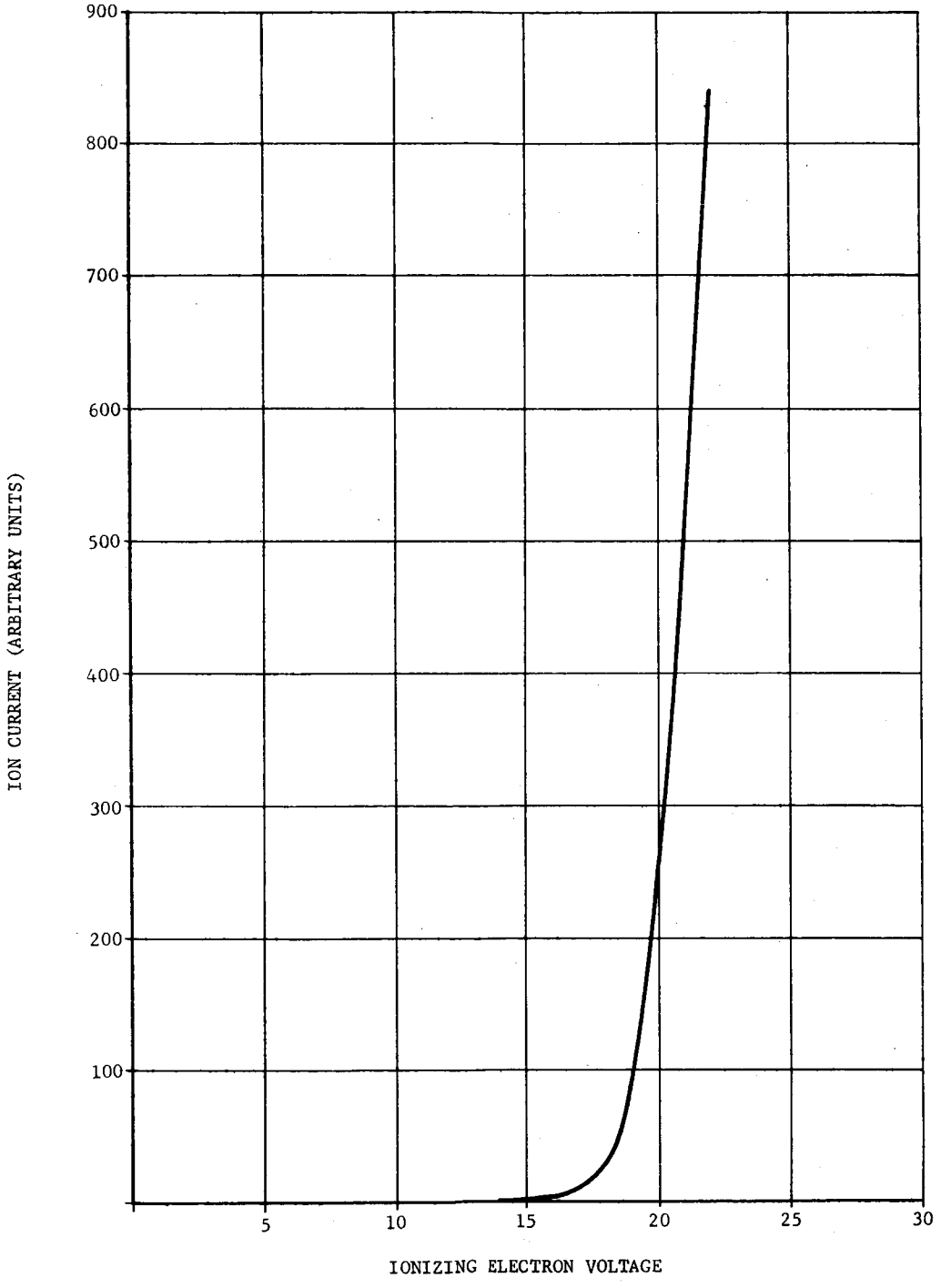


FIGURE 4-41
IONIZATION OF HELIUM AS A FUNCTION OF ELECTRON ENERGY

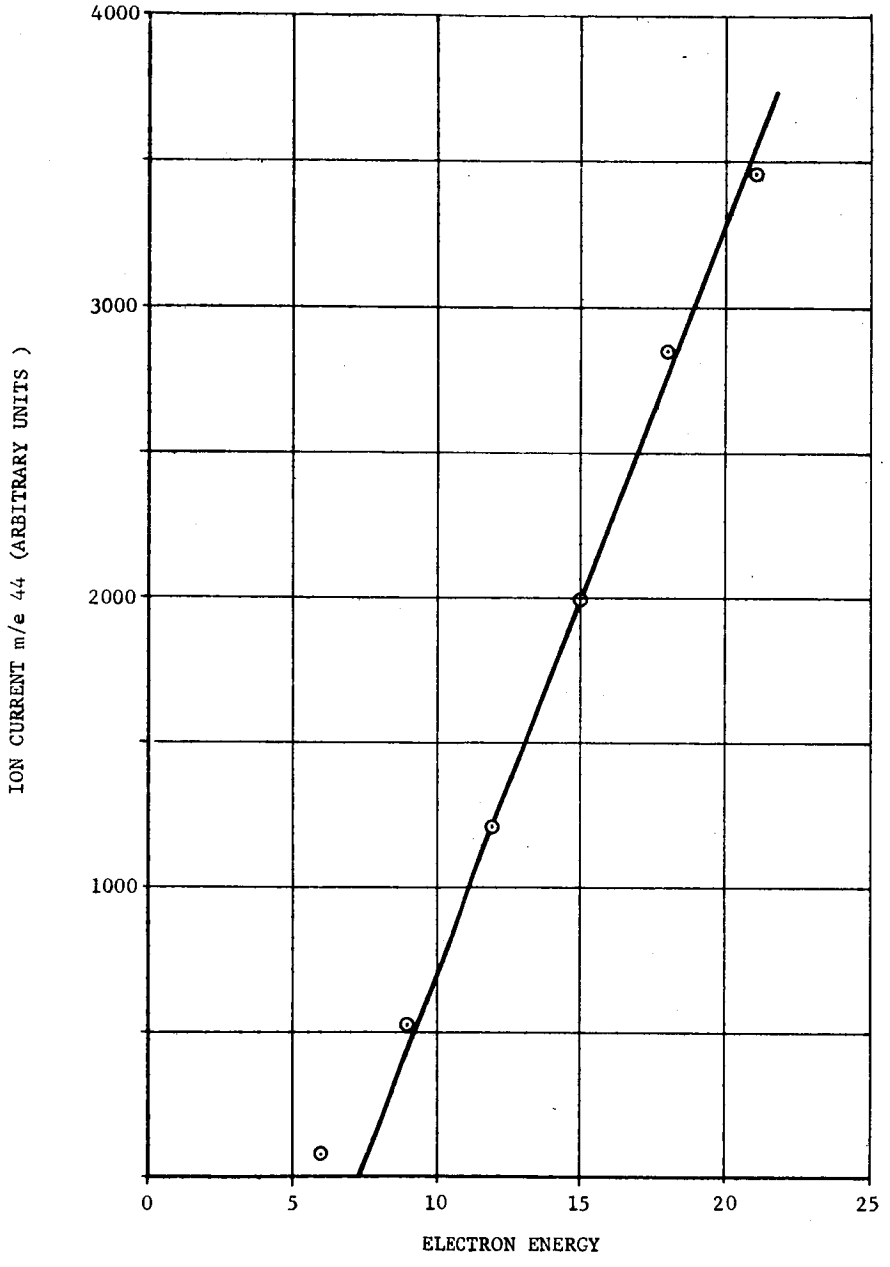


FIGURE 4-42
IONIZATION OF CARBON DIOXIDE AS A FUNCTION OF ELECTRON ENERGY

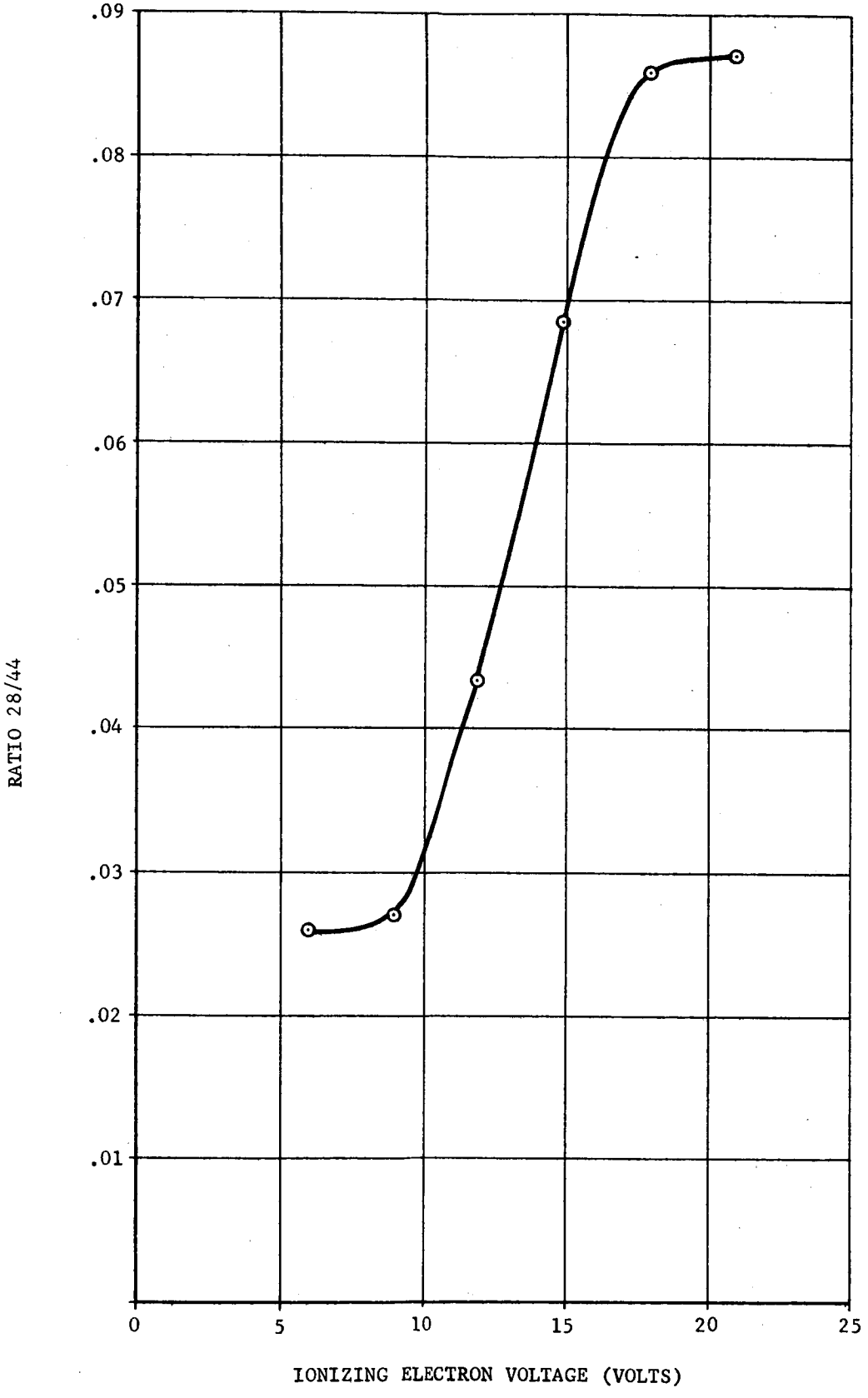
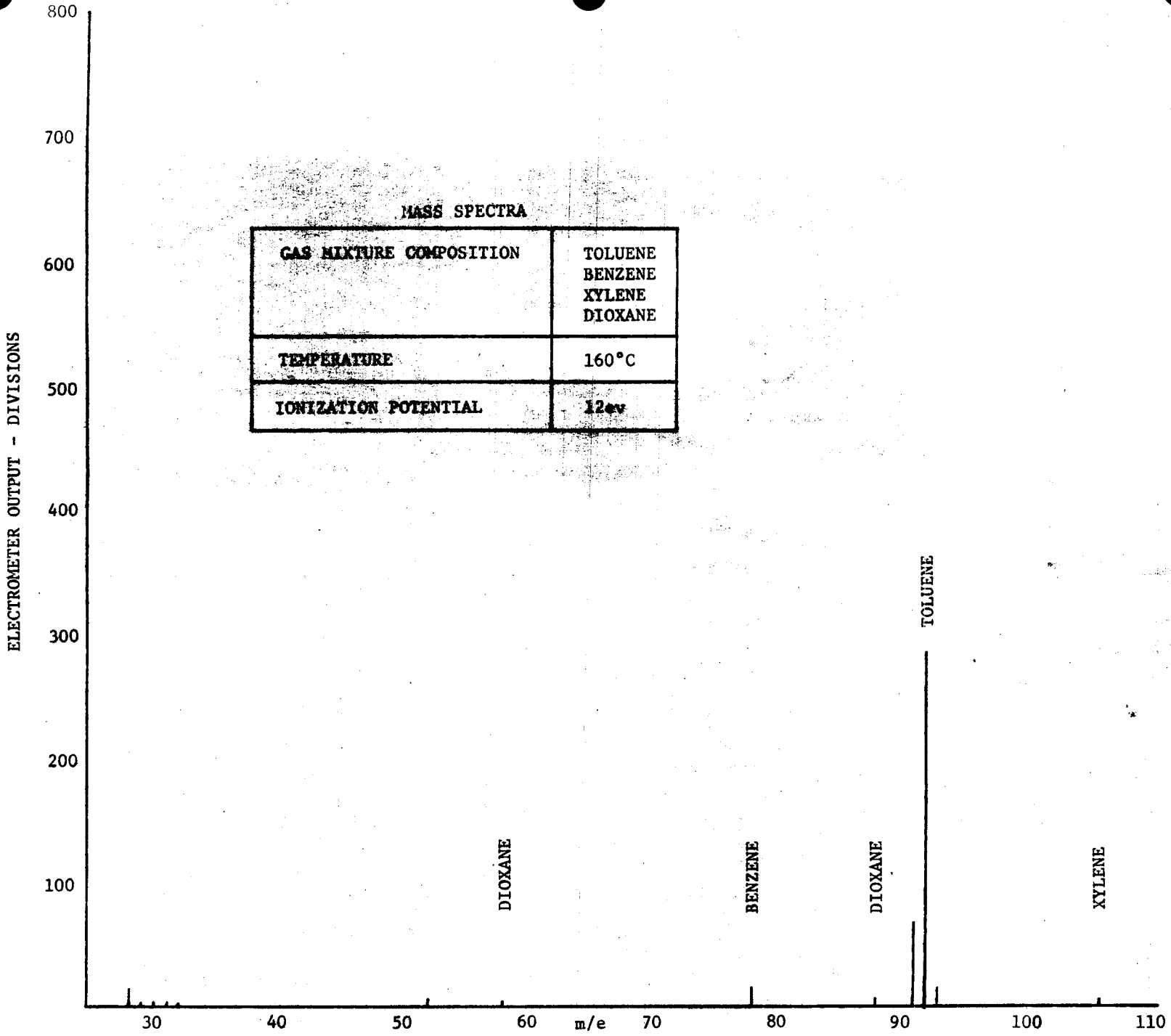


