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FINAL REPORT

FEASIBILITY STUDY ON ANALYTICAL TECHNIQUES FOR DETECTION OF GLYCOL VAPOR

By

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CONTRACT NAS 9 - 7570
EXHIBITS A, B, & C

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INTRODUCTION

The present work is a by-product of extensive studies conducted at the INSTITUTE FOR RESEARCH for specificity and steric factors for the detection of ethylene glycol vapors without interferences from other polysubstituted compounds. The preparation, stability and perceptible reaction characteristics of a multitude of reagents is described in the text of the final report for Exhibits A & B. The work described in this final report (Exhibit C) gives a detailed discussion of the physical and chemical properties of ethylene glycol and the silica gel adsorbent. The mechanism, specificity, effect of flow rate, effect of gas composition, effect of dew point (hygroscopicity), storage life, effect of temperature and methods of quantitation in various environments is elucidated.

The purpose of this investigation was to establish limits of detectability (sensitivity) and perform comprehensive laboratory studies on the mechanisms of reaction of ethylene glycol.

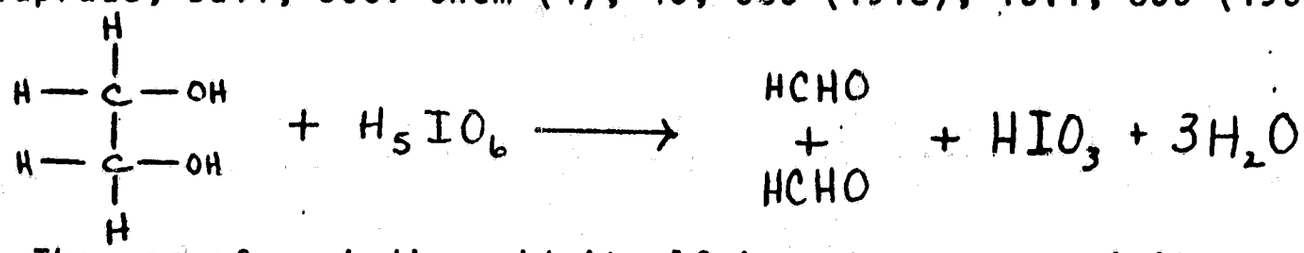
THEORY

Experimental work perfcrmed in this laboratory has shown that aliphatic aldehydes as formaldehyde can be detected at extremely low concentrations as well as be detected in a variety of environments. Consistent with this fact is the report, that in the gas phase, formaldehyde, unlike other low molecular weight aliphatic aldehydes is moderately stable in the presence of air or oxygen.

For a more thorough understanding of the detection of formaldehyde, a comprehensive program was initiated to develop methods which could be used for the detection&rapid estimation.

OXIDIZING AGENT

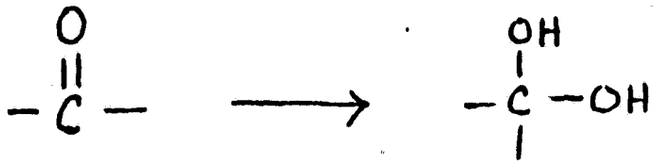
Innumerable oxidizing agents were investigated on the conversion of polyhydric alcohols as ethylene glycol to formaldehyde, however, the action of periodic acid and periodates was found to open up a new field for the rapid specific conversion of ethylene glycol to formaldehyde. The reaction of ethylene glycol with periodic acid is given by the following equation: (Malaprade, Bull, Soc. Chem (4), 43, 683 (1918), 1511, 833 (1939)



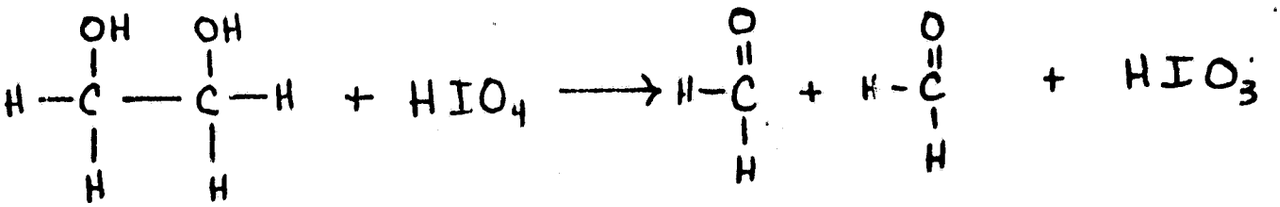
The use of periodic acid itself is not a pre-requisite, a periodate in the presence of non-interfering acid (dilute sulfuric acid) will have the same effect. The metaperiodates of sodium and potassium, the dimesoperiodate of potassium also introduces no complications.

Oxidizing Agents - continued

With consideration of compounds containing carbon hydrogen and oxygen, periodic acid oxidation are limited to those which provide two hydroxyl radicals attached to two adjacent carbons (in the alpha portion) aldehydes as formaldehyde assumed to be hydrated as follows:



The quantitative reaction is then represented by



It is thus possible stepwise to follow the reactions of periodic acid, in ethylene glycol. The nature of the other radicals attached to the carbon atom bearing hydroxyls is not without influence on the speed of the reaction which makes this reaction extremely valuable for the specific determination of ethylene glycol.

Physical Properties of Ethylene Glycol

Ethylene glycol is a colorless, practically odorless liquid with a sweetish taste. It is relatively viscous and nonvolatile, and is completely miscible with water and many organic liquids.

1. Azeotropes - Table I for the most part is taken from a compilation of data. It includes typical compounds that have been investigated for possible azeotrope formation with ethylene glycol. Water is listed first and then organic systems according to ascending number of atoms in the order C, H, Br, Cl, I, N, and O. All compounds with the same number of carbon atoms are placed together.
2. Flammability - Since flammability tests attempt to duplicate the conditions under which materials susceptible to combustion are stored, transported, and handled, such values as flash point and fire point are usually determined on the commercial product rather than on the pure chemical. A survey of the available data indicates that ethylene glycol has a flash point of 240°F. and a fire point of 250°F. The variations in the results of several investigators do not exceed the tolerance of 5°F. customary for these tests. The flash and fire points of aqueous solutions of ethylene glycol are shown in Table II.

TABLE I

Azeotropes of Ethylene Glycol

Name	Boiling Point of Azeotrope, °C. at 760 mm.	Ethylene Glycol, % by Wt.
Water	no azeotrope	
Nitromethane	no azeotrope	
Tetrachloroethylene	199.1	6
Acetamide	no azeotrope	
Bis(2-chloroethyl) ether	164	17.8
Glycol monoacetate	184.75	25
1-Butanol	no azeotrope	
2-(2-Methoxyethoxy)ethanol	192	30
Bromobenzene	150.2	12.5
Chlorobenzene	130.05	5.6
Nitrobenzene	185.9	59
Benzene	no azeotrope	
Aniline	190.55	24
Cyclohexane	no azeotrope	
Cyclohexanol	no azeotrope	
1-Hexanol	no azeotrope	
2-(2-Ethoxyethoxy)ethanol	196.0	54.5
o-Nitrotoluene	188.55	48.5
Toluene	110.20	6.3
Benzyl alcohol	193.1	56
p-Cresol	195.2	53.5
Methylcyclohexane	100.8	4
n-Heptane	98.3	3
n-Heptyl alcohol	174.1	17
Acetophenone	185.65	52
Ethylbenzene	133.0	13.5
o-Xylene	139.6	16
Diethyl maleate	193.1	55
Dibutyl ether	140.0	10
2-(2-Butoxyethoxy)ethanol	196.2	72.5
Bis(2-ethoxyethyl) ether	178.0	48.1
Ethyl benzoate	186.1	46
3-Phenylpropanol	195.5	75
Phorone	184.5	12
Naphthalene	183.9	51
Menthol	198.55	51.5
Decyl alcohol	193.0	67
Diisoamyl carbonate	186.45	46
Biphenyl	192.25	66.5
Diphenyl ether	192.3	64.5
Dihexyl ether	112.8*	35.6

Other flammability data for ethylene glycol and its aqueous solutions have been reported. Values ranging from 780 to 975°F. for the "apparent ignition temperature in air" of ethylene glycol have also been determined. The results of experiments performed by the Bureau of Standards on the spontaneous ignition temperatures of ethylene glycol and its aqueous solutions are summarized in Table II .

Several researchers have investigated the flammable characteristics of aqueous ethylene glycol solutions. They found that inhibited ethylene glycol solutions containing as low a concentration of water as 40 per cent by volume (freezing point - 62°F.) did not burn when sprayed onto wood or gasoline fires. In fact, such solutions acted as control and extinguishing agents. The National Bureau of Standards has found that inhibited ethylene glycol-water solutions were nonflammable when sprayed on a hot engine exhaust manifold.

TABLE II

Flammability Values for Ethylene Glycol and Its Aqueous Solutions

Ethylene Glycol % by wt.	Flash Point °F.[a]	Fire Point °F.[b]	Spontaneous Ignition Temperature, °F.	
100	245	250	750	1170
95	260	270		
90	270	280		
85				
80			770	1200
75				
70				
65				
60			790	1230
50				
40			815	1270
20			840	1350

3. Freezing Point - The accurate determination of the freezing point of ethylene glycol is complicated by the high viscosity of the liquid near the freezing temperature. This condition tends to cause supercooling of the liquid, making equilibrium between liquid and solid phase difficult to attain. The most probable value for the freezing point is -13°C. (+8.6°F.) which is an average of the more reliable values given in the literature.

Ethylene glycol and water form a eutectic mixture in the range 58 to 80 per cent glycol by weight,

although the exact eutectic composition and temperature have not been accurately defined. Solutions up to 58 per cent by weight form ice crystals on cooling to the freezing point. A nonrigid "slush" formation results. Solutions in the 80 to 100 per cent glycol range form ethylene glycol crystals upon freezing. Such solutions have a pronounced tendency to "supercool" or remain liquid at temperatures below their true freezing point (Figure 1.)

Ethylene glycol solutions in the 0 to 58 per cent range in general expand continuously from their freezing points to -54°F. There is some evidence that the more dilute solutions go through a maximum volume and then contract a little on cooling to -54°F. Solutions in the 80 to 100 per cent range contract continuously on cooling below their freezing points.

