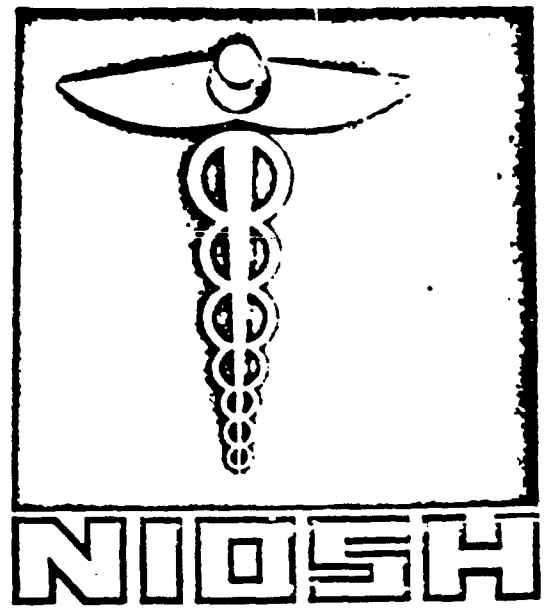

NIOSH MANUAL of ANALYTICAL METHODS

U.S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE
Public Health Service
Center for Disease Control
National Institute for Occupational Safety and Health

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PLAINTIFF'S EXHIBIT
CEL-292

ORGANIC SOLVENTS IN AIR

Physical and Chemical Analysis Branch

Analytical Method

Analyte:	Organic Solvents (See Table 1)	Method No:	P&CAM 127
Matrix:	Air	Range:	For the specific compound, refer to Tables I&II
Procedure:	Adsorption on charcoal desorption with carbon disulfide, GC		
Date Issued:	9/15/72	Precision:	10.5% RSD
Date Revised:	7/15/74	Classification:	See Table 1

1. Principle of the Method

   1.1 A known volume of air is drawn through a charcoal tube to trap the organic vapors present.

   1.2 The charcoal in the tube is transferred to a small, graduated test tube and desorbed with carbon disulfide.

   1.3 An aliquot of the desorbed sample is injected into a gas chromatograph.

   1.4 The area of the resulting peak is determined and compared with areas obtained from the injection of standards.

2. Range and Sensitivity

   The lower limit in mg/sample for the specific compound at 16 x 1 attenuation on a gas chromatograph fitted with a 10:1 splitter is shown in Table 1. This value can be lowered by reducing the attenuation or by eliminating the 10:1 splitter.

3. Interferences

   3.1 When the amount of water in the air is so great that condensation actually occurs in the tube, organic vapors will not be trapped. Preliminary experiments indicate that high humidity severely decreases the breakthrough volume.

   3.2 When two or more solvents are known or suspected to be present in the air, such information including their suspected identities, should be transmitted with the sample; since with differences in polarity, one may displace another from the charcoal.

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3.3 It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Hence, retention time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

3.4 If the possibility of interference exists, separation conditions (column packing, temperatures, etc.) must be changed to circumvent the problem.

4. Precision and Accuracy

4.1 The mean relative standard deviation of the analytical method is 8%. (Ref. 11.4).

4.2 The mean relative standard deviation of the analytical method plus field sampling using an approved personal sampling pump is 10% (Ref. 11.4). Part of the error associated with the method is related to uncertainties in the sample volume collected. If a more powerful vacuum pump with associated gas-volume integrating equipment is used, sampling precision can be improved.

4.3 The accuracy of the overall sampling and analytical method is 10% (NIOSH's unpublished data) when the personal sampling pump is calibrated with a charcoal tube in the line.

5. Advantages and Disadvantages of the Method

5.1 The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. The tubes are analyzed by means of a quick, instrumental method. The method can also be used for the simultaneous analysis of two or more solvents suspected to be present in the same sample by simply changing gas chromatographic conditions from isothermal to a temperature-programmed mode of operation.

5.2 One disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the sample value obtained for the backup section of the charcoal trap exceeds 25% of that found on the front section, the possibility of sample loss exists. During sample storage the more volatile compounds will migrate throughout the tube until equilibrium is reached (33% of the sample on the backup section).