FIGURE 4-43
FRAGMENTATION OF CARBON DIOXIDE AS A FUNCTION OF ELECTRON ENERGY

MASS SPECTRA

GAS MIXTURE COMPOSITION	TOLUENE BENZENE XYLENE DIOXANE
TEMPERATURE	160°C
IONIZATION POTENTIAL	12ev



MASS SPECTRA

GAS MIXTURE COMPOSITION	TOLUENE BENZENE XYLENE DIOXANE
TEMPERATURE	165°C
IONIZATION POTENTIAL	70 ev

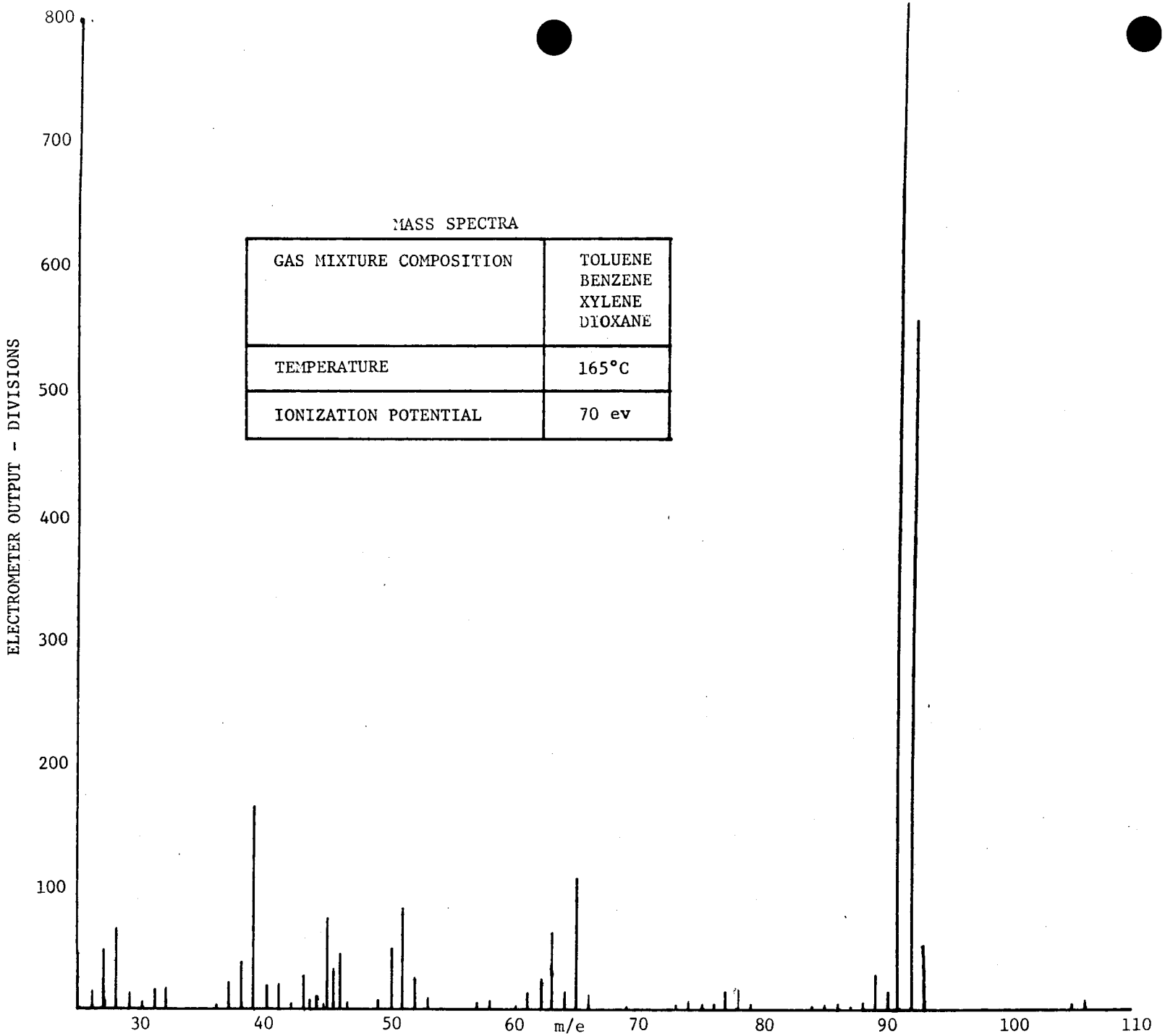


FIGURE 4-44

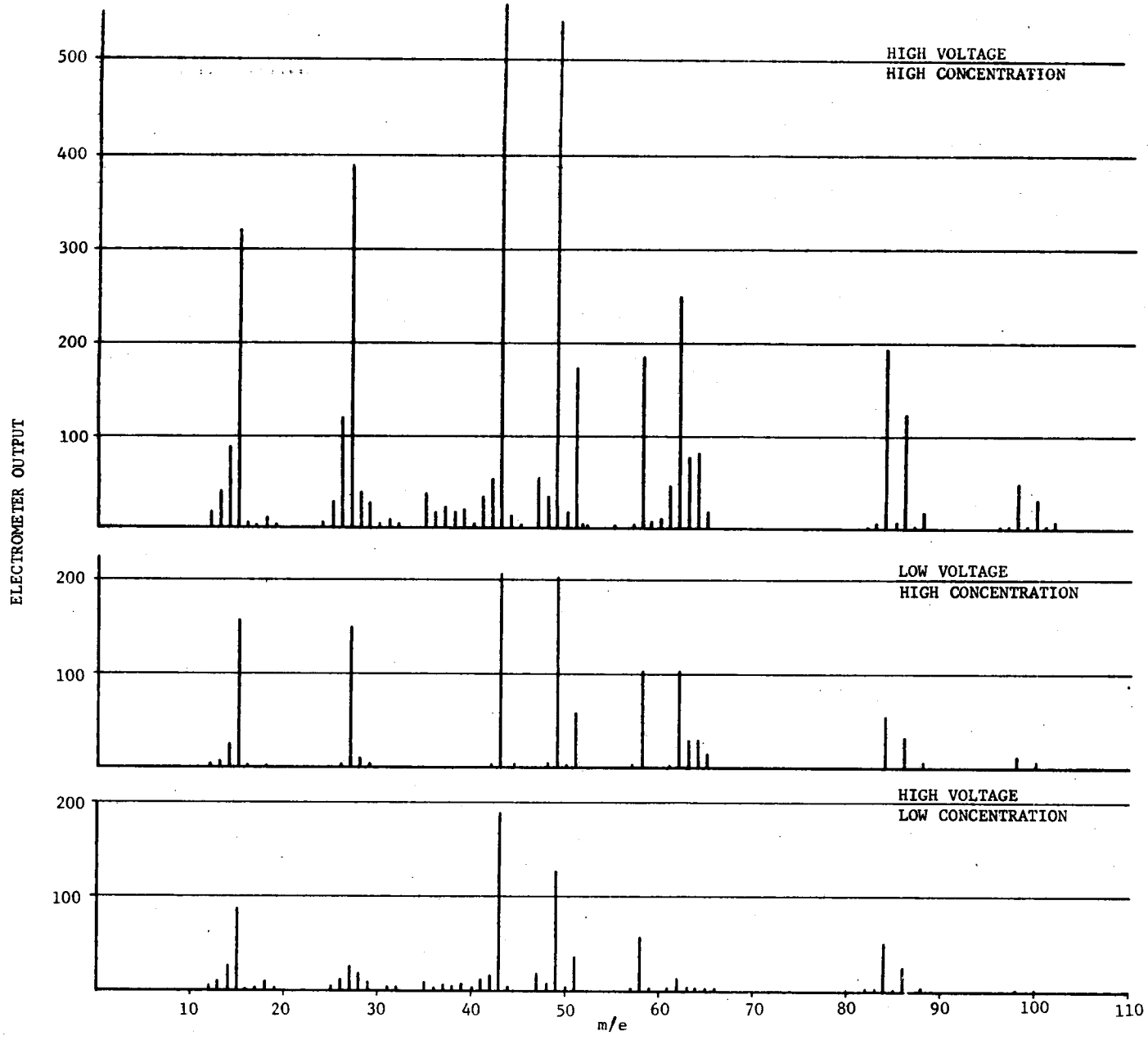


FIGURE 4-45

ACETONE, METHANOL METHYLENE CHLORIDE AND ETHYLENE DICHLORIDE

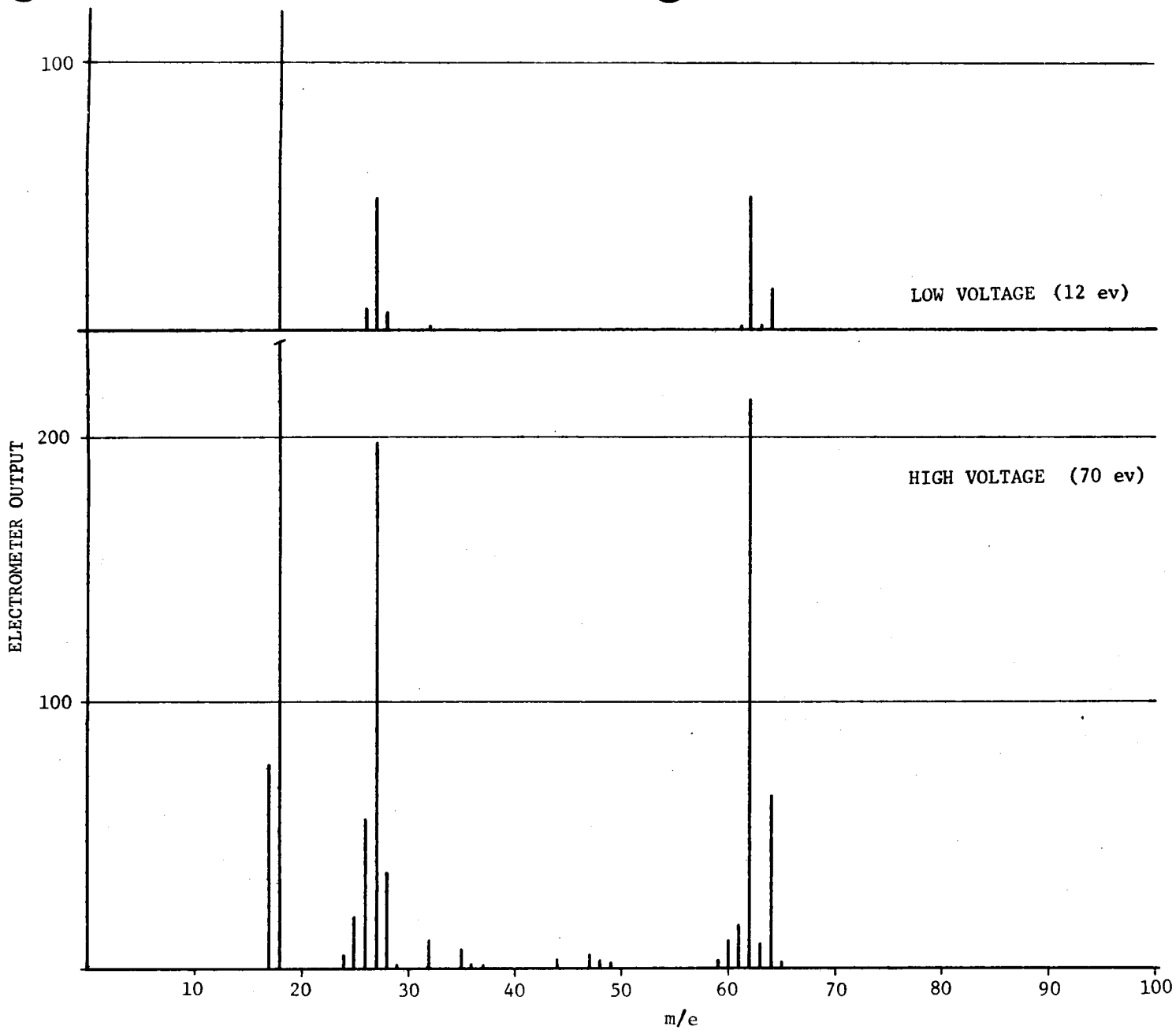


FIGURE 4-46A
VINYL CHLORIDE FREON-11 MIXTURE

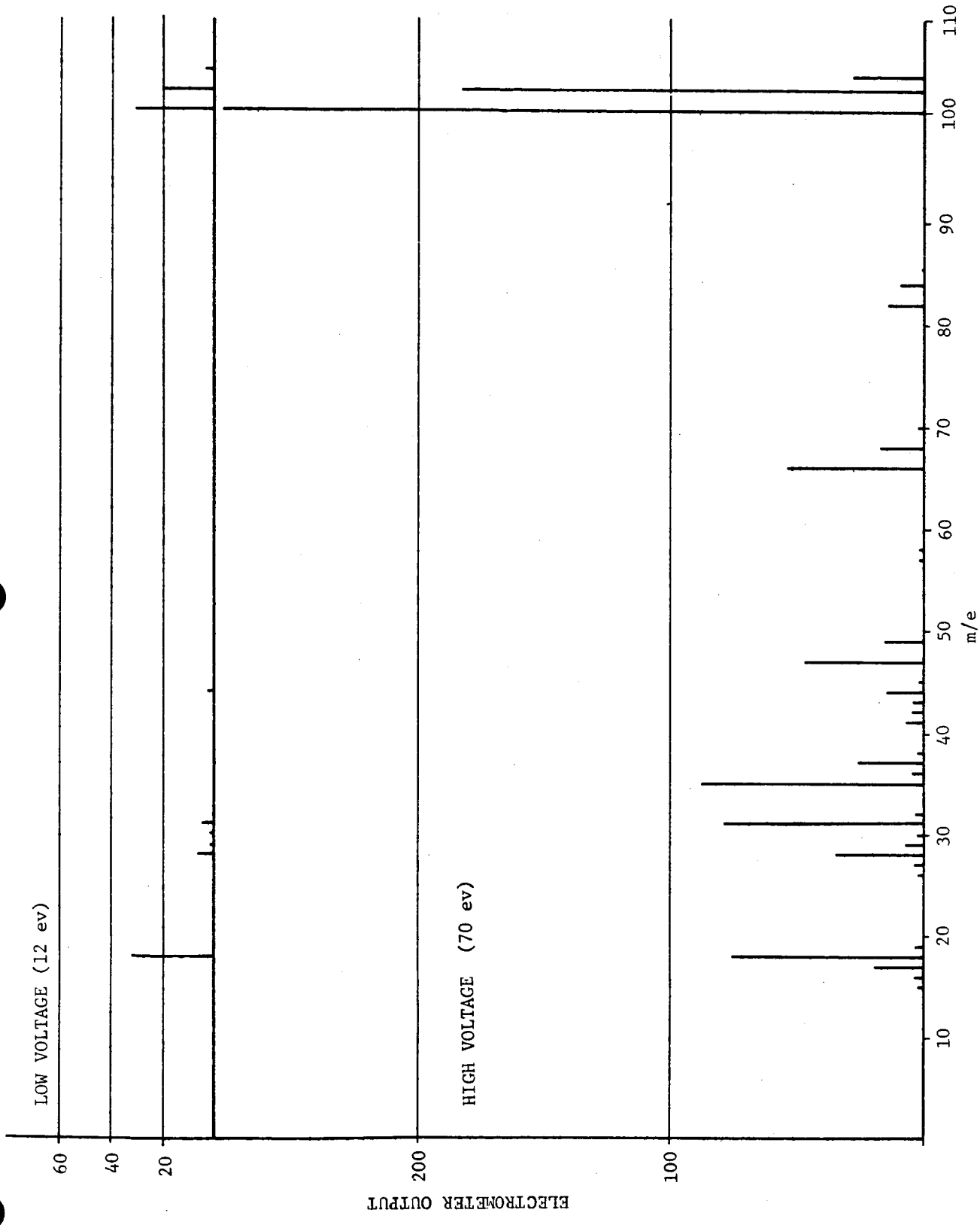


FIGURE 4-46B
VINYL CHLORIDE AND FREON-11 MIXTURE

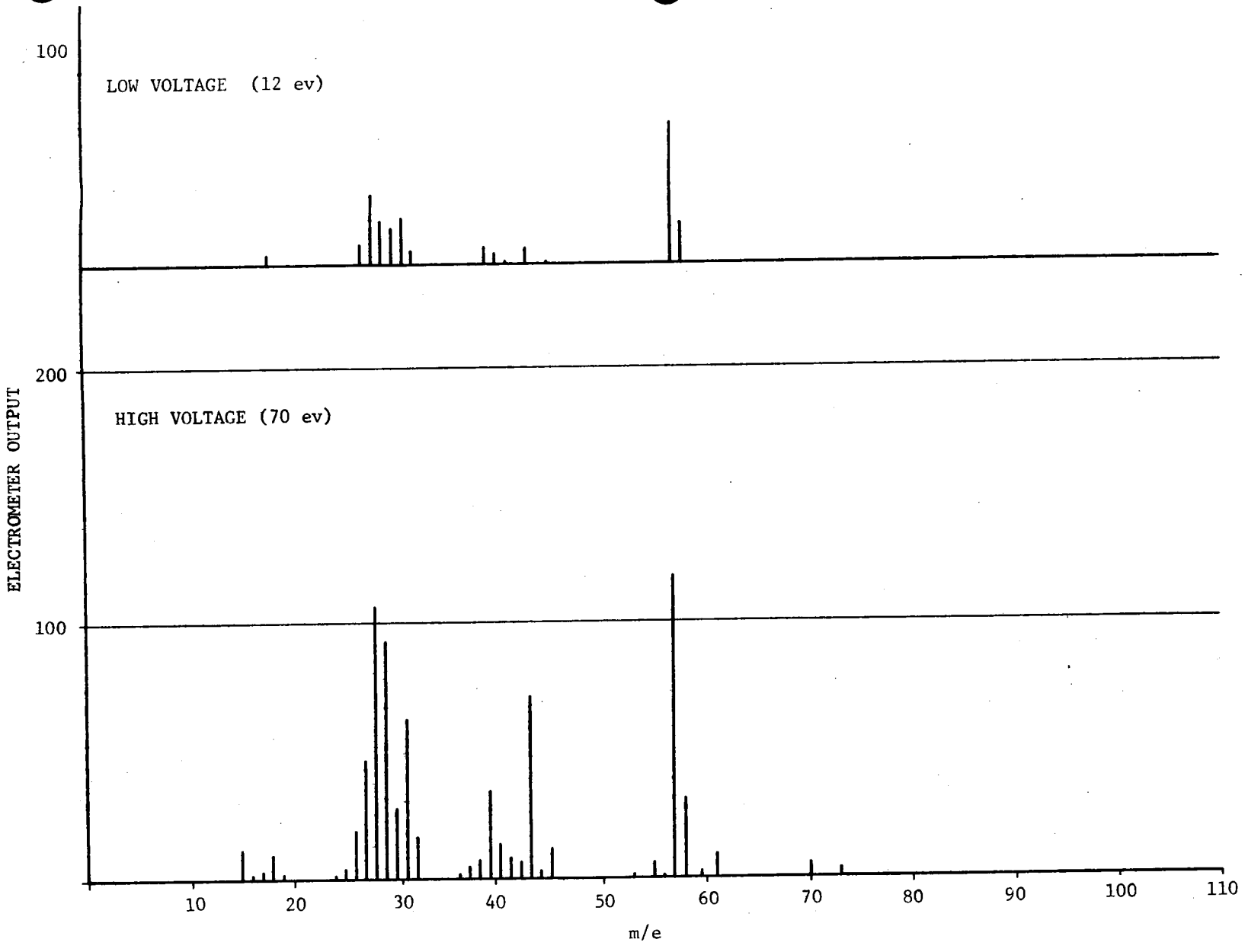


FIGURE 4-47A

MIXTURE OF ALLYL ALCOHOL AND ETHYL ACETATE

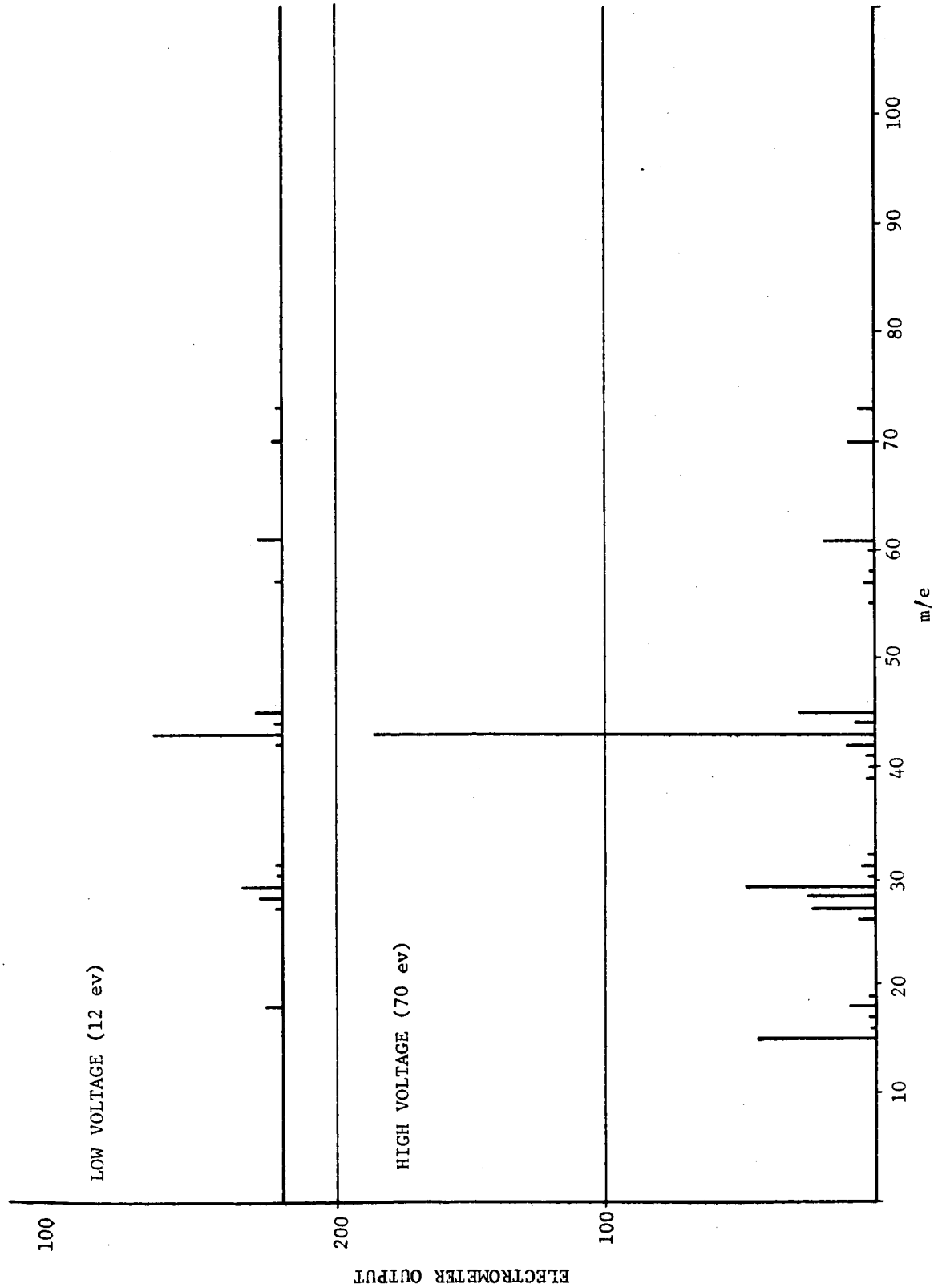


FIGURE 4-47B

MIXTURE OF ALLYL ALCOHOL AND ETHYL ACETATE

5. DISCUSSION OF RESULTS

There are two requirements to be considered in evaluating the performance of the Laboratory Contaminant Sensor; these are the capability for identification of contaminants and the capability for detecting contaminants at low concentrations. The results of the experimental program with respect to these factors is considered in a general way in the following sections.

5.1 IDENTIFICATION OF CONTAMINANTS

The capability of the Laboratory Contaminant Sensor for identifying the test contaminants has been satisfactorily demonstrated. The selectivity afforded by the sorption-desorption process overcomes the main limitation of the mass spectrometer for identification of contaminants - that of detecting a small amount of one compound in a mixture containing large amounts of other components with the same mass numbers.