4. Heat of Combustion - The most reliable value reported is 285.0 kcal./mol at constant pressure, both at 20°C. These data are based on the oxidation of the liquid glycol to liquid water and gaseous carbon dioxide.

5. Heat of Solution - Heat is liberated when ethylene glycol and water are mixed. The contraction of such mixtures has been studied and it has been concluded that a hydrate having the composition $C_2H_4(OH)_2 \cdot 2H_2O$ was formed and a heat of 0.60 calorie liberated.

A maximum effect was obtained by mixing 37 parts of glycol and 63 parts of water by weight, indicating the formation of a hydrate of composition $C_2H_4(OH)_2$ $6H_2O$.

6. Hygroscopicity - Although ethylene glycol is known to be very hygroscopic, very few quantitative data are available. It has been shown that ethylene glycol is about one and one-half times as hygroscopic as glycerol at room temperature and 100 per cent relative humidity.

Equilibrium dew points for gases in contact with aqueous solutions of ethylene glycol have been published by Dow. Their results are presented graphically in Figure 2 . Table III gives the hygroscopicity of ethylene glycol at 75°F.

TABLE III

Hygroscopicity of Ethylene Glycol at 75°F.

Relative Humidity %	Per Cent Water(Equilibrium Values)
25	10.3
30	12.3
35	15.0
40	18.0
45	21.7
50	26.5
55	32.0
60	39.0
65	47.0
70	57.0

Table IV contains relative humectant values for ethylene glycol. This is a property closely related to hygroscopicity in that it is the limiting concentration of water that will be absorbed in contact with air of a specified temperature and relative humidity. It also may be described as the composition of an aqueous solution that will remain in equilibrium with air of a given temperature and relative humidity.

TABLE IV

Relative Humectant Values of Ethylene Glycol

Air Temperature °F.	Relative Humidity, %							
	20	30	40	50	60	70	80	90
	Ethylene Glycol, % by wt. in water							
0	85.0	85.0	71.0	60.0	45.0			
10	93.0	85.0	71.0	62.5	47.0		30.0	
20	92.0	85.0	73.0	63.5	48.0	38.0	30.0	20.0
30	92.0	85.0	75.0	64.5	53.0	40.0	32.5	20.0
40	92.0	86.0	77.0	68.5	57.0	45.0	33.0	20.0
50	92.0	87.0	80.0	71.0	61.2	48.0	35.5	20.0
60	92.2	88.0	81.3	72.5	61.5	50.0	37.5	23.5
70	92.5	88.5	81.3	73.0	63.5	52.5	38.5	23.5
80	92.5	88.0	81.5	74.0	65.0	53.0	40.0	26.0
90	92.5	88.0	82.0	75.0	69.5	55.0	42.5	27.0
100	12.5	88.0	82.0	75.5	67.0	56.5	44.0	28.0
110	92.4	88.0	82.5	76.0	67.5	58.0	45.0	30.0
120	92.3	88.0	32.5	76.0	69.0	59.0	46.0	30.0

7. Refractive Index - The determination of refractive index affords a rapid and precise method of establishing the purity of ethylene glycol. Over the temperature range 15 to 35°C., the refractive index of the pure material varies linearly at the rate of 0.00026 per °C., the index at 20°C. being 1.4316 for a light of wavelength 5893 Å, corresponding to the sodium D line.

   The refractive index of aqueous solutions of ethylene glycol varies linearly with composition. This same relationship also holds for the systems ethylene glycol-diethylene glycol and ethylene glycol-propylene glycol.

8. Solubility - Ethylene glycol is completely miscible with water and the lower apiphatic alcohols, aldehydes, and ketones, but is practically insoluble in hydrocarbons and similar compounds. Solubility data on a number of ternary systems containing ethylene glycol, an aromatic hydrocarbon or hydrocarbon derivative, and ethanol or acetone as a mutual solvent has been reported. Of the compounds investigated, nitrobenzene has been shown to require the least amount of ethanol or acetone to effect complete solution; then, in order, benzene, chlorobenzene, bromobenzene, toluene, and xylene. Ethanol was found to be a more effective mutual solvent than

acetone.

Ethylene glycol is a satisfactory solvent for many substances. Solubilities of a number of common organic and inorganic materials are given in Table V .

9. Specific Heat - A tabulation of specific heat data reported by several investigators indicates that this property varies linearly with temperature:

$$x=0.538 + 0.00113t$$

where x is specific heat, cal/g./°C., and t is temperature, °C.

For pure ethylene glycol the specific heat at 20°C. is 0.561 calories per gram per °C. This value is numerically equal to the specific heat at 68°F. expressed as Btu per pound per °F.

10. Surface Tension - Reliable surface tension measurements on ethylene glycol have been reported and experimental data has shown that over the temperature range of 30 to 160°C., the empirical equation may be written as follows:

$$x=50.21 - 0.089t$$

where x is surface tension, dynes/cm., and t is temperature, °C.

11. Thermal Conductivity - For the pure compound, the change in thermal conductivity with temperature is a linear function which may be expressed (Figure 3):

$$x=7.25 \times 10^{-4} - 1.8t \times 10^{-7}$$

TABLE V

Solubility of Various Organic Solvents in Ethylene Glycol

Compound	Solubility, g./100g. of Ethylene Glycol
Acetic acid	∞
Acetone	∞
Benzene	6.0
Bis(2-chloroethyl) ether	11.8
Carbon disulfide	slightly soluble
Carbon tetrachloride	6.6
Chlorobenzene	6.0
Chloroform	slightly soluble
Dibutyl phthalate	0.5
o-Dichlorobe nzene	4.7
Diethanolamine	∞
Ethanol	∞
Ethyl ether	8.9
Furfural	∞
Glycerol	∞
Hexyl ether	0.09
Methanol	∞
Monoethanolamine	∞
Pentanol	∞
Phenol	∞
Phenyl ether	1.7
Pyridine	∞
Toluene	3.1
Xylene	slightly soluble

12. Vapor Pressure - An examination of the values reported for the boiling point of ethylene glycol at 760 mm reveals an appreciable variation. The rate of thermal decomposition of ethylene glycol at various temperatures has been reported and at 164.9°C. the rate is sufficient to increase the vapor pressure 1.3 mm/min.

A value of 197.6°C. has been selected as the most probable boiling point at 760 mm. This is the average of the more reliable determinations reported in the literature.

In order to determine the most probable values for the vapor pressure at various temperatures, all of the data were plotted on large-scale vapor pressure paper (log pressure vs. reciprocal of absolute temperature). After discarding obviously erroneous data, the best smooth curve was drawn through the remaining points so as to include a vapor pressure of 760 mm at 197.6°C. (Figure 4.)

It has been shown by work at the Bureau of Standards that an equation of the type

$$\log p = a - \frac{b}{c + t}$$

(where p is vapor pressure, mm., t is temperature, °C., and a, b, c are constants) represents the relationship between vapor pressure and temperature within the limits of experimental error over the range of 100 to

1500 mm. It may be used over a much wider range with small loss of precision. For ethylene glycol this equation may be written:

$$\log p = 7.8808 - \frac{1957}{193.8+t}$$

The values in Table VI were calculated from this expression.

The boiling points and vapor pressures of aqueous solutions of ethylene glycol may be calculated from the ideal-solution law:(Figure 5.)

$$P = x_1 p_1 + x_2 p_2$$

where P = total pressure at a constant temperature

x_1 = mol fraction of water

p_1 = vapor pressure of water

x_2 = mol fraction of ethylene glycol

p_2 = vapor pressure of ethylene glycol

Boiling point values reported by the National Bureau of Standards are given in Table VII. Vapor pressure data are presented in Table VIII.

13. Viscosity - The values in Table IX were derived from data published by the National Bureau of Standards giving the viscosity of pure ethylene glycol and its aqueous solutions from -50 to 350°F. The experimental points were not reported.

TABLE VI

	Vapor Pressure mm Hg	Temperature F.
100% Ethylene Glycol	0.025	50.0
	0.065	68.0
	0.13, 0.23	86.0
	0.28, 0.37	104.0
	0.70	122.0
	1.5, 2.07	140.0
	2.97	158.0
	5.86	176.0
90% Ethylene Glycol	1.85	40.0
	2.8	50.0
	4.2	60.0
	6.0	70.0
	8.2	80.0
80% Ethylene Glycol	2.88	40.0
	4.2	50.0
	6.5	60.0
	9.0	70.0
	12.7	80.0
70% Ethylene Glycol	3.3	40.0
	5.0	50.0
	7.8	60.0
	11.0	70.0
	15.3	80.0
50% Ethylene Glycol	4.1	40.0
	7.0	50.0
	9.8	60.0
	14.0	70.0
	19.0	80.0

TABLE VII

Boiling Point of Aqueous Solutions of Ethylene Glycol at One Atmosphere

Ethylene Glycol		Boiling Point, °F.
% by wt.	% by vol.	
0	0.0	212
10	9.1	214
20	18.4	216
25	23.2	217
30	28.0	218
35	32.8	219
40	37.8	221
45	42.8	223
50	47.8	225
55	52.9	227
60	58.0	230
70	68.4	238
80	78.9	252
85	84.1	262
90	89.4	279
95	94.7	309
100	100.0	388

TABLE VIII

Vapor Pressure of Ethylene Glycol and Its Aqueous Solutions

Ethylene Glycol % by vol.	0	18.4	37.8	58.0	68.4	78.9	89.4	94.7	100
Temperature °F.	Absolute Pressure, mm. at 0°C.								
140	149	139	125	105	-	-	-	-	-
160	245	229	206	172	147	115	70	40	3
180	388	363	326	272	234	183	112	65	6
200	596	557	501	419	360	282	173	101	11
220	889	830	748	625	538	422	261	154	21
240	1291	1206	1088	910	784	616	383	228	35
260	1832	1712	1545	1294	1116	879	550	331	59
280	2544	2378	2147	1801	1555	1228	772	470	94
300	3465	3240	2927	2458	2125	1682	1065	656	146
320	4636	4337	3920	3297	2853	2264	1443	899	221
340	6102	5711	5165	4350	3770	2999	1925	1213	326