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5.3 Furthermore, the precision of the method is limited by the reproducibility of the pressure drop across the tubes. This drop will affect the flow rate and cause the volume to be imprecise, because the pump is usually calibrated for one tube only.

6. Apparatus

6.1 An approved and calibrated personal-sampling pump for personal samples. For an area sample any vacuum pump whose flow can be determined accurately at 1 liter per minute or less.

6.2 Charcoal tubes: glass tube with both ends flame sealed, 7 cm long with a 6-mm O.D. and a 4-mm I.D., containing 2 sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600°C prior to packing. The absorbing section contains 100 mg of charcoal, the backup section 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of silylated glass wool is placed in frontof the absorbing section. The pressure drop across the tube must be less than one inch of mercury at a flow rate of 1 lpm.

6.3 Gas chromatograph equipped with a flame ionization detector.

6.4 Column (20 ft x 1/8 in) with 10% FFAP stationary phase on 80/100 mesh, acid-washed DMCS Chromosorb W solid support. Other columns capable of performing the required separations may be used.

6.5 A mechanical or electronic integrator or a recorder and some method for determining peak area.

6.6 Glass stoppered micro tubes. The 2.5-ml graduated microcentrifuge tubes are recommended.

6.7 Hamilton syringes: 10 µl, and convenient sizes for making standards.

6.8 Pipets: 0.5 ml delivery pipets or 1.0 ml type graduated in 0.1 ml increments.

6.9 Volumetric flasks: 10 ml or convenient sizes for making standard solutions.

7. Reagents

7.1 Spectroquality carbon disulfide (Matheson Coleman and Bell)

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7.2 Sample of the specific compound under study, preferably chromatoquality grade.

7.3 Bureau of Mines Grade A helium.

7.4 Prepurified hydrogen.

7.5 Filtered compressed air.

Procedure

8.1 Cleaning of Equipment. All glassware used for the laboratory analysis should be detergent washed and thoroughly rinsed with tap water and distilled water.

8.2 Calibration of Personal Pumps. Each personal pump must be calibrated with a representative charcoal tube in the line. This will minimize errors associated with uncertainties in the sample volume collected.

8.3 Collection and Shipping of Samples

8.3.1 Immediately before sampling, the ends of the tube should be broken to provide an opening at least one-half the internal diameter of the tube (2mm).

8.3.2 The smaller section of charcoal is used as a back-up and should be positioned nearest the sampling pump.

8.3.3 The charcoal tube should be vertical during sampling.

8.3.4 Air being sampled should not be passed through any hose or tubing before entering the charcoal tube.

8.3.5 The flow, time, and/or volume must be measured as accurately as possible. The sample should be taken at a flow rate of 1 lpm or less to attain the total sample volume required. The minimum and maximum sample volumes that should be collected for each solvent are shown in Table 1. The minimum volume quoted must be collected if the desired sensitivity is to be achieved.

8.3.6 The temperature and pressure of the atmosphere being sampled should be measured and recorded.

8.3.7 The charcoal tubes should be capped with the supplied plastic caps immediately after sampling. Under no circumstances should rubber caps be used.

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8.3.8 One tube should be handled in the same manner as the sample tube (break, seal, and transport), except that no air is sampled through this tube. This tube should be labeled as a blank.

8.3.9 Capped tubes should be packed tightly before they are shipped to minimize tube breakage during shipping.

8.3.10 Samples of the suspected solvent(s) should be submitted to the laboratory in containers furnished by NIOSH for such purpose. These liquid bulk samples should not be transported in the same container as the samples or blank tube. If possible, a bulk air sample (at least 50ℓ air drawn through tube) should be shipped for qualitative identification purposes.

8.4 Analysis of Samples

8.4.1 Preparation of Samples. In prepration for analysis, each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a small stoppered test tube. The separating section of foam is removed and discarded; the second section is transferred to another test tube. These two sections are analyzed separately.