The uniqueness of the mass spectra as a means of identification of compounds is well established. The use of mass spectrometry for the analysis of mixtures is also routine in cases where the general composition of the mixture is known and only the relative proportions of the various components are required. Problems arise in the analysis of unknown mixtures, not with the analysis of the major components which can usually be identified and determined if accurate calibration data are available, but with the detection of the presence of small amounts of other contaminants. This difficulty is compounded when the contaminants are present at low concentrations in air, so that the major portion of the sample entering the ion source for analysis is air and not those compounds which are of interest.

The Laboratory Contaminant Sensor overcomes these difficulties in two ways. First, the contaminants are concentrated by sorption and by precutting air from the accumulator cell. This results in a concentrated sample of contaminants for analysis. Secondly, by use of multiple sorbents and programmed temperature desorption, this mixture of contaminants is partially separated so that the probability of two contaminants with similar mass spectra appearing in the mass spectrometer for analysis at the same time is greatly reduced. The effectiveness of this technique is shown by the results presented in this report. These results are summarized in Figures 5-1 and 5-2 which show the temperature at the peak of the desorption curve for the test contaminants on charcoal and Porapak Q, and the major mass numbers associated with the contaminants. (In inspecting these figures, it should be remembered that the desorption curve extends over an approximately 80°C range, centered around the peak.) These figures show that the separation achieved is sufficient and that no difficulty is anticipated in identifying any of the test contaminants.

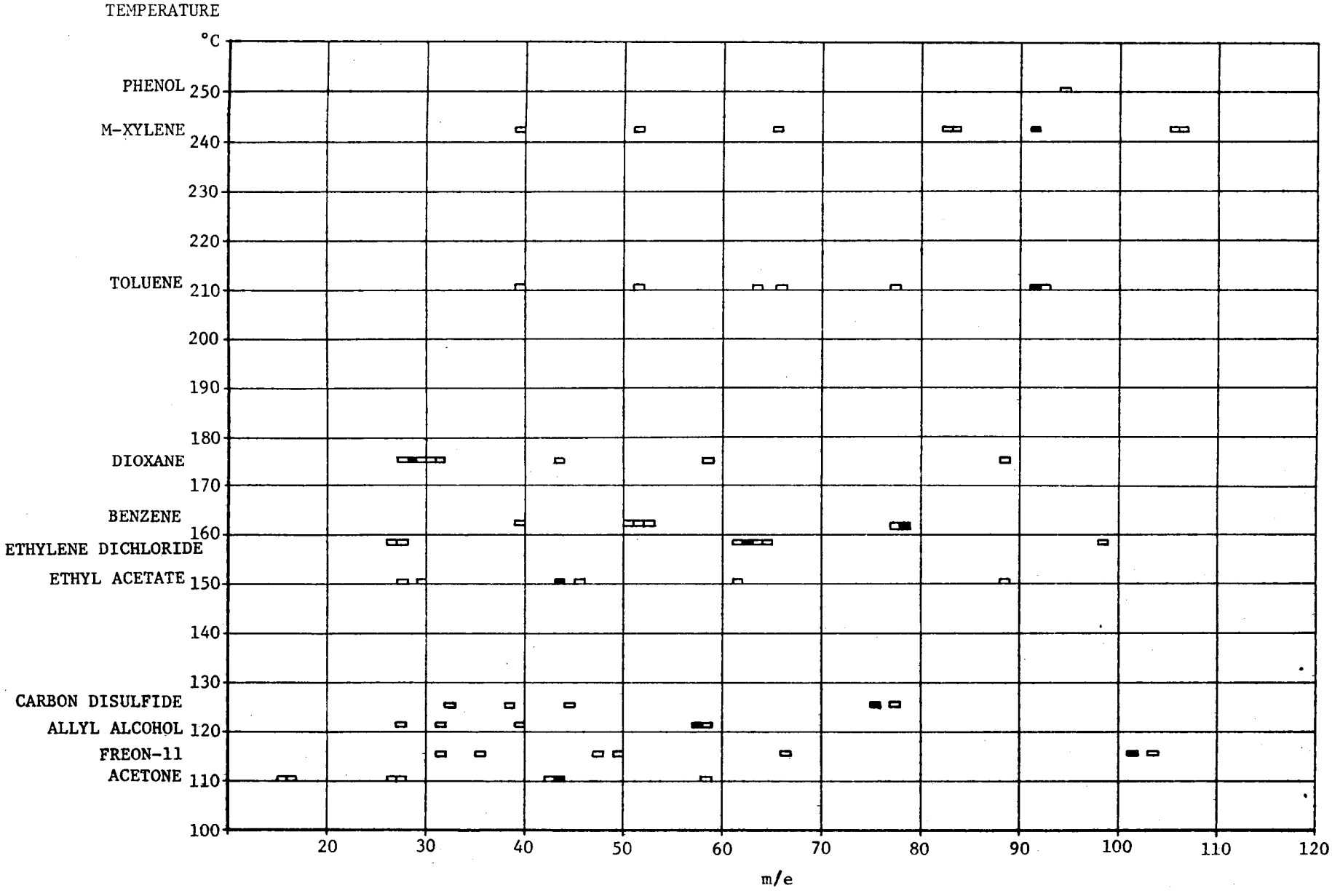


FIGURE 5-1
PORAPAK Q

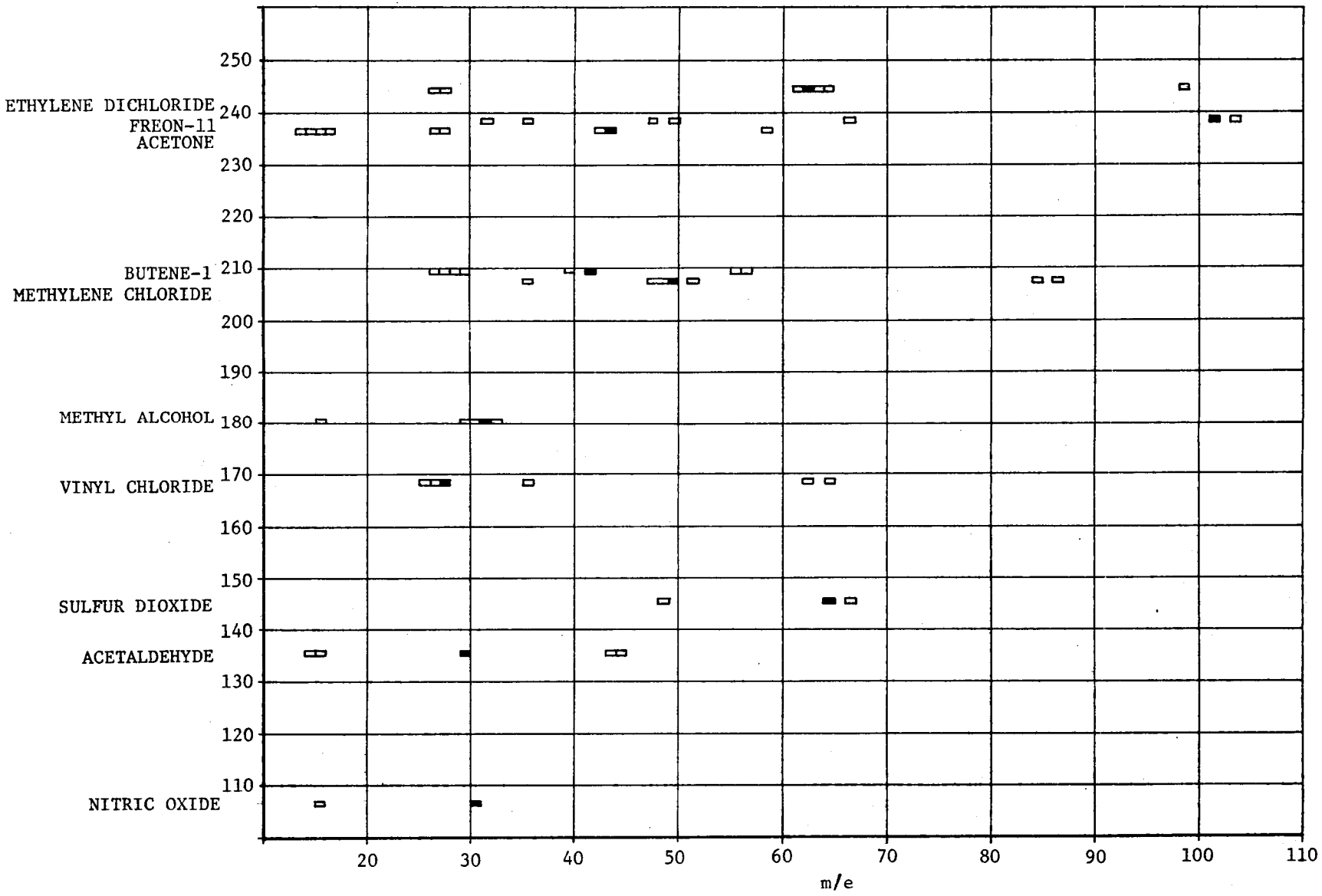


FIGURE 5-2
CHARCOAL (MI-1)

For example, if the desorption curve shown in Figure 4-29 was obtained by analysis of an unknown, reference to Figure 5-1 would indicate that the compound giving rise to m/e 57, 58 and 31 is allyl alcohol; in a similar manner, ethyl acetate could be identified. The desorption curves for m/e 27 and 29 suggest that there is a third component in the mixture, but this possibility is eliminated by refering to the mass spectra of allyl alcohol and ethyl acetate. From these spectra, it can be shown by calculation that the curves for m/e 27 and 29 represent the sum of contributions from allyl alcohol and ethyl acetate at each temperature. By this type of analysis, it should be possible to account for the intensity of each mass number at each temperature. (Not all the mass numbers are shown in Figure 4-29 for simplicity.) The mass spectra of the pure compounds in the particular instrument used must be known for this type of analysis.