TABLE IX

Absolute Viscosity of Ethylene Glycol and Its Aqueous Solutions

Ethylene Glycol, % by wt.		0	20	40	60	80	100
% by vol.		0	18.4	37.8	58.0	78.0	100
Temperature,		Viscosity, centipoises					
°F.	°C						
−50	−46				268.4	835	
−40	−40				161.9	449	
−30	−34				97.8	259	
−20	−29				62.4	158.2	
−10	−23			19.82	41.7	101.7	
0	−18			14.14	29.04	68.19	
20	−7		4.23	7.93	15.51	34.06	86.9
40	+4	1.55	2.74	4.91	9.19	19.08	45.0
60	16	1.12	1.90	3.28	5.89	11.60	26.66
80	27	0.86	1.39	2.32	4.03	7.58	15.82
100	38	0.68	1.07	1.72	2.89	5.23	10.38
120	49	0.56	0.85	1.33	2.17	3.78	7.17
140	60	0.47	0.69	1.06	1.68	2.83	5.17
160	71	0.40	0.58	0.86	1.34	2.19	3.88
180	82	0.35	0.49	0.72	1.09	1.74	2.97
200	93	0.30	0.43	0.61	0.91	1.41	2.34
220	104	0.27	0.37	0.53	0.77	1.17	1.89
240	116	0.24	0.33	0.46	0.66	0.97	1.56
260	127	0.22	0.30	0.41	0.58	0.84	1.30
280	138	0.20	0.27	0.37	0.51	0.73	1.10
300	149	0.18	0.25	0.33	0.45	0.64	0.95
320	160	0.17	0.23	0.30	0.41	0.57	0.83
340	171	0.16	0.21	0.28	0.37	0.51	0.72
360	177	0.15	0.20	0.26	0.35	0.48	0.68

TABLE X

Physical Properties of Ethylene Glycol

Acid dissociation constant at 19°C.	$K_a = 5.7 \times 10^{-15}$
Boiling point at 760 mm.	197.6°C.
Coefficient of expansion at 20°C.	0.00062/°C.
Density (true) at 20°C.	1.11336 g./ml.
Dielectric constant at 20°C. and 150 meters	38.66 esu
Dipole moment at 30°C.	$2.20 \quad 0.02 \times 10^{18}$ esu
Electrical conductivity at 25°C.	1.07×10^{-6} reciprocal ohms (mhos)
Entropy of formation at 25°C.	39.9 kcal./mol/°C.
Fire point	250°F.
Flash point	240°F.
Free energy of formation at 25°C.	-80.2 kcal./mol
Freezing point	-13°C.
Heat of combustion at constant pressure and 20°C.	-283.3 kcal./mol
Heat of formation at 20°C.	-108.1 kcal./mol
Heat of fusion	44.7 cal./g.
Heat of vaporization at 760 mm.	191 cal./g.
Molal entropy at 25°C.	-105.4 kcal./°C.
Molecular refraction at 20°C.	14.49
Molecular refractivity at 20°C.	24.03
Molecular weight, 1951	62.07
Parachor	148.9 (152.2 calculated)
Ramsay and Shields constant	1.06
Refractive index, n_D at 20°C.	1.4316
Specific Gravity(apparent)at 20/20°C.	1.1155
Specific heat at 20°C.	0.561 cal./g./°C.
Surface energy at the boiling point (total)	74.52 ergs

TABLE X (con't.)

Surface tension at 20°C.	48.4 dynes/cm.
Thermal conductivity at 20°C.	0.000690 cal.-cm./sec./cm.^{2}/°C.
Vapor pressure at 20°C.	0.06 mm.
Verdet constant at 25°C. and 5461 Å	0.01456 min./gauss cm.
Viscosity (absolute) at 20°C.	20.93 cp.

SUBSTRATE FOR SELECTIVE ADSORPTION

A wide variety of substrates were investigated to observe the color and interaction between the organic indicating reagent and oxidation product of the ethylene glycol (formaldehyde).

Silica gel was found to be the most suitable substrate. The granular silica gel found to be most suitable was extremely pure silica (99.7%) with only trace amounts of metallic impurities. The selectivity of a particular grade of silica gel in the preferential adsorption of one compound over another depends upon the pore diameter mesh size and percolation rate. Particle sizes ranging from 35 to 60 mesh were found to be suitable as a selective adsorbent for the sulfuric acid. An excess amount of sulfuric acid was used to insure complete surface coverage of the silica gel surface as well as permeation into the pores. Davison (Grace Chemical Co.) granular silica gels (Grades 59 & 81) were used as the selective adsorbent. These silica gels exhibited the highest adsorptive capacity.

Glass beads of different sizes was combined with the silica gel to reduce the "closest-close" packing in the column thus permitting laminar flow through the tube. Movement of the band was observed to be a function of flow-rate.

Physical Properties of Silica Gel

1. Size and Shape - In applications where adsorbents are used under static equilibrium conditions, the size and shape of particles is unimportant. However, in dynamic operations, the kinetics of mass transfer and considerations of pressure drop exert much more influence. As a rule, the kinetics of a system require small particle size for rapid transfer of an adsorbate to the adsorbent. Optimization of this factor cannot always be tolerated because of the increased pressure drop resulting from small particles. In any system, the pressure drop requirements must be balanced against the adsorption efficiency of a given size of particles. The shape of the particles also influences mass transfer because of variations in external particle surface per quantity of adsorbent. Thus the irregular granular shape of silica gel improves kinetics even when a large average particle size is utilized to minimize pressure drop.
2. Density - The particle density of an adsorbent is largely dependent on the volume of pores within the structure. As less pore volume is built into an adsorbent, the density will increase. As pore volume is increased, it becomes easier for adsorbates to diffuse within a particle; but at the same time, the skeleton of the particle becomes more delicate.

3. Strength - The physical strength of an adsorbent is partially a function of the internal pore structure. In addition to the strength imparted by the basic structure of the gel, most silica gels are "pre-attrited" prior to packaging to knock off any cracked corners which could produce dust, or fines, in normal use.
4. Silica Structure - The fact that silica gel is an amorphous rather than a crystalline form of silica is also very important. Such a form will not contribute to possible physiological effects.

Performance Characteristics of Silica Gel

The behavior of silica gel, in adsorbing a component or components in a gaseous phase is dependent upon specific physical factors. Some important parameters are presented below:

A. Dehydration

When silica gel is used primarily for water and gas adsorption, gas composition, pressure, temperature and particle size are influential in its performance.

1. In considering gas composition the water content is critical, since it will influence both the amount of water which will be adsorbed by the gel and the rate at which it will be adsorbed.

The maximum amount of water which can be adsorbed is defined by a measurable equilibrium relationship between the water in the gas phase and the water adsorbed in the gel. This relationship at atmospheric pressure is graphically illustrated in Figure 6. The directional effect of inlet gas water content on the maximum useful capacity of the gel is shown by the following:

Assume two gas streams, each at the same temperature, 80°F., and the same pressure. Stream "A" has a water vapor partial pressure of .20 in Hg., so the maximum water content of gel in equilibrium would be 11.5% (from Figure 6). If stream "B" contains more water, say a partial pressure of .40 in Hg., the maximum water content of gel in equilibrium would be 21% (from Figure 6).

The rate at which the water is adsorbed will influence the time required for contact between the gel and the gas for a given degree of dehydration. The unsteady state conditions present in a desiccant bed under dynamic adsorption operation makes accurate determination of the water transfer rate beyond the scope of this presentation. However, a qualitative understanding of this effect is presented below. The rate at which silica gel

will adsorb water vapor from a gas in turbulent flow as:

$$\frac{dw}{d\theta} = \alpha G^n \Delta p$$

when: w = water content of silica gel

G = mass velocity of the gas based on specified area of gel

Δp = difference between the vapor pressure of water in the gas and in the gel

α, n = constants

From this expression it can be seen that the rate of adsorption is a direct function of the vapor pressure differential, so higher vapor pressures of water in the gas will increase the initial rate of adsorption. As the mass transfer zone develops the effect of inlet water content of the gas is masked by other factors. For practical purposes it can be assumed that the length of this transfer zone, or the contact time for a gas to reach a given dryness, will increase with inlet water content.

2. Polar molecules as ethylene glycol in the gas stream also influence gel performance. Silica gel will preferentially adsorb water so that theoretically glycols will not be strongly adsorbed until they pass beyond the zone of water

adsorption. This distinction is not 100% efficient, however, and some glycols and hydrocarbons are actually adsorbed within the water adsorption zone. As more water enters the zone it will displace most of these adsorbed less polar materials and they will move down the column to be adsorbed again. This displacement slows down the rate of water adsorption and increases the length of the water adsorption zone. Some glycols and hydrocarbons, because of their molecular size or type, will be more strongly held by the silica gel and will not be completely displaced.

3. Gas contaminants such as CO_2 have adsorption characteristics similar to hydrocarbons as butane. During water adsorption, most of the CO_2 previously adsorbed will be displaced, but some are concentrated in the adsorbed water or hydrocarbons. In this phase they have a minimum effect on adsorption capacity.

   Alcohols behave very much like water in the silica gel. They have no lasting effect, but compete with the water vapor for adsorption capacity.

   Certain amines have a deleterious effect on the capacity and life of silica gel. They are readily adsorbed, and during regeneration are decomposed.

The ammonia resulting from the decomposition attacks the internal structure of the gel particles. As the internal structure deteriorates, the pores become larger, and the surface area is reduced. This attack, if carried to extremes, will reduce adsorption capacity.

4. The operating temperature of a silica gel column within the range usually encountered aboard the spacecraft has little effect on its performance. In general, lower temperatures result in greater capacity, although the increase in equilibrium capacity at any level of relative saturation is increased only about 5% over the temperature range 120°F. to 70°F. Above 120°F., capacity decreases rapidly.

5. The total pressure of a system has very little effect on silica gel capacity for water, providing it is above 100 psi. Below this pressure most gases do not have sufficient heat capacity to dissipate the heat of adsorption. The heat of adsorption is the sum of the heat of condensation for the water and the heat of wetting of the silica surface (about 325 BTU per lb. of water).