8.4.2 Desorption of Samples. Prior to analysis, one-half ml of carbon disulfide is pipetted into each test tube. (All work with carbon disulfide should be performed in a hood because of its high toxicity.) Tests indicate that desorption is complete in 30 minutes if the sample is stirred occasionally during this period. The use of graduated glass-stoppered, microcentrifuge tubes is recommended so that one can observe any apparent change in volume during the desorption process. Carbon disulfide is a very volatile solvent, so volume changes can occur during the desorption process depending on the surrounding temperature. The initial volume occupied by the charcoal plus the 0.5 ml CS_2 should be noted and corresponding volume adjustments should be made whenever necessary just before GC analysis.

8.4.3 GC Conditions. The typical operating conditions for the gas chromatograph are:

1. 85 cc/min. (70 psig) helium carrier gas flow.
2. 65 cc/min. (24 psig) hydrogen gas flow to detector.
3. 500 cc/min. (50 psig) air flow to detector.
4. 200°C injector temperature.

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5. 200°C manifold temperature (detector)
6. Isothermal oven or column temperature - refer to Table 1 for specific compounds.

8.4.4 Injection. The first step in the analysis is the injection of the sample into the gas chromatograph. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 µl syringe is first flushed with solvent several times to wet the barrel and plunger. Three microliters of solvent are drawn into the syringe to increase the accuracy and reproducibility of the injected sample volume. The needle is removed from the solvent, and the plunger is pulled back about 0.2 µl to separate the solvent flush from the sample with a pocket of air to be used as a marker. The needle is then immersed in the sample, and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

8.4.5 Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

8.5 Determination of Desorption Efficiency

8.5.1 Importance of determination. The desorption efficiency of a particular compound can vary from one laboratory to another and also from one batch of charcoal to another. Thus, it is necessary to determine at least once the percentage of the specific compound that is removed in the desorption process for a given compound, provided the same batch of charcoal is used. The Physical and Chemical Analysis Branch of NIOSH has found that the desorption efficiencies for the compounds in Table 1 are between 81% and 100% and vary with each batch of charcoal.

8.5.2 Procedure for determining desorption efficiency. Activated charcoal equivalent to the amount in the first section of the sampling tube (100 mg) is measured into a 5cm, 4-mm I.D. glass tube, flame-sealed at one end (similar to commercially available culture tubes). This charcoal must be from the same batch as that used in obtaining the samples and can be obtained from unused charcoal tubes. The open end is capped

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with Parafilm. A known amount of the compound is injected directly into the activated charcoal with a microliter syringe, and the tube is capped with more Parafilm. The amount injected is usually equivalent to that present in a 10-liter sample at a concentration equal to the federal standard.

At least five tubes are prepared in this manner and allowed to stand for at least overnight to assure complete absorption of the specific compound onto the charcoal. These five tubes are referred to as the samples. A parallel blank tube should be treated in the same manner except that no sample is added to it. The sample and blank tubes are desorbed and analyzed in exactly the same manner as the sampling tube described in Section 8.3.

Two or three standards are prepared by injecting the same volume of compound into 0.5 ml of CS_2 with the same syringe used in the preparation of the sample. These are analyzed with the samples.

The desorption efficiency equals the difference between the average peak area of the samples and the peak area of the blank divided by the average peak area of the standards, or

$$\text{desorption efficiency} = \frac{\text{Area sample} - \text{Area blank}}{\text{Area standard}}$$

9. Calibration and Standards

It is convenient to express concentration of standards in terms of mg/0.5 ml CS_2 because samples are desorbed in this amount of CS_2. To minimize error due to the volatility of carbon disulfide, one can inject 20 times the weight into 10 ml of CS_2. For example, to prepare a 0.3 mg/0.5 ml standard, one would inject 6.0 mg into exactly 10 ml of CS_2 in a glass-stoppered flask. The density of the specific compound is used to convert 6.0 mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/0.5ml versus peak area.

NOTE: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations and variations during the same day of the FID response.