The advantage of using more than one sorbent is illustrated by the analysis of mixture #8 on Porapak Q and charcoal. (Figures 4-26 and 4-27.) On Porapak Q the desorption curve of mass number 49 (CH_2Cl) overlaps both mass numbers 84 and 62, and by calculation, it could be shown that the intensity of mass number 49 is derived from two compounds. On charcoal, the relation of 49 to 84 is clearly seen because desorption of ethylene dichloride as indicated by mass number 62 is only starting at the end of the desorption run.

From the preceding discussion, it can be seen that identification of contaminants is accomplished through use of the mass spectra and a reference chart for desorption temperature. The instrument must be calibrated to obtain data for both references. Even with extensive calibration, it must be expected that previously unanalyzed compounds will be encountered. These should be detected either directly from the mass spectra obtained during desorption or from residuals at mass numbers associated with known compounds when the whole desorption curve and associated spectra are analyzed.

The desorption temperature and the sorbent on which the compound is detected can be of some use in choosing among possible identifications. If the contaminants tested in this program are arranged in the order of their desorption temperatures from charcoal and Porapak Q, there appears to be a rough correlation with boiling point. This is illustrated in Table 5-1. The compounds which are gases at room temperature are more strongly sorbed on charcoal than would be expected from their boiling point; the oxygenated organics, acetaldehyde, methyl alcohol and acetone desorb in the predicted order. The desorption temperature of water on charcoal is also lower than predicted on the basis of boiling point. The only irregularities on Porapak Q are the rather low desorption temperature for allyl alcohol and a high desorption temperature for Freon-11. Actually allyl alcohol is in line with methanol which desorbs at temperatures below 100°C from Porapak Q, and water which is not retained on Porapak Q.

As more data on other compounds is obtained it should be possible to establish relations among types of chemical compounds. This information, in conjunction with the mass spectra information, should prove most useful in identifying unknown contaminants.

Another feature of the Laboratory Contaminant Sensor that has potential application to the problem of contaminant identification is the availability of ionization by low voltage electrons. Limited data on this mode of operation is presented in

TABLE 5-1
Contaminants in Order of Desorption Temperature

SORBENT	CONTAMINANT	DESORPTION TEMPERATURE (°C)	BOILING POINT (°C)
CHARCOAL	Nitric oxide	106	-151.8
	Water	130	100
	Acetaldehyde	135	20.8
	Sulfur dioxide	145	-10
	Vinyl chloride	165	-13.9
	Methyl alcohol	180	65
	Butene-1	209	-6.3
	Methylene chloride	210	40
	Acetone	>230	56
PORAPAK Q	Acetone	110	56
	Carbon disulfide	113	45
	Allyl alcohol	115	97
	Freon-11	~115	25
	Benzene	146	80.1
	Ethylacetate	150	77
	Ethylene dichloride	158	84
	Dioxane	171	101
	Toluene	201	110.6
	Xylene	>240	139
	Phenol	>240	182

Section 4 of this report. Mass spectra resulting from this mode of operation are considerably simplified, i.e., the number of fragmentation peaks is reduced. With fewer peaks coming from each contaminant, the probability of one contaminant masking another should be reduced. At present the loss in sensitivity resulting from the use of low voltage electrons is a limitation of its use. However, it is possible to increase the sensitivity of the electrometer amplifier of the mass spectrometer and, under these conditions, this limitation may be largely eliminated. Considerable calibration data would be required to exploit the potential of low voltage ionization, but this could prove rewarding in development of the ultimate identification capability of the Laboratory Contaminant Sensor.

5.2 QUANTITATIVE DETERMINATION

The characteristics which describe an instrument's capability for quantitative determination are sensitivity, precision, and accuracy. Freedom from interference by other components of the mixture is also an important consideration. The measure of quantitative response used in the experimental work was the electrometer output (in divisions) at the maximum of the desorption curve measured for a selected contaminant. There appears to be no advantage in using peak area measurements based on the width of the peak at one-half the maximum peak height.

The precision of this measurement is indicated by the difference between the experimentally measured output and that predicated from the line relating output to amount sorbed or concentration. These data are shown in Figure 4-5 through 4-25. For most of the data, the precision appears to be within that measured for the gas proportioner unit. A statistical analysis of the data was not carried out for most of the contaminants because of the limited data for the individual contaminants. For Freon-11, statistical analysis yields a standard deviation of two percent for the slope of the line relating output to amount sorbed. This corresponds to a precision of 10 percent at the 15 ppm level.

The accuracy and sensitivity for the individual contaminants depends on the accuracy of the vendor's analysis and the ability to obtain a representative sample of the contaminant air mixture from the cylinder. The generally good precision obtained in measuring output versus concentration, indicates that samples taken at reasonably close time intervals have the same composition. However, there is a considerable time lapse and much cylinder handling occurs between the time of the vendor's analysis and sampling in our laboratory. This is probably partially responsible for the discrepancy between the analysis performed at Perkin-Elmer Aerospace Systems and that supplied by the vendor. Other sources of error in our analysis are the use of sensitivity data and mass spectral data from the literature rather than actual calibration data which is unavailable. For these reasons, the sensitivity values quoted are based on the vendor's analyses in most cases. At present, the best estimate for accuracy is based on the comparison of our analysis with the vendor's and on one comparison of two mixtures containing the same contaminant from the vendor. This estimated accuracy is $\pm$30%.

The problem of obtaining accurately analyzed samples of trace contaminants for calibration is common to any instrument or technique used for this purpose. For relatively concentrated mixture (>100 ppm) the mass spectrometer can be used for

analysis of single contaminant air mixtures or for multiple contaminant air mixtures as long as the contaminants are chosen to avoid interferences. However, for accurate analysis the mass spectrum and the sensitivity for the contaminant must be determined by calibration with the pure contaminant. If the analysis of contaminant mixtures were performed at nearly the same time that the sorption experiments were carried out, a better estimate of the accuracy of the Laboratory Contaminant Sensor could be obtained.

The sensitivity of the Laboratory Contaminant Sensor for the test contaminants is reported in terms of divisions (at the desorption curve maximum) per microliter (STP) of contaminant sorbed. Values ranging from 0.7 to 17 divisions/$\mu\ell$ are observed. These sensitivities may be related to the concentration of contaminant by multiplying by the sample volume, which was three liters for the quantitative measurements. Thus, the sensitivities on a concentration basis range from 2.1 to 51 divisions/ppm. Assuming a ten division signal can be detected, the detectable limits range from 5 to 0.5 ppm. However, in some cases, notably the halogenated organics, the detectable limit is set by fixed losses of the contaminant in the system.

These limits are actually conservative estimates; the full capability of the mass spectrometer was not used in determining sensitivity. The ionizing electron current can be increased by a factor of two to three without increasing the noise level so that lower concentrations can be determined. The ten division signal selected is about ten times the noise level in the instrument. It was chosen because, for some contaminants, it might be necessary to detect a fragment ion, at ten percent intensity for identification. For a number of contaminants this is not a requirement. However, since there are some fixed losses in the system, there appeared to be no advantage to trying to increase the sensitivity until the cause of these losses is established and corrected. These effects were discussed for the individual contaminants in Section 4. A summary of these results is presented in Table 5-2.

The factors which affect the sensitivity value for the different contaminants merit some discussion. One of the most important of these is the inherent sensitivity of the mass spectrometer for the compounds; sensitivity values vary over a ten-fold range. These sensitivities are dependent on the chemical nature of the compound and on ion source conditions in the individual mass spectrometer. All other factors being equal, it would be expected that sensitivities determined for the Laboratory Contaminant Sensor would parallel those of the mass spectrometer. However, other factors such as those involved in determining the peak shape are also important in determining the sensitivity. The peak height, that is, the signal at the maximum of the desorption curve, is used as the measure of sensitivity. This gives reasonably consistent results for determination of different amounts of the individual contaminants. Comparisons between different contaminants will be affected by the peak shape. The factors which determine the peak shape are the heat of desorption and the pumping speed through the micrometer valve. At constant pumping speed, contaminants with large heats of desorption exhibit sharply rising desorption curves, while those with lower heats of desorption show a more gradual increase in pressure with temperature. The peak height is expected to be relatively higher for compounds with large heats of desorption.

TABLE 5-2

CONTAMINANT	SORBENT	PEAK TEMP. (°C)	m/e	LITERATURE	LABORATORY CONTAMINANT SENSOR	SENSITIVITY AT PEAK (DIVISION/μℓ)
Acetone	Charcoal or	230	43	100	100	4.8 (charcoal)
	Porapak Q	110	58	27.1	28.4	5.8 (Porapak)
Acetaldehyde	Charcoal	135	29	100	100	2.8
			44	45	54	1.6
			43	26	30	1.0
Allyl alcohol	Porapak Q	115	57	100	100	1.6
			31	32.4	62	1.0
			39	23	30	
Ammonia			17	100		
			16	80		
Benzene	Porapak Q	146	78	100		17.9 (12.7)*
			51	21		
			39	14		
Butene-1	Charcoal	209	41	100		5.6
			56	37.1		2.04
Carbon dioxide	Molecular Sieve 5A	140	44	100	100	
	Charcoal	>230	28	11		
Carbon disulfide	Porapak Q	113	76	100	100	10.6
			78	8.9	8.7	
			38	6.5	11.6	
			32	20.4	13.3	
Carbon monoxide	Palladium-charcoal	190	28	100	100	1.45
1,4 Dioxane	Porapak Q	171	28	100	100	16.2 (9.2)
			58	24	20	(2.2)
			88	31.5	24	3.46 (2.1)

TABLE 5-2 (Continued)

CONTAMINANT	SORBENT	PEAK TEMP. (°C)	m/e	LITERATURE	LABORATORY CONTAMINANT SENSOR	SENSITIVITY AT PEAK (DIVISION/μℓ)
Ethyl acetate	Porapak Q	150	43	100	100	6
			61	10.9	11.8	0.7
			88	3.9		
			45	13.6	13.7	
Ethylene dichloride	Porapak Q	158	62	100	50	1.38, 1.23
			98	13.7	9.0	
			27	91	100	
Formaldehyde						
Freon-11	Charcoal	>230	101			2.6
Hydrogen chloride						
Hydrogen sulfide						
Methane						
Methyl alcohol	Charcoal	180	31	100	100	2.3
			32	67		
			15	36		
Methylene chloride	Charcoal	207	49	100	100	3.7
			84	78.4	45	1.6
Nitric Oxide	Charcoal	106	30	100		2.4
Nitrous Oxide	Molecular Sieve 5A	132	44	100		.66
			30	40		
			28	15.81		
Phenol	Porapak Q	>230				

TABLE 5-2 (Continued)

CONTAMINANT	SORBENT	PEAK TEMP. (°C)	m/e	LITERATURE	LABORATORY CONTAMINANT SENSOR	SENSITIVITY AT PEAK (DIVISION/$\mu\ell$)
Sulfur dioxide	Charcoal	145	64	100	100	2.8
			48	49.5	44.8	
Toluene	Porapak Q	201	91	100		11.6 (7.3)
			92	77		
			65	12.5		
			39	18		
Vinyl chloride	Charcoal	165	27	100	100	3.8
			62	76.2	93	3.5
m-Xylene	Porapak Q	240	106			

* Values in parenthesis are based on analysis of the mixture by Aerospace Systems.

For viscous flow through the metering valve, the pumping speed varies inversely with the gas phase viscosity of the contaminants. The peak shape will tend to be high and narrow for compounds with large heats of desorption and low gas phase viscosity. For molecular flow out of the metering valve, the peak shape will depend on the molecular weight of the compounds. By use of the equation derived in Section 2 of this report, it should be possible to predict the relative sensitivity of the Laboratory Contaminant Sensor for various compounds if accurate data for the mass spectrometer sensitivity, the heat of desorption, and the gas phase viscosity are available.

The use of teflon coating appears questionable since a number of compounds are apparently irreversibly sorbed to a small extent in the system. This irreversible sorption is probably due to absorption or solution of these compounds in the surface coating. On the other hand, if metallic surfaces are employed it is expected that certain contaminants will react irreversibly with the surface. The solution to this problem must lie in minimizing the surface area and choosing a surface which is unreactive to the largest number of contaminant types.

The effect of water on determination of the contaminants was investigated to a limited extent. From the available data, it appears that there is no significant effect on either the desorption temperature or the quantative determination of the contaminants tested. A thorough study of the effect of water might be carried out for one or two selected compounds to confirm this observations, and possible interactions must always be considered for any contaminant. Water interferes with the determination of ammonia because of coincidence of the mass ratios m/e 17 and m/e 16. No separation of these two compounds was achieved for any of the sorbents tested and it appears that it may be necessary to seek a specific sorbent for this process.