6. Velocity - In the design and operation of the ethylene glycol detection system, the velocity

must be carefully considered.

The length of a mass transfer zone varies with gas velocity, because contact time is a direct function of this factor. However, the length of zone to velocity relationship is modified by increased mass transfer rates across the solid-gas interface at higher velocity. Thus, the mass transfer zone length is not directly proportional to velocity. This assumes, of course, that the minimum velocity is high enough to be above the laminar range flow, but below a level which might cause movement of the silica gel. At very low velocity the effects of channelling or wall effects may cause very poor gas distribution.

Adsorption

The general mechanism of adsorption is analogous to ion exchange and miscible displacement of fluids, in terms of the variation of effluent concentration with time. Several mechanisms are occurring simultaneously - diffusion and dispersion through the gas phase, condensation on the surface and imbibition (internal diffusion) of the liquid from the outer surfaces of the particle into the interstices. The fact that these occur simultaneously makes it difficult to pinpoint the exact role of any one

mechanism or to quantitatively describe the process in academic detail. It appears that gaseous diffusion and dispersion within the particle play a minor role and may be ignored.

The effects of surface liquid "film" and internal diffusion on the rate of adsorption is of interest. The predominance of either can influence optimum flow rates, geometry of packed column and particle size for a dynamic system. At the present time, however, not enough is known about their relative influences to make much difference. Commonly used techniques which assume a "film" resistance to calculate mass transfer rates do so more out of convenience than as a matter of fact.

In spite of the exact mechanism, a given adsorbate will continue to collect on an active surface as long as free surface is available and there is a positive concentration driving force from gas to liquid. Adsorption can continue to occur after all available surface "sites" are covered. A concentration driving force exists even though the surface forces have been satisfied.

The concentration of a given adsorbate follows a sequential pattern. The leading edge of an adsorption zone moves into a portion of the column that contains none of that particular adsorbate. The degree of saturation at the inlet increases until the first layer of gel is saturated.

Once this has occurred a so-called adsorption or mass transfer zone has been formed. This zone grows in length but rapidly stabilizes and moves through the column with no further effective change in length. As the leading edge of this front reaches the exit of the column, "breakthrough" of the particular adsorbate occurs and the concentration in the exit gas rapidly approaches that of the inlet.

Chemical Properties

Silica gel is an extremely pure form of silicon dioxide (99.7+% SiO_2). It is manufactured under carefully controlled conditions from sulfuric acid and sodium silicate. The fact that silica gel is the result of controlled reaction between other manufactured chemicals frees it from any deviation which might be introduced by naturally occurring raw materials.

Silica (silicon dioxide) is an extremely inert material. Only strong alkalies or hydrofluoric acid react with it to any appreciable extent. It is insoluble in all common solvents. A typical analysis of silica gel is given as follows (Table XI):

TABLE XI

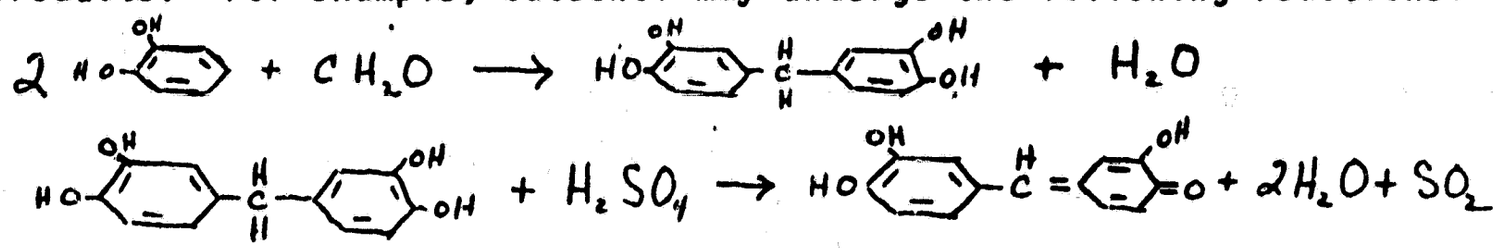
Properties of Silica Gel

Silica as SiO_2	99.84%
Iron as Fe_2O_3	.01%
Aluminum as Al_2O_3	.07%
Titanium as TiO_2	.04%
Calcium as Ca	.01%
Sodium as Na_2O	.02%
Zirconium as Zr_2O	.01%
Pore Volume	0.43 cc./gm.
Average Pore Diameter	22 Angstroms
Surface Area	750-800 sq. meters/gm.
Total Volatile at 1750°F	5.0 to 6.5%
Specific Heat	0.22 BTU/lb./°F.
True Density of Silica (no porosity)	137 lbs./cu. ft.
Particle Density	75 lbs./cu. ft.
Bulk Density	45 lbs./cu. ft.
Thermal Conductivity	1 BTU/sq.ft./hr./F./in.
Reactivation Temperature Range	250-600°F

REAGENTS FOR FORMALDEHYDE DETECTION

Concentrated sulfuric acid containing formaldehyde readily reacts with aromatic hydrocarbons, particularly, with hydroxyl substituted benzene functional groups. These reactions may be conducted at room temperature or on gentle warming. Ordinarily, red, violet or green colorations or precipitation occurs if formaldehyde is added to solutions as suspensions of the organic compounds. The addition of concentrated sulfuric acid greatly enhances the speed of reactions. The precise composition of the reaction product is not known:

The concentrated sulfuric acid which is both an oxidant and dehydrant probably brings about first a condensation of the aromatic compounds with formaldehyde, and then oxidizes the resulting di-arylmethylene compound to colored P-quinoidal products. For example, catechol may undergo the following reactions:



In accord with this explanation (LeRosen Anal. Chem. 24 (1952), 1338) which can apply to various derivatives of benzene, the color reaction occurs with only those aromatic compounds which possess a free para position as a para hydroxyl group in order that an oxidation to colored p-quinoidal compounds can ensue through the action of the concentrated sulfuric acid. Certain benzene substituted compounds which are sterically hindered may not react as readily to form colored quinoidal products. However, certain ethers, such as a dimethyl ether derivative of catechol readily form a colored complex without any hindrance of reaction whatsoever.

PROPOSED GLYCOL DETECTION SYSTEM

The proposed glycol detection system is shown on the accompanying flow diagram. The ethylene glycol vapor comes in contact with a strong oxidizing agent as periodic acid and is oxidized to formaldehyde. The formaldehyde vapor reacts with an organic reagent such as a substituted catechol to form a colored methylene substitution compound. This colored complex is selectively adsorbed on a silica gel substrate which has been treated with sulfuric acid. The color reaction is enhanced and catalyzed by the polar acidic character (hydrosulfate) of the silica gel and the rate of reaction determined by the intensity of the color band developed or possibly by frontal analysis (i.e, movement of band as a function of time). The concentration of ethylene glycol may therefore be quantitated rapidly and precisely. (Figure 7)

SPECIFICITY

The color reaction between formaldehyde and a dialkyl ether of catechol was observed to be unaffected by the various reagents listed below:

1) Aldehydes, C_1 to C_5
2) Ketones - Methyl Ethyl Ketone & Methyl Isobutyl Ketone
3) Alcohols, C_1 to C_5
4) Ammonia
5) Benzene
6) Acrolein
7) Acids, C_1 to C_5
8) Chlorobenzene
9) Cyclohexanol
10) p-dioxane
11) Ethyl Acetate
12) Mercaptans: Ethyl, Methyl and Propyl Mercaptan
13) Freon 11
14) Hydrogen Chloride
15) Hydrogen Sulfide
16) Dichloromethane
17) Phenol
18) Hydrocarbons, C_1 to C_4
19) Toluene
20) Propylene
21) Trichloroethylene
22) Xylene

This technique has been thoroughly evaluated for all of the compounds listed and has been found to be specific for ethylene glycol. No interferences have been observed experimentally.

Effect of Flow Rate

Table XII shows the effect of flow rate on ethylene glycol reaction time at various temperatures. Flow rates in the range of 20 to 85 standard cc per minute (ccm) give sensibly constant values, whereas flow rates of the order of 10 ccm generally require longer times for the reaction to occur. A possible explanation of the longer response time is the non-equilibrium condition at this lower flow rate. Figure 8 graphically shows the effect of flow rate at the various temperatures.

TABLE XII

Effect of Flow Rate on Reaction Time at Various Temperatures

Glycol Flow Rate - 80 ccm
Air-Water Flow Rate - 30 ccm

Temperature °F.	Mixed Flow Rate 10.1 ccm	22.5 ccm	57.3 ccm	85.1 ccm
100	7	8	8	8
95	14	14	15	13
90	18	20	16	16
85	22	22	21	21
80	29	26	26	27
75	35	30	32	33
70	45	39	39	41
65	50	44	45	46
60	50	54	51	51
55	62	58	55	57
50	69	64	60	60
45	67	61	61	63
40	69	67	67	60

Ethylene Glycol-Water Dew Points

Table XIII gives the dew point of varying ratios of ethylene glycol-water mixtures in the temperature range of 40 to 80°F. The concentration of ethylene glycol was observed to be independent of the water vapor or humidity content over the ranges of dew points investigated.

Effect of Oxygen on Ethylene Glycol Determination

An experiment was performed at ambient conditions of temperature (75°F.) and a reduced pressure of 250 mm. Pure oxygen was allowed to flow over water and glycol at flow rates of 30 and 80 ccm respectively. The combined flow rate was adjusted to be 57.3 ccm and the glycol concentration measured by means of the glycol detection tube and polarographically. The response time of the tube was observed to be 30 seconds and the concentration calculated to be exactly 1.0 ppm. This is in excellent agreement with the results obtained using air and nitrogen. Pure oxygen at reduced pressures, therefore, does not alter the response to the glycol detection tubes.

Storage Life

Thirty glycol detection tubes were sealed in polyethylene and their response times measured over a period of 3 months. The response time was not observed to deviate more than 10 per cent over this extended period. The glycol tubes are therefore stable to periods in excess of 3 months.