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10. Calculations

10.1 The weight, in mg, corresponding to each peak area is read from the standard curve for the particular compound. No volume corrections are needed, because the standard curve is based on mg/0.5 ml CS_2 and the volume of sample injected is identical to the volume of the standards injected.

10.2 Corrections for the blank must be made for each sample.

$$\text{Correct mg} = mg_s - mg_b$$

where:

mg_s = mg found in front section of sample tube

mg_b = mg found in front section of blank tube

A similar procedure is followed for the backup sections.

10.3 The corrected amounts present in the front and backup sections of the same sample tube are added to determine the total measured amount in the sample.

10.4 This total weight is divided by the determined desorption efficiency to obtain the total mg per sample.

10.5 The volume of air sampled is converted to standard conditions of of 25°C and 760 mm Hg.

$$V_s = V \times \frac{P}{760} \quad \frac{298}{T+273}$$

where:

V_s = volume of air in liters at 25°C and 760 mm Hg

V = volume of air in liters as measured

P = Barometric pressure in mm Hg

T = Temperature of air in degree centigrade

10.6 The concentration of the organic solvent in the air sampled can be expressed in mg per m^3, which is numerically equal to µg per liter of air

$$mg/m^3 = \mu g/l = \frac{\text{total mg (Section 10.4) x 1000 (µg/mg)}}{V_s}$$

10.7 Another method of expressing concentration is ppm, defined as µl of compounds per liter of air

$$ppm = \mu l \text{ of compound}/V_s$$

$$ppm = \frac{\mu l \text{ of compound}}{V_s} \times \frac{24.45}{MW}$$

where:

24.45 = molar volume at 25°C and 760 mm Hg

MW = molecular weight of the compound (Table 1)

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11. References

11.1 White, L.D., D.G. Taylor, P.A. Mauer, and R.E. Kupel, "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," *Amer. Ind. Hyg. Assoc. J.*, 31:225 (1970).

11.2 Young, D.M. and A.D. Crowell, Physical Adsorption of Gases, Butterworths, London, 1962, pp. 137-146.

11.3 Federal Register, 37 (#202), 22139-22142 (October 18, 1972).

11.4 NIOSH Contract HSM-99-72-98, Scott Research Laboratories, Inc., "Collaborative Testing of Activated Charcoal Sampling Tubes for Seven Organic Solvents," pp. 4-22, 4-27 (1973).

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TABLE I

PARAMETERS ASSOCIATED WITH P&CAB ANALYTICAL METHOD NO. 127

Organic Solvent	Method Classification	Detection limit (mg/sample)	Sample Volume (ℓ) Minimum[a]	Maximum[b]	GC Column Temperature(°C)	Molecular Weight
Acetone	D	-	0.5	7.7	60	58.1
Benzene	A	0.01	0.5	55	90	78.1
Carbon tetrachloride	A	0.20	10	60	60	154.0
Chloroform	A	0.10	0.5	13	80	119
Dichloromethane	D	0.05	0.5	3.8	85	84.9
p-Dioxane	A	0.05	1	18	100	88.1
Ethylene dichloride	D	0.05	1	12	90	99.0
Methyl ethyl ketone	B	0.01	0.5	13	80	72.1
Styrene	D	0.10	1.5	34	150	104
Tetrachloroethylene	B	0.06	1	25	130	166
1,1,2-trichloroethane	B	0.05	10	97	150	133
1,1,1-trichloroethane (Methyl Chloroform)	B	0.05	0.5	13	150	133
Trichloroethylene	A	0.05	1	17	90	131
Toluene	B	0.01	0.5	22	120	92.1
Xylene	A	0.02	0.5	31	100	106

(a) Minimum volume, in liters, required to measure 0.1 times the OSHA standard

(b) These are breakthrough volumes calculated with data derived from a potential plot (reference 11.2) for activated coconut charcoal. Concentrations of vapor in air at 5 times the OSHA standard (reference 11.3) or 500 ppm, whichever is lower, 25°C, and 760 torr were assumed. These values will be as much as 50% lower for atmospheres of high humidity. The effects of multiple contaminants have not been investigated, but it is suspected that less volatile compounds may displace more volatile compounds (See 3.1 and 3.2)