6. CONCLUSIONS AND RECOMMENDATIONS

The concept of a Laboratory Contaminant Sensor based on extraction and desorption of contaminants and analysis by mass spectrometry has been tested and shows good capability for identification and quantitative determination of contaminants. Identification of contaminants is based on mass spectra obtained as a function of temperature, and the peak desorption temperature. Detection limits based on sensitivity are conservatively set at 0.5 to 5 ppm for individual contaminants; in some cases, fixed losses in the system limit detectability to slightly higher values.

The results of this development program have demonstrated the potential of this system for contaminant analysis. One limitation on the test results is the uncertainty about the accuracy of the method. This uncertainty can be eliminated by calibration of the mass spectrometer with pure compounds and analysis of the contaminant test gas mixtures. Some modifications to the inlet system are required for this purpose and should be considered in future development programs.

Future development efforts should be directed toward increasing the number of contaminants tested and increasing the sensitivity of detection. Modifications to the electrometer amplifier can be made which will produce a ten-fold increase in the sensitivity for detection by the mass spectrometer. With these modifications the analytical technique should be re-evaluated to establish the factors which limit the sensitivity of the method. Tests with additional contaminants will serve to improve the evaluation of the capability of this technique for identification of contaminants. In this regard, also, the use of low ionization voltage should be investigated more extensively. As a starting point, the low voltage spectra of the contaminants tested in this program could be determined for the pure compounds with the modifications to the inlet system suggested above.

The formulation of the sorbent system and analytical technique to be used for analysis of unknown samples should be established and tested under the expected operating conditions. A limited effort was made toward this on the present program, but this should be expanded and revised as new information becomes available. Since the amount of data produced in routine operation is enormous, some thought should be given to the use of automated data reduction methods and computerized data interpretation.

Finally, an optimized analytical technique should be selected on the basis of the results of the program outlined above, and the necessary instrumentation designed to meet the constraints of space flight hardware.

APPENDIX A

Test Data on Matheson Gas Proportioner Model 665

Series 1 Tests - Glass wool in mixing tube, capillary inlet system. Oxygen was used with the R600 flowmeter; Nitrogen in R602. Sensitivity of mass spectrometer, pure N_2 5500 divisions; pure oxygen 4210 divisions.

FLOW RATE (ml/min)		PEAK HEIGHT (DIVISION)		COMPOSITION			
				CALCULATED FROM FLOW RATE		CALCULATED FROM MASS SPECTROMETER RESPONSE	
Oxygen R600	Nitrogen R602	m/e 32	m/e 28	O_2	N_2	O_2	N_2
7.2	404	80.4	6060	0.0175	0.982	0.0172	0.984
46.8	24	3180	2010	0.661	0.339	0.681	0.314
22.4	146	639	5220	0.133	0.867	0.137	0.845
16.8	838	95.1	5980	0.0198	0.988	0.0204	0.969
135.2	79.9	2950	2260	0.629	0.371	0.632	0.355
53.2	416	535	5350	0.1135	0.888	0.1143	0.867
7.6	856.8	37.8	6070	0.0088	0.993	0.0075	0.992
13.4	540	94.8	5370	0.0243	0.976	0.0225	0.978
27.2	540	218	5290	0.0479	0.952	0.0510	0.948
12.4	540	84.6	5400	0.0225	0.978	0.0200	0.979
32.8	540	246	5210	0.0573	0.943	0.0582	0.942
77.2	540	554	4750	0.125	0.875	0.130	0.870
77.2	202	1188	3950	0.277	0.724	0.282	0.718
77.2	32	3050	1635	0.706	0.294	0.710	0.290
77.2	212	1170	3960	0.267	0.734	0.278	0.720
77.2	64	2300	2500	0.546	0.453	0.546	0.455
77.2	10	3800	654	0.895	0.115	0.884	0.175

Series 2 Tests - Teflon in mixing tube, LCS inlet system.
Sensitivity: Nitrogen 6100 divisions/300μ; oxygen 4630 divisions/300μ.

FLOW RATE (ml/min)		PEAK HEIGHT (DIVISION)		COMPOSITION			
				CALCULATED FROM FLOW RATE		CALCULATED FROM MASS SPECTROMETER RESPONSE	
Oxygen R600	Nitrogen R602	m/e 32	m/e 28	O_2	N_2	O_2	N_2
139.2	850	756	5860	0.141	0.86	0.142	0.86
12.8	54	710	4300	0.192	0.81	0.174	0.827
133.6	54	3000	1740	0.712	0.288	0.687	0.313
12.8	848	65	6000	0.0149	0.985	0.0135	0.986
25.6	184	560	5200	0.122	0.878	0.121	0.881

NASA CR-66606-A

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LABORATORY CONTAMINANT SENSOR
FINAL REPORT
CR-66606
ADDENDUM

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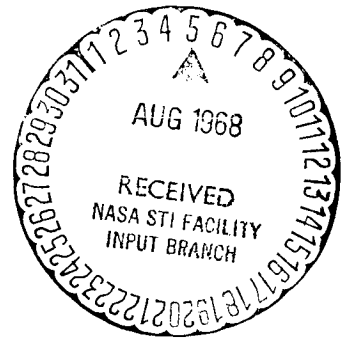
Hampton, Virginia



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PREFACE

This report is an addendum to the Laboratory Contaminant Sensor Final Report NASA CR-66606. It contains data on the sensitivity and mass spectra for the compounds tested as contaminants in the development of the Laboratory Contaminant Sensor. These data were obtained with the mass spectrometer used in the Laboratory Contaminant Sensor, hereinafter referred to as the sensor.

SUMMARY

Data are presented for the mass spectra and sensitivity of twenty-three compounds tested as contaminants in the development of the sensor. (See Final Report NASA CR-66606.) These data were obtained with the mass spectrometer used in that program at two energies of ionizing electrons, 70 and 12 eV.

1. INTRODUCTION

In the development of the sensor, mass spectral analysis was used to determine the identity and the amounts of contaminants extracted from air samples as they were desorbed from an accumulator cell. The sensitivity of this instrument was determined from mass spectrometer response at the peak of the desoprtion curve for known amounts of contaminants. Analyzed gas mixtures containing contaminants at low concentrations in air were purchased for this purpose. The sensitivities presented in the final report were based on the vendor's analysis of the test gas mixtures. These sensitivities relate to the overall process - sorption, desorption and mass spectral analysis. It was recognized that the results of the desorption experiments would be more meaningful, if the sensitivity of the mass spectrometer to the pure compounds was known. With this information, the pressure developed in the inlet system during desorption of contaminants could be calculated. Knowledge of the sensitivity is also a requirement for material balance calculations and for analysis of test gas mixtures. Therefore, the original effort was extended to include determination of the spectra and sensitivity of mass spectrometer to the pure contaminants.

Modifications to the inlet system, to permit samples of pure materials to be introduced at known pressures, are described in the following section of the report. Results of the determinations are presented in Section 3.

2. INLET SYSTEM

Modifications to the inlet system consisted of the addition of a closed arm manometer, a small sample volume in which gas samples at known pressure could be isolated for introduction to the inlet system, a large expansion volume in the inlet to provide the pressure reduction required, and the associated valves and tubing. The modified inlet system is shown schematically in Figure 2-1.

Samples for analysis were introduced from a cylindrical container made of stainless steel which has a volume of approximately 74 ml. It is equipped with two Whitey valves. A quick disconnect fitting is used to attach the sample container to the tube leading to the manometer and the small sample volume. The closed arm manometer has a pressure range of 100 mm; it is connected to the system through a standard taper joint which is sealed with Apiezon W wax. The small sample volume, $\approx$11 ml, is made of 3/8 inch stainless tubing (0.035 inch wall) and is closed with Nupro bellow valves. The large expansion volume is a stainless steel cylinder with a volume of 2250 ml; it is also equipped with a Nupro bellow valve. All connections in the system are made with 3/8 inch stainless steel tubing and Swagelok fittings. An additional valved sample port was provided for the introduction of measured amounts of liquid or solid samples through a rubber septum directly into the expansion volume. However, this port was not used since it proved more convenient to use the sample container and measure the pressure of these samples directly, as described subsequently.

The following procedures were used to obtain samples of gases at known pressures in the inlet system. The sample container was filled with the test gas from a pressurized cylinder. The container was valved off and attached to the inlet system with the quick disconnect fitting. The entire system up to the sample container was evacuated and the exit valve of the sample volume was closed, and the sample container valve was opened slowly to allow the sample gas to enter the sample volume at a pressure measured on the closed arm manometer. The sample volume was isolated by closing the valve connecting it to the line with the manometer and the sample volume. The inlet system was valved off from the vacuum pump by closing valve E. (See Figure 2-1.) Valve C was closed, isolating the gold leak, and the exit valve of the sample volume was opened allowing the sample to expand into the inlet system. Valve C was opened to allow the sample to enter the mass spectrometer ion source.

In order to introduce liquid samples to the sensor, a silicone rubber septum was attached to the sample container with a Swagelok fitting. The sample container which was attached to the inlet system was evacuated up to the rubber septum. The sample container was valved off from the vacuum system by closing valve F, and a few microliters of the test liquid were injected into the container from a syringe. Valve G on the container was closed, and the sample

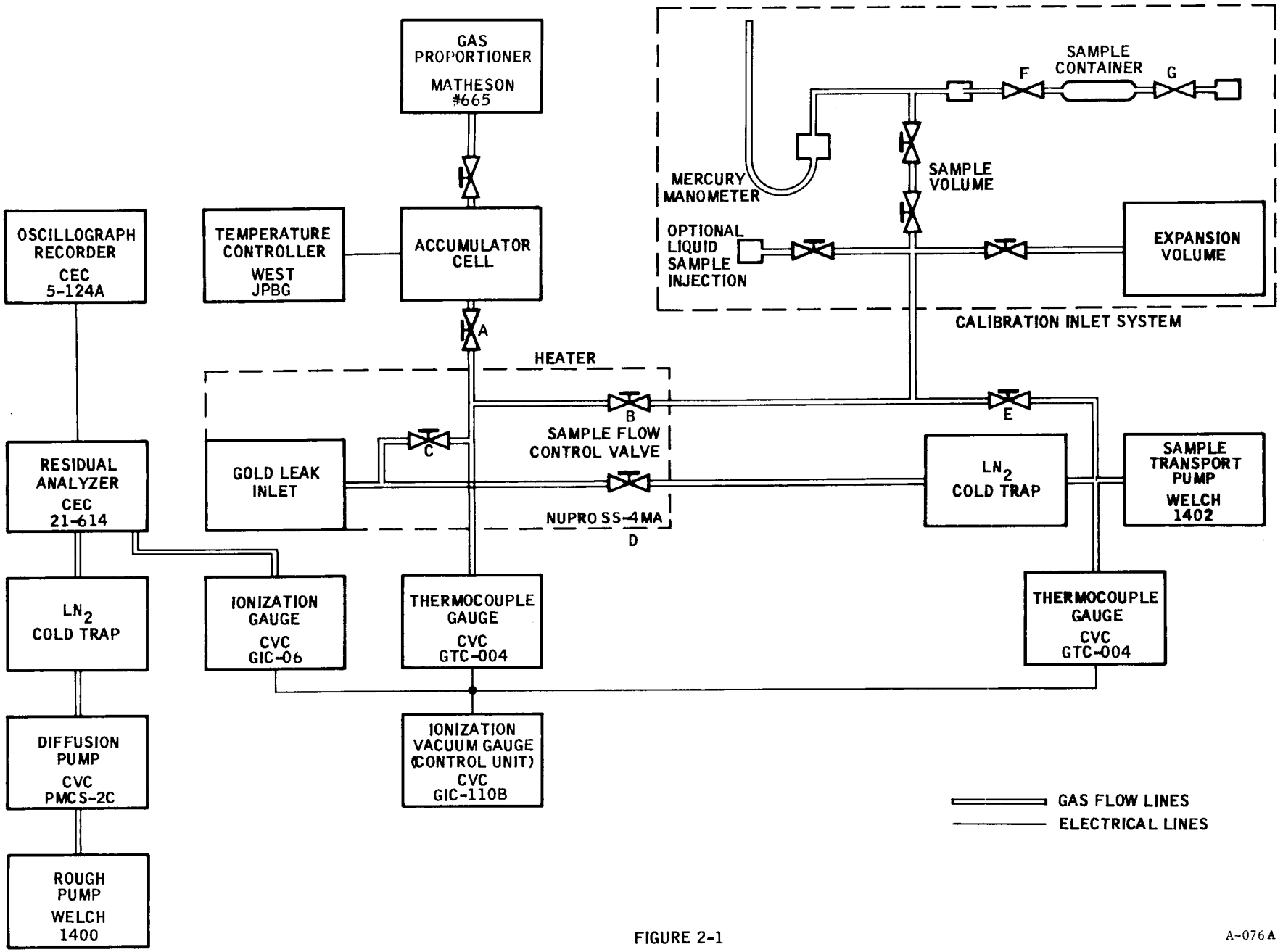

FIGURE 2-1

A-076A

Laboratory Contaminant Sensor Schematic Diagram

was introduced into the inlet system in the manner described for gas samples. The liquid samples tested are volatile enough at room temperature to permit their pressure to be measured on the manometer. The amount of sample introduced into the sample volume could be controlled either at the sample container valve or by the amount of liquid injected. This procedure worked satisfactorily for all the materials tested except phenol which has a vapor pressure at room temperature too low to be measured on the manometer.