TABLE XIII

Composition	Water Bath Temperature, °F.	Dew Point, °F.
99% Ethylene Glycol	40	-23
	50	-18
	60	-11
	70	- 8 or -7
	80	- 1
90% Ethylene Glycol	40	12
	50	20
	60	28
	70	35
	80	44
80% Ethylene Glycol	40	22
	50	31
	60	40
	70	49
	80	58
70% Ethylene Glycol	40	27
	50	35
	60	44
	70	53
	80	62
60% Ethylene Glycol	40	31
	50	40
	60	49
	70	58
	80	67
50% Ethylene Glycol	40	35
	50	44
	60	54
	70	64
	80	73

Sensitivity

The sensitivity of the detector tube was established by taking an aliquot sample of the ethylene glycol and affecting *a priori* oxidation to formaldehyde (see Fig. 9, schematic of Glycol Apparatus). The oxidation of the ethylene glycol proceeds according to the following equation:

$$CH_2OH \quad CH_2OH + HIO_4 \rightarrow HCHO + HIO_3 + H_2O$$

The formaldehyde content therefore gives a measure of the ethylene glycol concentration. Figure 8 gives a plot of the current as a function of response time (dark line). A plot is given on the same graph of the current versus the temperature of the glycol and water bath (dotted line). The current is empirically related to the concentration according to the following expression:

$$i = nFACD^{\frac{1}{2}}\sqrt{\frac{1}{\pi t}}$$

i = current, microamperes
n = number electrons
F = Faradays
A = area of electrode surface (cm^2)
C = concentration (moles/liter)
D = diffusion coefficient (cm^2/sec.)
π = constant
t = time, seconds

A calibration curve of a pure formaldehyde standard is given in Figure 10.

Ethylene glycol was determined to concentration levels as low as 0.1 ppm. At ambient conditions of temperature (75°F.), the ethylene glycol concentration was observed to be 0.99 ppm at a glycol flow rate of 80 ccm, air-water flow rate of 30 ccm, and a mixed flow rate (glycol-water vapor) of 57.3 ccm. An average response time for the reaction to occur on the substrate was of the order of 30 seconds. Excellent agreement was obtained on several consecutive runs. A typical polarogram is shown in Figure 11.

Future Work

A) Optimization of glycol detector tube

1) Seal between reagent - study boundary effect
2) Particle size of reagents and adsorbents
3) Geometry of tube
4) Frontal analysis of chromatographic band
5) Rate of movement of band as function of flow rate
6) Method of quantitation, e.g., use of calibrated syringe to displace known amount of air at a specified rate

B) Fabrication of tubes - Prepare 25 tubes and air displacement apparatus for evaluation in environmental chambers

CONCLUSIONS

Ethylene glycol is readily oxidized by periodic acid to formaldehyde. Formaldehyde may be specifically determined without any interferences by its reaction with a substituted catechol compound. The color development is enhanced by an acid precursor which is adsorbed into a specially purified grade of silica gel. Quantitation of the amount of ethylene glycol is made by rapidity of of color development as well as rate of movement of the color band. The proposed system is specific for ethylene glycol and the catechol dimethyl ether gives a well defined lavender band which is extremely sensitive to ethylene glycol.

Institute for Research
1714 Rice Boulevard
Houston, Texas 77005

August 1, 1969

Figure 1

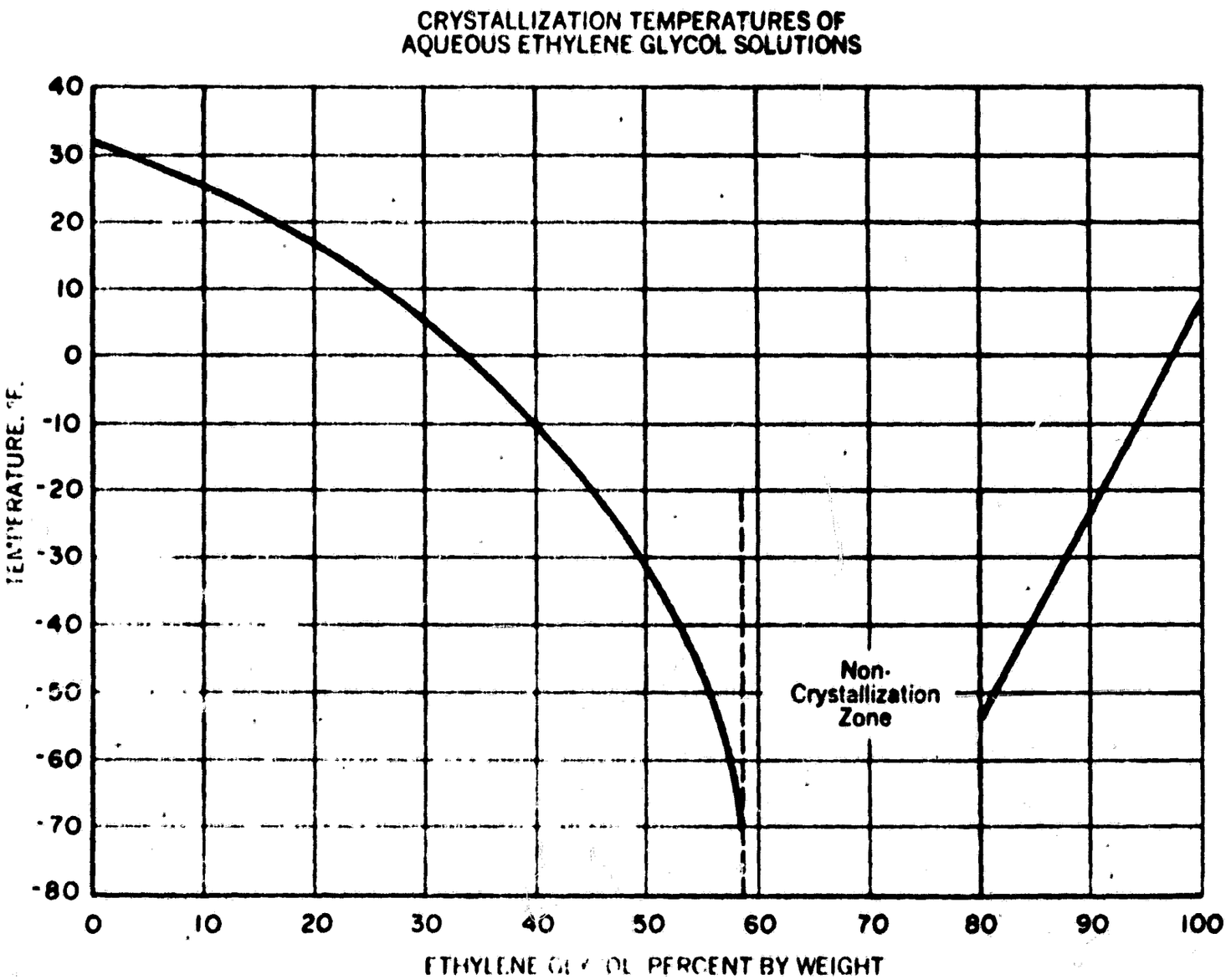

CRYSTALLIZATION TEMPERATURES OF
AQUEOUS ETHYLENE GLYCOL SOLUTIONS
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
TEMPERATURE, °F.
Non-
Crystallization
Zone
0
10
20
30
40
50
60
70
80
90
100
ETHYLENE GLYCOL PERCENT BY WEIGHT

Figure 2

WATER VAPOR DEW POINT OVER
AQUEOUS ETHYLENE GLYCOL SOLUTION

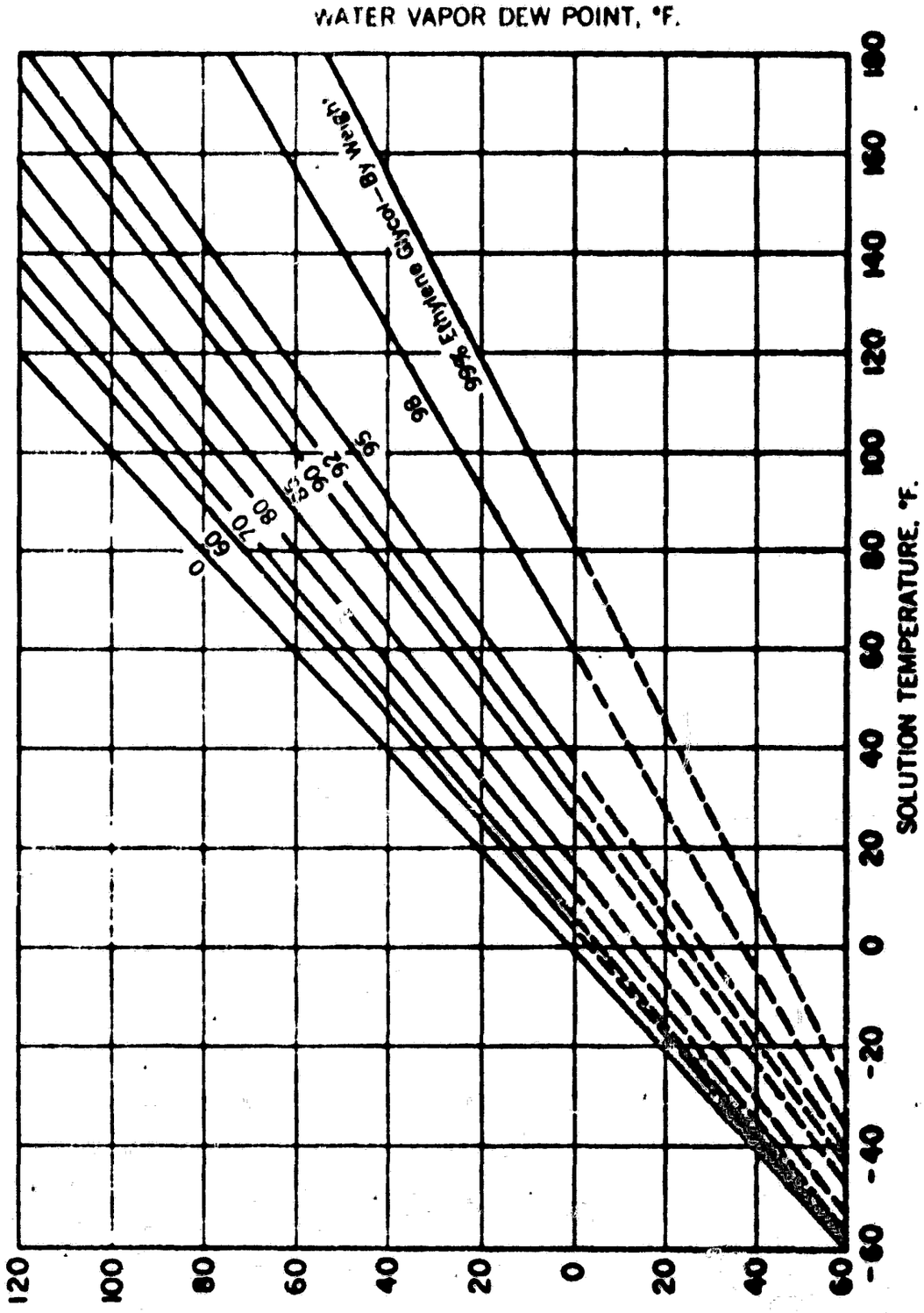


Figure 3

THERMAL CONDUCTIVITY OF
ETHYLENE GLYCOL—WATER MIXTURES

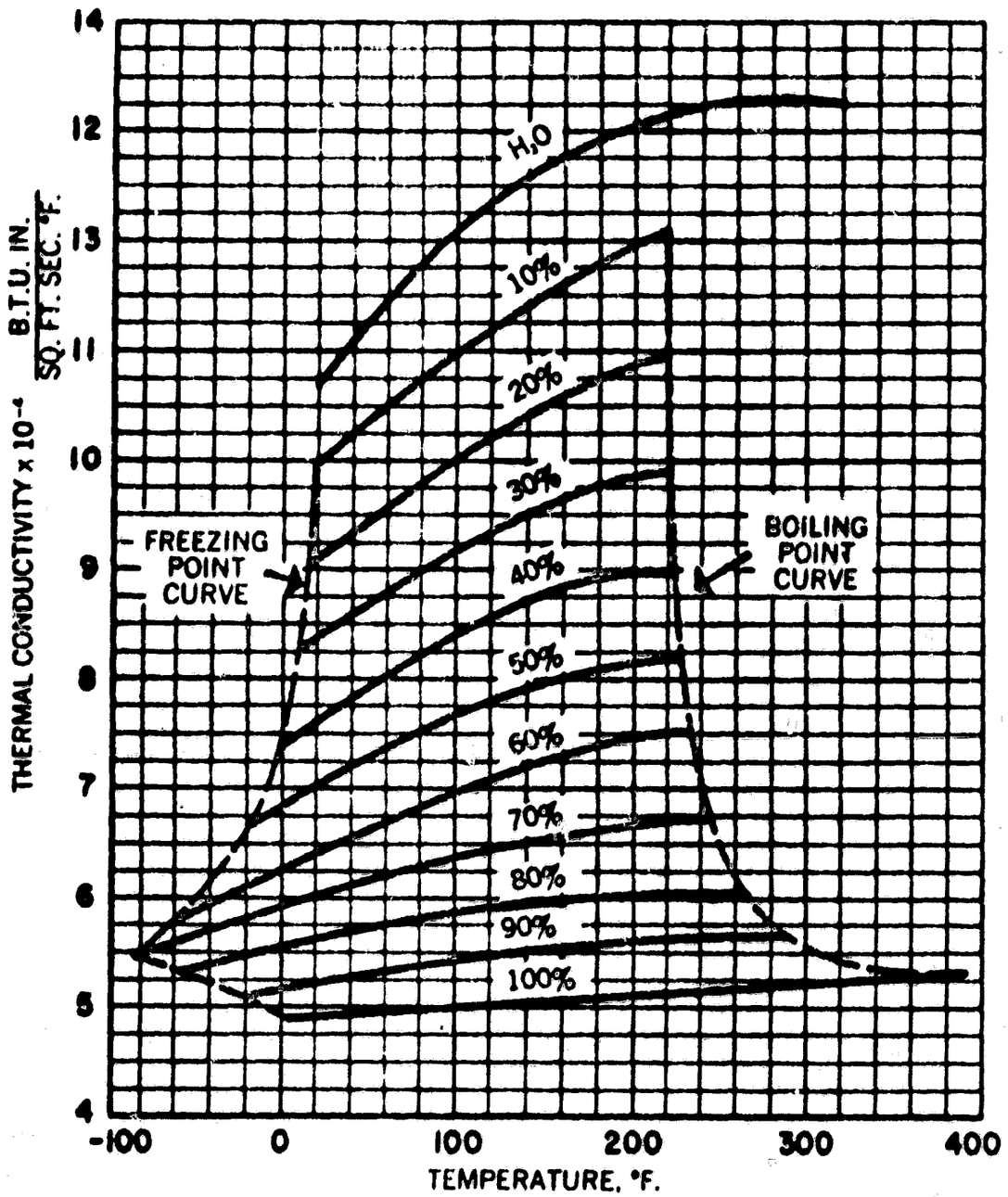
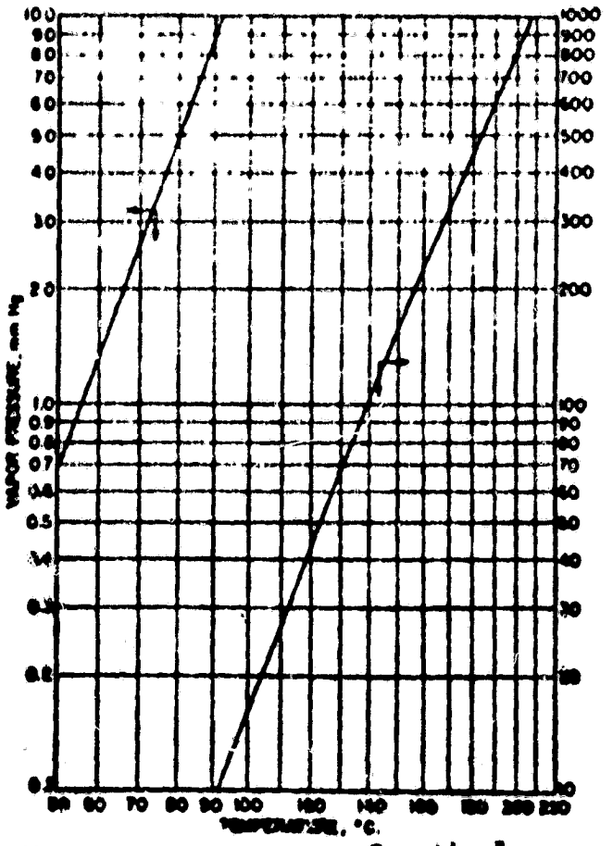
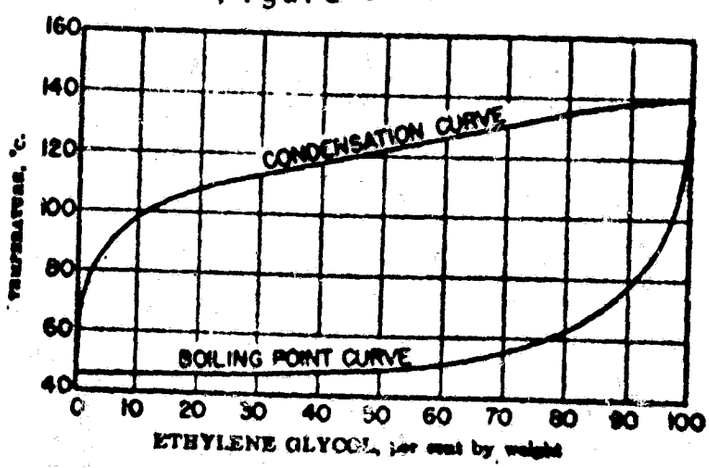


Figure 4



Vapor pressure of ethylene glycol at various temperatures.

Figure 5



Boiling point diagram for ethylene glycol-water system.