The pressure in the inlet system was determined from the pressure measured on the manometer and the ratio of the sample volume to the inlet system volume. This ratio was determined to be 4.4×10^{-3} by calibration. The volume of the sample loop was determined by calibration with water; the dead volume of the values was obtained from vendor's literature. The volume of the inlet system was determined by calibrating the expansion volume with water and estimating the volume of the associated tubing from length and diameter measurements.

Background spectra of the inlet system were recorded immediately before the sample was introduced. Mass spectra were recorded at 70 and 12 eV ionization energy at an electron current of 30μA. Scan speed 3 and the low sensitivity mode of operation were employed. These conditions are identical to those used in the Laboratory Contaminant Sensor Development program.

3. RESULTS

The mass spectral patterns for the contaminants are shown in Tables 3-1 through 3-25 for 70 and 12 eV ionization voltages. The sensitivities relative to nitrogen in air are also shown in the tables. Nitrogen in air is used as a reference rather than pure nitrogen or n-butane because data on the sensitivity to nitrogen in air are available for the time period during which the contaminant studies were performed.

The mass spectral patterns were corrected for air in the sample from the oxygen mass 32 peak for those compounds for which mass 32 is not a part of the sample spectrum. For some compounds, the correction was based on the mass 28 nitrogen peak. The air correction was equivalent to about one torr of air in the worst case. Sensitivity values for the mass spectrometer were obtained by measuring the output of the major peak at three or four different pressures. The pressure readings were corrected for air and the sensitivity values were obtained from the slope of the line relating output to pressure. For gas sample, pressures in the range from 5 to 40 torr were used in the sample volume. For liquids, the pressure range was usually from 3 to 20 torr; for xylene; which has a relatively low volatility, the pressure range was from one to four torr.

The sensitivity to nitrogen in air was based on measurements at eight different inlet pressures performed on one day. A sensitivity of 47 divisions/micron was measured; this sensitivity was independent of inlet system pressure up to about 150 microns. The standard deviation of the daily monitoring of the response to nitrogen in air indicated a variation of approximately two percent during the period in which most the samples were run. Spectra for benzene, vinyl chloride, nitrous oxide and butene-1 were determined at a period of lower instrument sensitivity and their relative sensitivity was derived from a comparison with the nitrogen (in air) sensitivity for that time period. The relative sensitivity values are believed to be accurate to about fifteen percent.

Two compounds exhibited somewhat unique behavior. The data for methanol indicated some holdup of methanol in the inlet system. The amount of the holdup was equivalent to one torr of methanol in the sample volume. This could be due to air in the sample since it is not possible to correct the spectra for air in this case. For m-xylene, the sensitivity appeared to increase with pressure; since only relatively small pressures of this compound were used, the observation could result from erroneous pressure measurements, but the data appear too regular to permit this explanation.

In determining the mass spectra of formaldehyde a solution of formaldehyde in water was used. The spectra and sensitivity data obtained had to be corrected for a large amount of water and a smaller amount of methanol, which results in a larger uncertainty in the sensitivity and mass spectral pattern of this compound. There appears to be a high molecular component in this mixture also.

The vapor pressure of phenol was too low to permit measurement of sample pressure with the manometer. The sensitivity to this compound was not determined.

The sensitivities of organic compounds relative to nitrogen measured with this mass spectrometer appear to be lower than values reported for American Petroleum Institute spectra. The chlorinated compounds are an exception. In order to establish whether the lower sensitivity is due to the fact that the inlet system was not heated, a temporary heater was wrapped on the large sample volume, the system was heated to 100°C, and the sensitivities were measured for methanol, acetone, benzene, toluene, and m-xylene. Within the accuracy of the sensitivity measurement, heating the inlet system appeared to make no difference. However, this is an area which could be further investigated. The lower relative sensitivities may be due to the use of a rhenium filament instead of a tungsten filament, conditioned with butane and to differences in conditions in the ion source.

Mass spectral patterns for 12 eV ionization potentials generally confirm the observations made in the final report. The patterns of the aromatics are most strikingly simplified; the oxygenated compounds still fragment appreciably at 12 eV. The sensitivities of organics relative to nitrogen in air is greater at 12 eV than 70 eV ionization potential; this is expected from the ionization potentials which are lower for organics than for nitrogen. The sensitivity to nitrogen in air is reduced by a factor of 6.3 at 12 eV; the sensitivities to organics is reduced but by a smaller factor depending on the compound.

The data presented in the final report were briefly reviewed with respect to the calibration results. The use of the sensitivities contained in this report to calculate the analysis of purchased contaminant mixtures generally results in higher values for the concentration than those reported in Table 3-1 of the Final Report, NASA CR-66606. If these higher values for concentration are used to estimate the sensitivity of the overall process, the sensitivity of the technique would appear to be lower than reported. A cursory inspection of the data indicates that the difference is less than a factor of two in most cases. Sensitivities to methanol, dioxane, toluene and m-xylene may be lower by larger factors. However, until the differences between the vendor's analysis and our data can be resolved, the sensitivities given in the final report should be regarded as the most representative values.

TABLE 3-1

Mass Spectral Pattern for Acetaldehyde

m/e	70 eV	12 eV
12	.028	.006
13	.073	.030
14	.196	.256
15	.518	.893
16	.075	.141
17	.002	.004
18	.003	.003
24	.010	
25	.032	
26	.063	.008
27	.035	.012
28	.036	.004
29	1.000	1.000
30	.011	.012
31	.004	.004
40	.009	
41	.036	
42	.092	.013
43	.305	.413
44	.566	.913
45	.013	.022
	.001	.002
*Relative Sensitivity	.008	.016

*Relative to nitrogen (mass 28) in air.

TABLE 3-2

Mass Spectral Pattern for Acetone

m/e	70 eV	12 eV
12	.009	.001
13	.025	.004
14	.089	.043
15	.471	.717
16	.006	.008
17	.001	.001
18	.001	.002
19	.005	
19.5	.003	
20	.002	
24	.003	
25	.013	
26	.053	.006
27	.077	.027
28	.023	.015
29	.045	.025
30	.001	.001
31	.006	.004
36	.005	
37	.018	
38	.020	
39	.035	.003
40	.008	.003
41	.018	.002
42	.068	.018
43	1.000	1.000
44	.022	.022
45	.002	.002
51	.001	
52	.001	
53	.013	
55	.002	.001
57	.008	.007
58	.301	.490
59	.010	.017
60	.001	.001
*Relative Sensitivity	1.1	2.3

*Relative to nitrogen (mass 28) in air.

TABLE 3-3

Mass Spectral Pattern for Air

m/e	70 eV	12 eV
14	.074	.037
16	.019	.017
17	.001	
18	.005	.003
20	.002	
28	1.000	1.000
29	.010	.007
32	.210	.205
40	.015	.012
44	.002	
*Relative Sensitivity	1.0	1.0

*Relative to nitrogen (mass 28) in air.

TABLE 3-4

Mass Spectral Pattern for Allyl Alcohol

m/e	70 eV	12 eV
12	.012	
13	.017	
14	.0351	.0077
15	.0545	.0481
16	.0027	.0006
17	.0048	
18	.0045	.0006
19	.0083	.0026
19.5	.0030	
20	.0025	
20.5	.0009	

TABLE 3-4 (Continued)

Mass Spectral Pattern for Allyl Alcohol

m/e	70 eV	12 eV
24	.0073	
25	.0338	
26	.1624	.0197
27	.3663	.1600
27.5	.0012	
28	.2009	.2160
28.5	.0077	
29	.7264	5458
30	.2456	.3097
31	.5531	.3538
36	0083	
37	.0437	
38	.0617	
39	3033	.1027
40	.1078	.0929
41	.0693	.0439
42	.0187	.0080
43	.0464	.0387
44	.0018	.0013
45	.0030	.0026
52	.0024	
53	.0131	
54	.0036	.0013
55	.0495	.0103
56	.0055	.0039
57	1.000	1.000
58	.2712	.3399
59	.0062	.0103
60	.0023	.0019
*Relative Sensitivity	.6	1.9

*Relative to nitrogen (mass 28) in air.

TABLE 3-5

Mass Spectral Pattern for Benzene

m/e	70 eV	12 eV
12	.005	
13	.002	
14	.001	.002
15	.005	
16	.000	
17		
18	.001	.001
24	.001	
25	.004	
26	.029	.002
27	.029	.002
28	.003	.004
29		.001
31	.003	
35	.003	
36	.005	
36 5	.001	
37	.043	
37.5	.017	
38	.061	
38.5	.006	
39	.160	.032
39.5	.004	
40		
47	.002	
48	.002	
49	.022	
50	.145	.002
51	.179	.003
52	.208	.047
53	.011	.002
54		
55		
56		
57		
58		
59		
60	.003	
61	.005	
62	.007	

TABLE 3-5 (Continued)

Mass Spectral Pattern for Benzene

m/e	70 eV	12 eV
63	.024	.001
64	.002	.002
65		
66		
67		
68		
69		
70		
71		
72		
73	.014	
74	.041	
75	.016	
76	.039	.005
77	.179	.024
78	1.000	1.000
79	.069	.066
*Relative Sensitivity	1.6	5.0

*Relative to nitrogen (mass 28) in air.

TABLE 3-6

Mass Spectral Pattern for Butene-1

m/e	70 eV	12 eV
12	.0040	
13	.0048	
14	.0224	.004
15	.0316	.015
16	.0013	
19	.0004	
20	.0004	
24	.0013	
25	.0101	
25.5	.0119	
26	.0883	.011

TABLE 3-6 (Continued)

Mass Spectral Pattern for Butene-1

m/e	70 eV	12 eV
26.5	.0022	
27	.2495	.068
27.5	.0001	
28	.4048	.369
29	.1309	.107
30	.003	.003
36	.0022	
37	.0202	
38	.0347	
39	.2982	.111
40	.0606	.048
41	1.000	1.000
42	.0347	.032
43	.001	.001
44	.0018	.001
48	.0022	
49	.0119	
50	.0408	
51	.0334	
52	.0101	
53	.0501	.011
54	.0189	.017
55	.1660	.140
56	.3492	.029
57	.0167	.029
58	.0009	.001
*Relative Sensitivity	1.1	3.0

*Relative to nitrogen (mass 28) in air.

TABLE 3-7

Mass Spectral Pattern for Carbon Dioxide

m/e	70 eV	12 eV
12	.051	.019
16	.083	.151
18	.002	.004
22	.022	
28	.068	.017
44	1.000	1.000
45	.012	.012
*Relative Sensitivity	1.1	1.0

*Relative to nitrogen (mass 28) in air.

TABLE 3-8

Mass Spectral Pattern for Carbon Disulfide

m/e	70 eV	12 eV
12	.031	.029
14	.001	
16	.002	
25.3	.002	
28	.013	.003
32	.120	.108
33	.001	.001
34	.005	.004
38	.115	
38.5	.003	
39	.010	
40	.001	

TABLE 3-8 (Continued)

Mass Spectral Pattern for Carbon Disulfide

m/e	70 eV	12 eV
44	.115	.019
45	.002	
46	.005	.001
64	.011	
66	.001	
76	1.000	1.000
77	.026	.025
78	.088	.086
79	.002	.002
80	.002	.002
*Relative Sensitivity	1.8	5.6

*Relative to nitrogen (mass 28) in air.

TABLE 3-9

Mass Spectral Pattern for Carbon Monoxide

m/e	70 eV	12 eV
12	.026	.0043
13	.0003	
14	.0104	
16	.0071	
17	.0002	
18	.0002	.0007
28	1.000	1.000
29	.0108	0.0102
30	.0021	.0026
*Relative Sensitivity	1.4	1.8

*Relative to nitrogen (mass 28) in air.