Figure 6

EQUILIBRIUM ADSORPTION OF WATER BY SILICA GEL

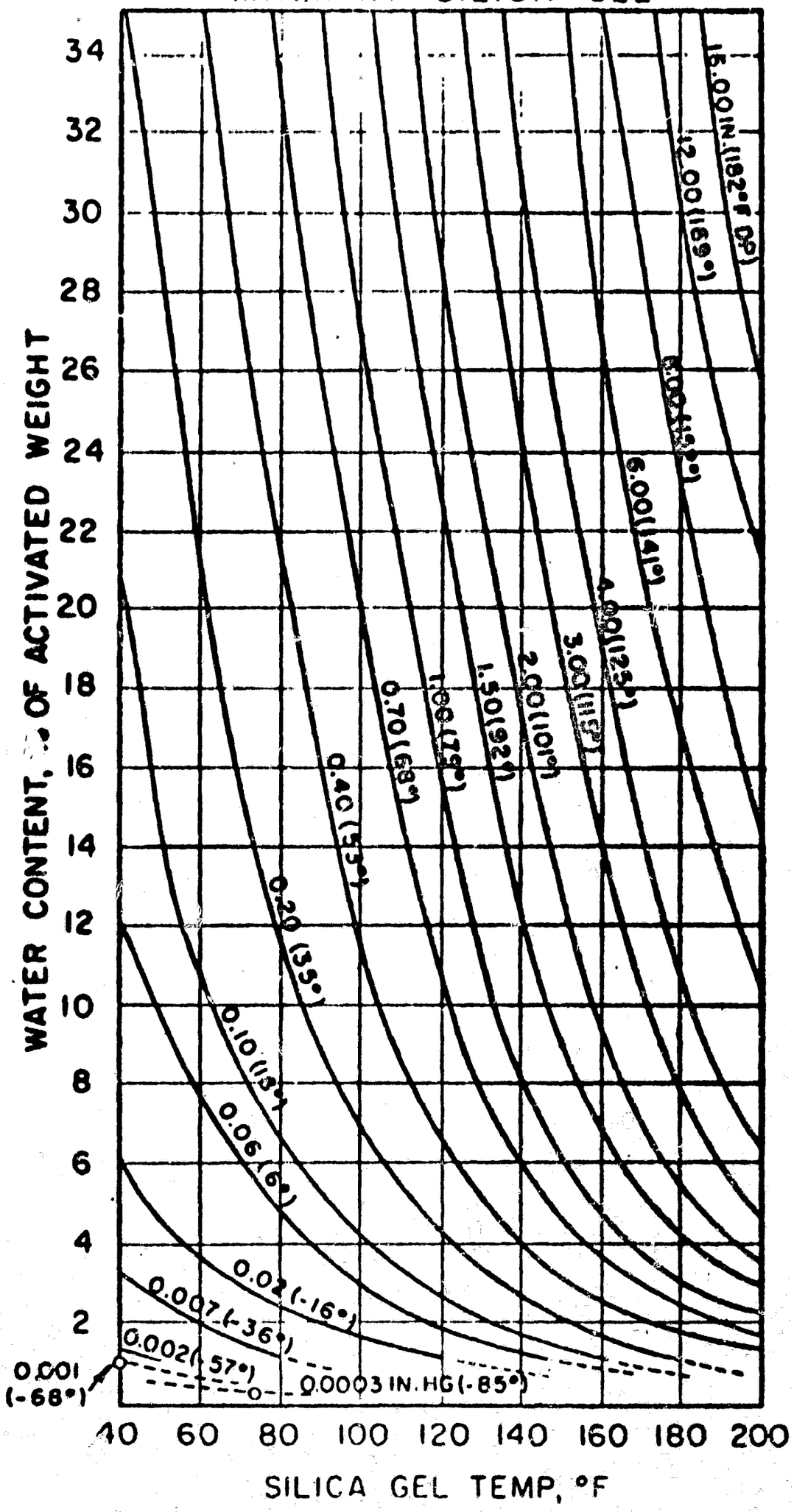
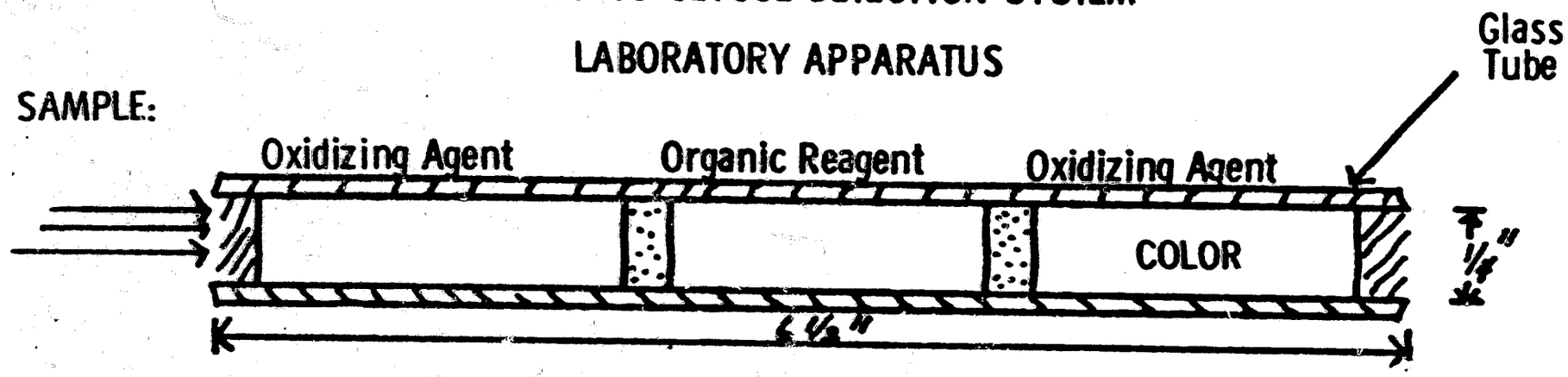


Figure 7

COLORIMETRIC GLYCOL DETECTION SYSTEM

LABORATORY APPARATUS



PRINCIPAL OF OPERATION

(1) GLYCOL + ACID $\xrightarrow{\text{OXIDATION}}$ ALDEHYDE

(2) ALDEHYDE + REAGENT $\xrightarrow{\text{CONDENSATION}}$ METHYLENE COMPOUND

(3) METHYLENE COMPOUND + ACID $\xrightarrow{\text{OXIDATION}}$ COLOR CHANGE

CHEMICALS SELECTED

(1) OXIDIZING AGENT - PERIODIC ACID

(2) ORGANIC REAGENT - CATECHOL DIMETHYL ETHER

(3) OXIDIZING AGENT - SULFURIC ACID
(WET/LAB : DRY/FLIGHT)

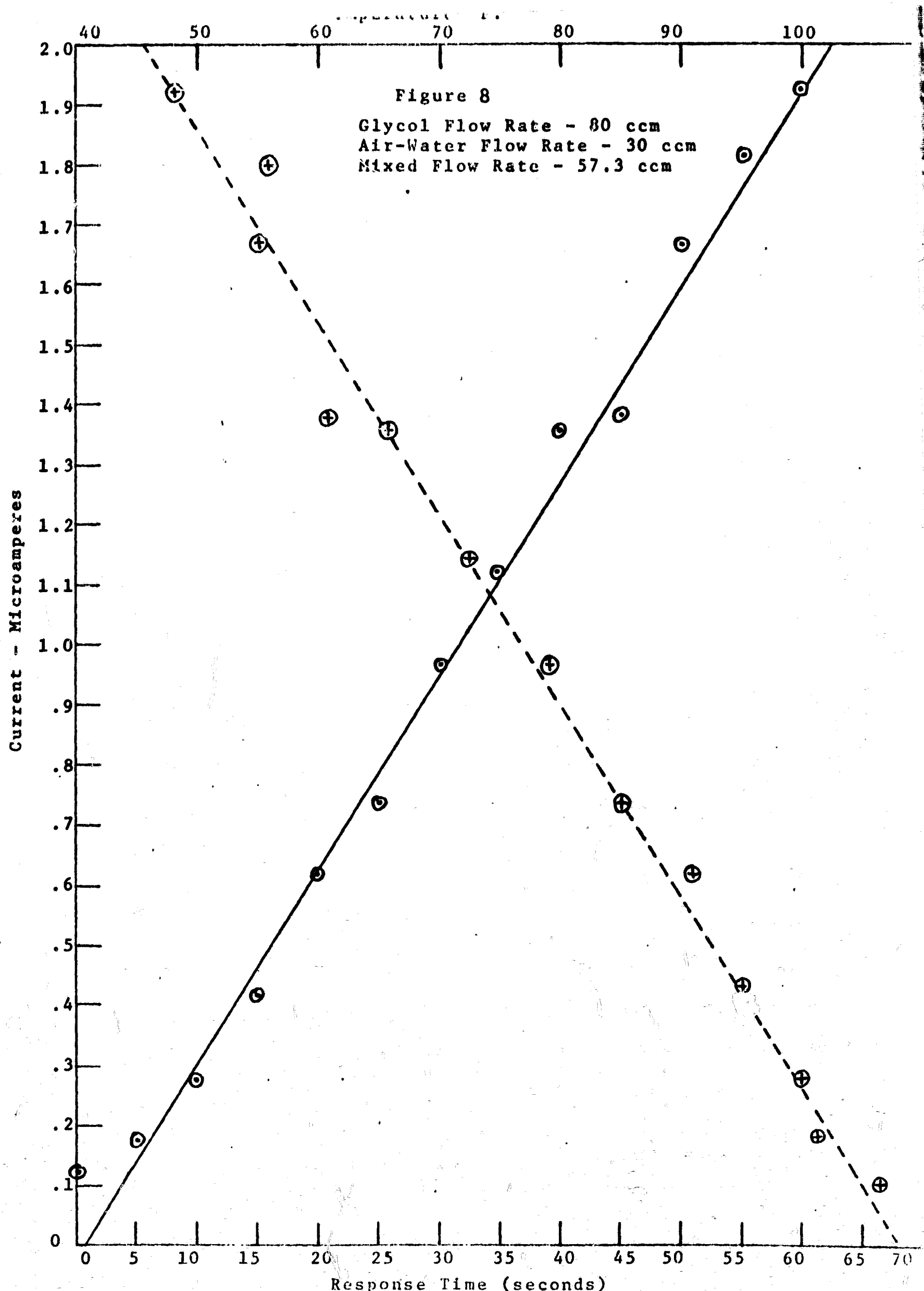


Figure 8
Glycol Flow Rate - 80 ccm
Air-Water Flow Rate - 30 ccm
Mixed Flow Rate - 57.3 ccm
Current - Microamperes
Response Time (seconds)
40
50
60
70
80
90
100
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70

Figure 9

GLYCOL APPARATUS

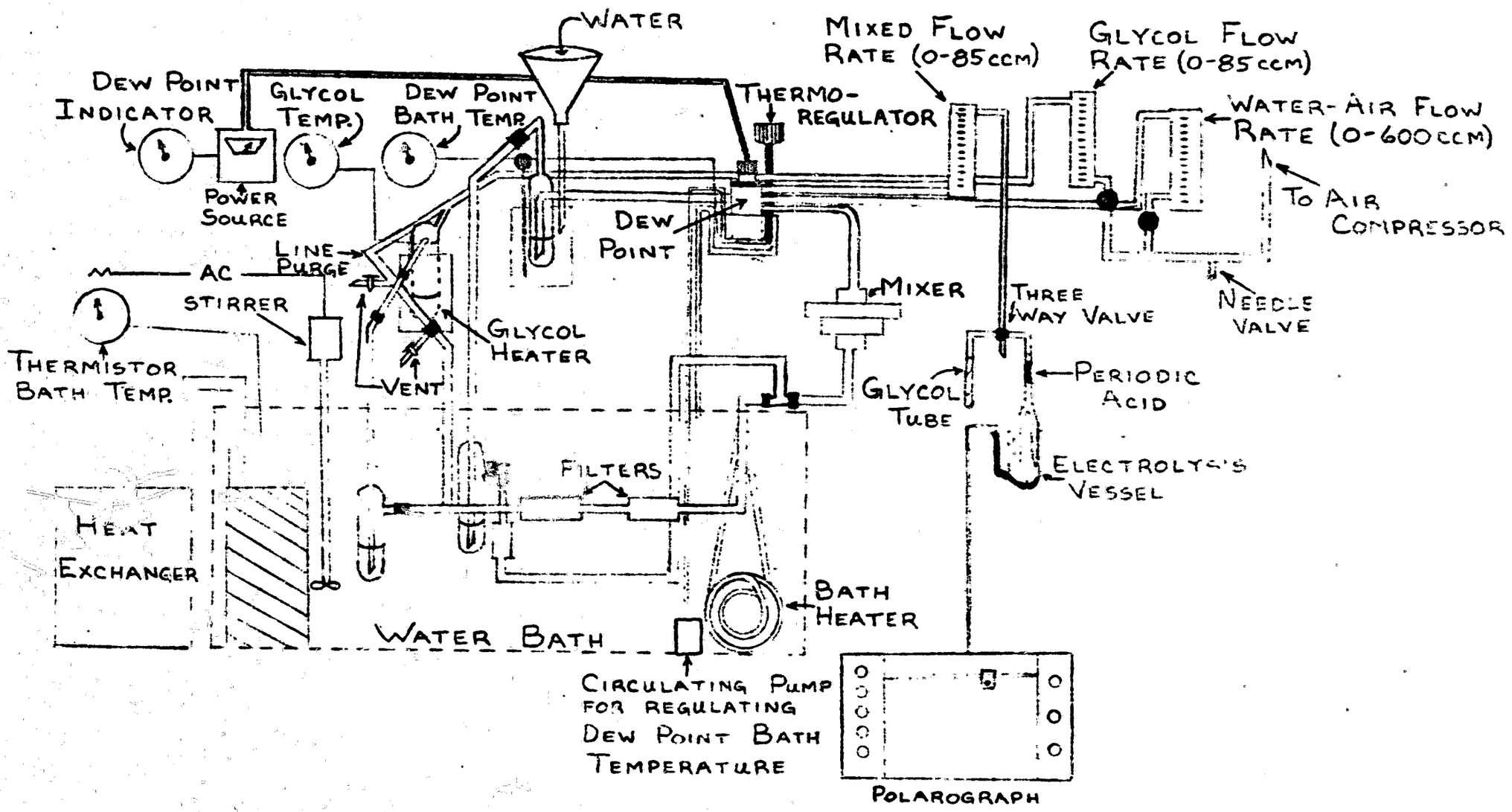


Figure 10

Standard Working Curve for
Reagent Grade Formaldehyde

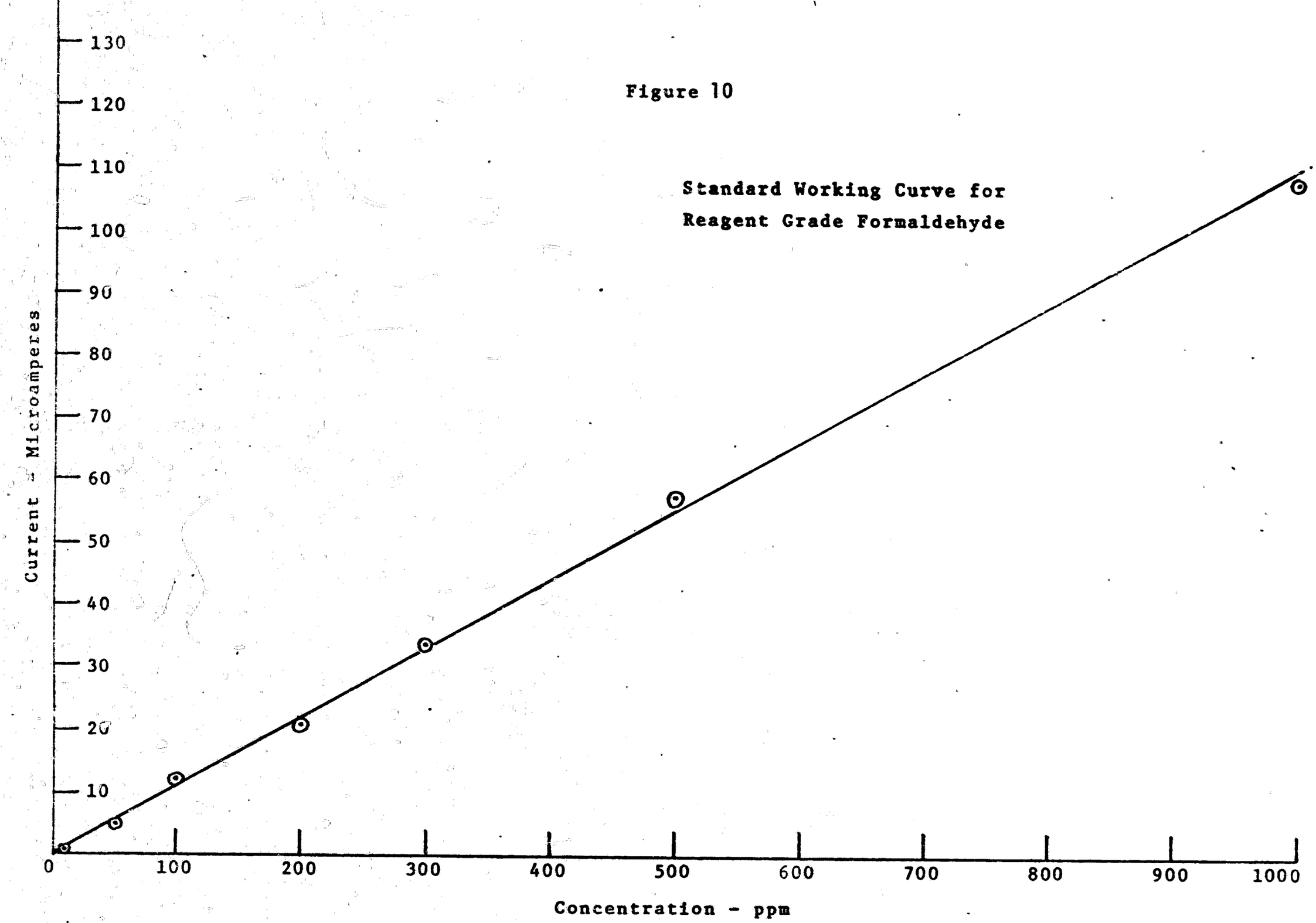


Figure 11

65° BATH TEMP

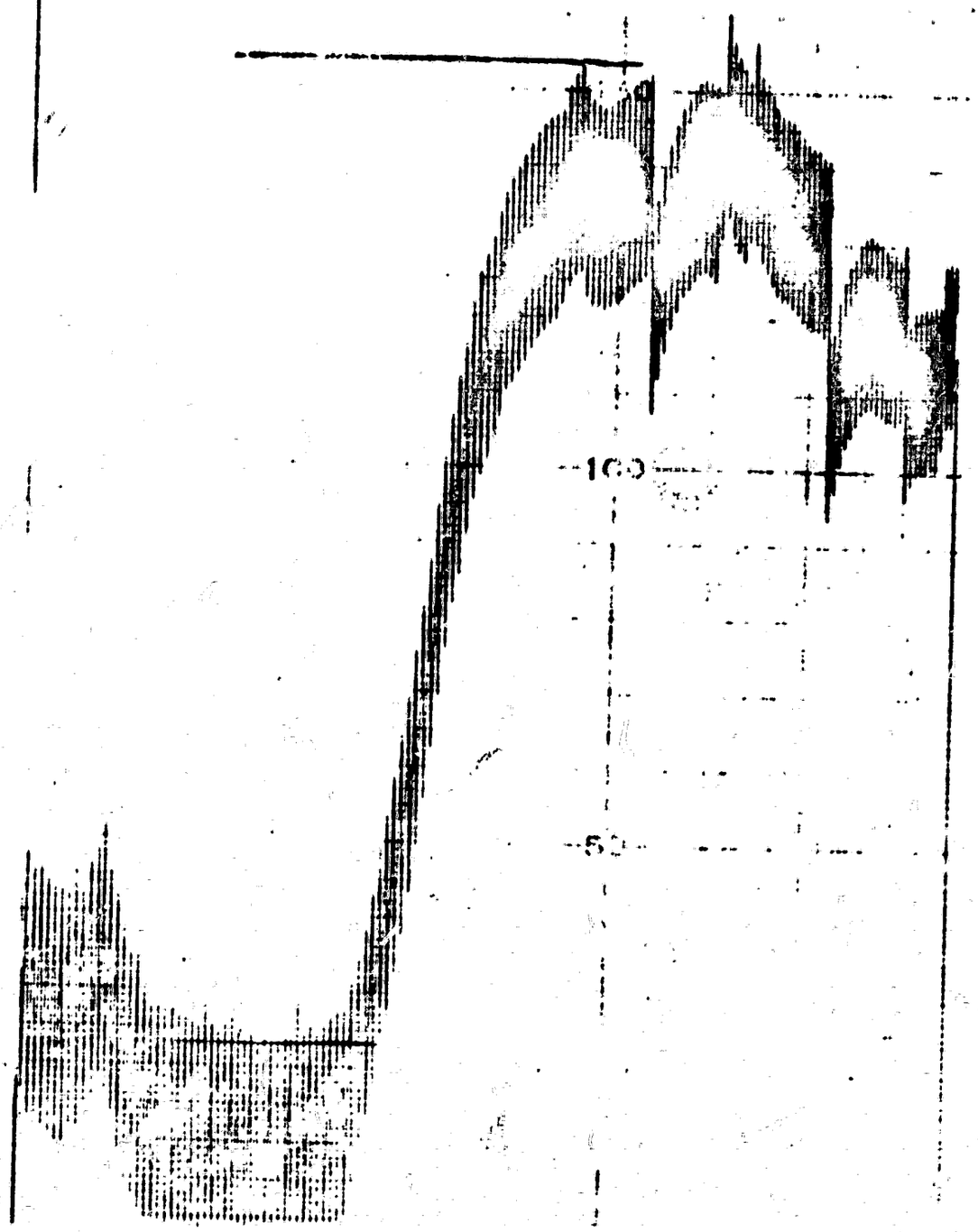
TUBE RESPONSE = 46.8 sec

d.p = 2.1

G_f = 30 ccm/min

A_f = 30 ccm/min

M_f = 25 ccm/min

SENSI = .010

CONC. = 0.67 ppm