TABLE 3-10

Mass Spectral Pattern for 1,4-Dioxane

m/e	70 eV	12 eV
12	.002	
13	.008	
14	.038	.003
15	.149	.163
16	.005	.003
17	.001	.001
18	.003	.003
19	.004	.003
25	.002	
26	.058	.014
27	.106	.020
28	1.000	1.000
29	.300	.190
30	.118	.146
31	.143	.099
32	.014	.008
33	.001	
39	.002	.001
40	.002	.002
41	.004	.002
42	.012	
43	.086	.040
44	.025	.031
45	.030	.026
46	.001	
57	.057	.056
58	.219	.270
59	.011	.014
60	.002	.002
61	.002	
87	.018	.018
88	.242	.333
89	.011	.015
90	.001	.002
*Relative Sensitivity	1.4	3.3

*Relative to nitrogen (mass 28) in air.

TABLE 3-11

Mass Spectral Pattern for Ethyl Acetate

m/e	70 eV	12 eV
12	.004	.001
13	.012	.001
14	.049	.006
15	.174	.164
16	.005	.004
17		.001
18	.001	.001
19	.005	.008
25	.002	
26	.025	.001
27	.095	.032
28	.042	.039
29	.204	.255
30	.008	.005
31	.009	.005
36	.001	.003
38		.001
40	.001	
41	.004	
42	.051	.020
43	1.000	1.000
44	.029	.025
45	.141	.229
46	.003	.005
55	.001	.001
58	.001	.001
59	.001	
60	.007	.010
61	.117	.208
62	.003	.004
63	.001	.001
70	.057	.093
71	.003	.004
73	.033	.049
74		.002
87	.002	.002
88	.031	.033
89	.002	.002
*Relative Sensitivity	1.8	2.8

*Relative to nitrogen (mass 28) in air.

TABLE 3-12

Mass Spectral Pattern for Ethylene Dichloride

m/e	70 eV	12 eV
12	.011	
13	.017	.001
14	.035	.010
15	.0065	.004
16	.003	
18		.001
24	.0096	
25	.054	
26	.213	.022
27	1.000	1.000
28	.181	.092
29	.002	.001
30.5	.003	
31.5	.004	
32	.023	.009
33	.001	
35	.038	
36	.020	
37	.014	
38	.007	
39	.001	
40	.002	
43	.003	
47	.018	
48	.031	
49	.399	.262
50	.011	.001
51	.130	.077
52	.002	
58	.001	.001
59	.004	
60	.023	
61	.105	.012
62	.522	.504
63	.170	.162
64	.178	.165
65	.042	.047
66	.002	
67	.001	

TABLE 3-12 (Continued)

Mass Spectral Pattern for Ethylene Dichloride

m/e	70 eV	12 eV
70	.001	
94	.001	
95	.004	.001
96	.002	
97	.006	.002
98	.095	.056
99	.003	
100	.060	.036
101	.001	
102	.009	.005
*Relative Sensitivity	.7	1.6

*Relative to nitrogen (mass 28) in air.

TABLE 3-13

Mass Spectral Pattern for Formaldehyde

m/e	70 eV	12 eV
12	.031	
13	.039	
14	.086	
15*	.424	.88
16	.172	.1
27*	.043	
28	.359	.20
29	1.000	.96
30	.675	1.00
31	.016	.85
32	.075	.03
33	.009	
42*	.039	
43*	.486	.38
44*	.031	.04
45*	.539	.43
46*	.012	

*Due to some higher molecular weight species, possibly methyl formate

*Relative		
Sensitivity	0.15	.37

*Relative to nitrogen (mass 28) in air.

TABLE 3-14

Mass Spectral Pattern for Freon-11

m/e	70 eV	12 eV
17.5	.003	
18	.001	.005
18.5	.001	
19	.006	
20	.001	
28	.007	.018
31	.203	.057
35	.231	
36	.010	
37	.069	
38	.004	
39	.003	
40	.001	
41	.017	
42	.009	
43	.001	
44	.001	
47	.139	
48	.002	
49	.044	
50	.001	
50.5	.049	
51.5	.031	
52.5	.006	
58	.002	
59	.004	
60	.005	
61	.004	
66	.175	
67	.003	
68	.055	
70	.007	

TABLE 3-14 (Continued)

Mass Spectral Pattern for Freon-11

m/e	70 eV	12 eV
72	.006	
82	.048	
84	.030	
86	.004	
101	1.000	1.000
103	.611	.625
105	.106	.096
117	.022	
119	.021	
121	.007	
*Relative Sensitivity	.35	.76

*Relative to nitrogen (mass 28) in air.

TABLE 3-15

Mass Spectral Pattern for Hydrogen Sulfide

m/e	70 eV	12 eV
16	.010	.001
17	.017	.001
18	.009	.006
32	.356	.166
33	.367	.175
34	1.000	1.000
35	.025	.015
36	.044	.039
*Relative Sensitivity	1.2	5.0

*Relative to nitrogen (mass 28) in air.

TABLE 3-16

Mass Spectral Pattern for Methyl Alcohol

m/e	70 eV	12 eV
12	.013	.002
13	.023	.002
14	.061	.046
15	.298	.398
16	.007	.004
17	.008	.002
18	.006	.004
19	.003	.002
28	.154	.033
29	.454	.151
30	.067	.040
31	1.000	1.000
32	.695	.829
33	.010	.011
34	.002	
*Relative Sensitivity	.7	2.0

*Relative to nitrogen (mass 28) in air.

TABLE 3-17

Mass Spectral Pattern for Methylene Chloride

m/e	70 eV	12 eV
12	.024	.019
13	.046	.049
14	.044	.124
15	.001	.002
16	.001	
17	.001	
17.5	.005	
18	.002	.003
24	.001	
24.5	.003	
25.5	.001	
26	.001	
28	.003	.002
35	.065	
36	.017	.005
37	.021	
38	.006	.002
40	.001	
41	.079	
41.5	.003	
42	.047	
43	.002	
47	.139	.011
48	.078	.039
49	1.000	1.000
50	.037	.021
51	.284	.294
52	.004	.003
82	.005	
83	.016	.009
84	.521	.384
85	.016	.010
86	.309	.237
87	.005	.003
88	.052	.036
89	.001	
*Relative Sensitivity	.9	2.2

*Relative to nitrogen (mass 28) in air.

TABLE 3-18

Mass Spectral Pattern for Nitric Oxide

m/e	70 eV	12 eV
14	.037	.016
15	.031	
16	.006	.004
17		
18	.001	.001
28	.013	.005
30	1.000	1.000
31	.004	.004
32	.003	.002
*Relative Sensitivity	1.15	2.3

*Relative to nitrogen (mass 28) in air.

TABLE 3-19

Mass Spectral Pattern for Nitrous Oxide

m/e	70 eV	12 eV
14	.077	.048
16	.032	.070
18	.002	
28	.072	.033
29	.001	.001
30	.189	.082
31	.001	
44	1.000	1.000
45	.008	.007
46	.002	.002
*Relative Sensitivity	.9	1.3

*Relative to nitrogen (mass 28) in air.

TABLE 3-20

Mass Spectral Pattern for Phenol

m/e	70 eV	12 eV
37	.09	
38	.20	
39	.31	
40	.25	
41	.04	
42	.04	
47	.09	
49	.04	
50	.08	
52	.04	
53	.04	
54	.04	
55	.10	
59	.04	
60	.04	
61	.04	
62	.04	
63	.09	
64	.04	
65	.17	
66	.17	.10
67	.06	
68	.04	
69	.02	
70	.02	
76	.21	.21
77	.04	
78	.06	.10
91	.02	
92	.02	
93	.04	
94	1.00	1.00
95	.10	.014

TABLE 3-21

Mass Spectral Pattern for Sulfur Dioxide

m/e	70 eV	12 eV
14	.003	
16	.027	.017
18	.001	.006
24	.016	
25	.001	
32	.091	.009
33	.001	
34	.003	
48	.432	.067
49	.003	
50	.019	.003
64	1.000	1.000
65	.009	.006
66	.048	.044
*Relative Sensitivity	.68	.65

*Relative to nitrogen (mass 28) in air.

TABLE 3-22

Mass Spectral Pattern for Toluene

m/e	70 eV	12 eV
12	.001	
13	.001	
14	.002	
15	.006	
16		
17	.001	.001
18	.002	.003
25	.001	
26	.014	
27	.044	.004
28	.004	.006
29	.001	
36	.002	
37	.018	
38	.039	
39	.158	.001
40	.020	.001
41	.021	
42	.002	
42.5	.001	
43	.025	
43.5	.006	
44	.008	
44.5	.007	
45	.080	
45.5	.011	
46	.050	
46.5	.005	
49	.006	
50	.050	
51	.083	
52	.021	
53	.010	
54	.001	
60	.002	
61	.014	
62	.031	
63	.073	
64	.017	

TABLE 3-22 (Continued)

Mass Spectral Pattern for Toluene

m/e	70 eV	12 eV
65	.119	.002
66	.015	.001
67	.001	
70	.001	
71	.001	
72		
73	.002	
74	.008	
75	.005	
76	.003	
77	.006	
78	.001	
85	.005	
86	.007	
87	.005	
88	.001	
89	.036	
90	.018	
91	1.000	.267
92	.714	1.000
93	.063	.082
*Relative Sensitivity	1.4	3.5

*Relative to nitrogen (mass 28) in air.

TABLE 3-23

Mass Spectral Pattern for Vinyl Chloride

m/e	70 eV	12 eV
12	.023	.003
13	.028	.005
14	.020	.015
15	.004	.002
18	.004	.002
24	.025	
25	.104	.003
26	.296	.156
27	1.000	1.000
28	.039	.040
29	.001	
30	.002	
30.5	.005	
31	.001	
31.5	.002	
35	.034	.005
36	.015	
37	.011	
38	.005	
47	.024	
48	.011	
49	.018	
50	.003	
51	.001	
55	.001	
56	.001	
57	.001	
60	.019	
61	.076	
62	.980	
63	.057	
64	.302	
*Relative Sensitivity	.012	.037

*Relative to nitrogen (mass 28) in air.

TABLE 3-24

Mass Spectral Pattern for Water

m/e	70 eV	12 eV
16	.018	.002
17	.242	.115
18	1.000	1.000
19	.001	
20	.002	
*Relative Sensitivity	.60	1.7

*Relative to nitrogen (mass 28) in air.

TABLE 3-25

Mass Spectral Pattern for m-Xylene

m/e	70 eV	12 eV
14	.008	
15	.017	
17	.001	
18	.003	.003
26	.012	
27	.095	.008
28	.013	.009
27	.005	
31	.001	
37	.011	
38	.027	
39	.152	
40	.017	
41	.023	
42	.001	
43	.005	.001
44	.001	
44.5	.001	
45.5	.003	

TABLE 3-25 (Continued)

Mass Spectral Pattern for m-Xylene

m/e	70 eV	12 eV
49	.007	
50	.005	
51	.171	
51.5	.008	
52	.091	
52.5	.005	
53	.036	
54	.003	
55	.002	
56	.001	
57	.002	.002
60	.001	
61	.008	
62	.020	
63	.054	
64	.011	
65	.077	
66	.011	
67	.003	
68	.001	
69	.001	
70	.001	
71	.001	
72	.001	
73	.003	
74	.013	
75	.009	
76	.008	
77	.119	
78	.058	.012
79	.062	.004
80	.005	
81	.001	
82	.001	
83	.001	
84	.001	
85	.002	
86	.003	
87	.003	
89	.018	
90	.006	

TABLE 3-25 (Continued)

Mass Spectral Pattern for m-Xylene

m/e	70 eV	12 eV
91	1.000	.418
92	.096	.053
97	.001	
98	.002	
99	.001	
101	.002	
102	.009	
103	.049	
104	.023	
105	.226	.047
106	.514	1.000
107	.045	.092
*Relative Sensitivity	1.1**	3.8

*Relative to nitrogen (mass 28) in air.

**Initial value

4. CONCLUSIONS

Mass spectra at 70 and 12 eV ionization voltages were measured for the contaminants tested in the sensor program. The sensitivity values relative to nitrogen in air were determined. The relative sensitivity values are somewhat lower for organics than expected from reference spectra. This difference is tentatively attributed to differences in filament and ion source conditions in the mass spectrometer.

At 12 eV, the sensitivities of organics relative to nitrogen is increased as expected from ionization potentials. The absolute sensitivity of the instrument for nitrogen is reduced by a factor of 6.3.