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TABLE II

CHEMICALS WHICH HAVE GREATER THAN 80% DESORPTION EFFICIENCY BUT HAVE NOT BEEN THOROUGHLY TESTED BY NIOSH

Class E (Proposed)

Acrylonitrile
Allyl glycidyl ether
n-Amyl acetate
2-Butoxyethanol
n-Butyl acetate
n-Butyl alcohol
n-Butylglycidyl ether
Chlorobenzene
Cyclohexane
Cyclohexanone
o-Dichlorobenzene
p-Dichlorobenzene
Diethyl ether
N,N-Dimethyl aniline
Epichlorohydrin
2-Ethoxylethyl acetate
Ethyl acetate
Ethylbenzene
Ethyl butyl ketone
Fufural
Heptane
Hexane
Isoamyl acetate
Isobutyl acetate
Isobutyl alcohol
Isooctane
Isophorone
Isopropyl acetate
Isopropyl glycidyl ether
2,6-Lutidine
Methyl acetate
Methyl acrylate
Methyl n-butyl ketone
Methyl ethyl ketone
Methyl isobutyl ketone
Methyl methacrylate
α-Methyl styrene
p-Methyl styrene
n-Octane
3-Octanone
Pentane
2-Pentanone
α-pinene
n-Propyl acetate
1,1,2,2-Tetrachloroethane
Tetrahydrofuran
Trichlorotrifluoroethane (Freon 113)

Recommended Sample Size = 10ℓ

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FORMALDEHYDE IN AIR BY CHROMOTROPIC ACID

Scope:

This method describes a procedure for the determination of formaldehyde in air. Compounds yielding formaldehyde under color development conditions will interfere with the chromotropic acid test; they are 1) paraformaldehyde, 2) trioxane, 3) Celcon, and 4) sugars (PE and TMP). These compounds will generally be present as particulates and can be eliminated by placing a filter on the sample inlet.[1] Acetone, acrolein, acetaldehyde, diacetone alcohol, methanol and methylal[2] can interfere if present in sufficient concentration (Table I).

The method is sensitive to 375 micrograms per cubic meter of air (0.3 ppm) based on a sample collection rate of 1 SCFH. It takes advantage of the fact that formaldehyde forms a purple color with 1,8-dihydroxy-3, 6-naphthalene disulfonic acid (chromotropic acid) in the presence of sulfuric acid. The absorbance is measured at 580 mμ against a reagent blank.

Equipment:

1. Mine Safety Appliances Company Permissible Portable Pump Model G or equivalent.
2. 30 ml gas scrub bottles with spargers
3. 100 and 25 ml volumetric flasks
4. 1 and 5 ml Mohr Pipette
5. 2, 3, 5 and 10 ml volumetric pipettes
6. 10 and 50 ml burettes
7. Beckman Model DB-G Spectrophotometer, 1 cm silica cells
8. Ice bath
9. Boiling water bath
10. Millipore Field Monitors (0.8 μ pore size paper): Aerosol type Cat. No. MAW Go 37Ao

Reagents:

1. 100 μg/ml Stock Solution - Enough fine paraformaldehyde powder to assay 100 mg of formaldehyde (HCHO), 10 grams of sodium bisulfite, dissolve and dilute to one liter with water. Stable for at least two months.

2. 0.5% Chromotropic Acid (salt) solution - Dissolve 0.5 gram of 4,5-dihydroxy-2, 7-naphthalene disulfonic acid or 1,8-dihydroxy-3, 6-naphthalene disulfonic acid (disodium salt) in 100 ml of water. Keep refrigerated, stable for two weeks.

3. Reagent grade concentrated sulfuric acid.

4. 1% aqueous sodium bisulfite.

Standard Curve Preparation:

1. Label nine 100 ml volumetric flasks 0.1, 0.3, 0.5, 0.7, 1.0, 3.0, 5.0, 7.0, and 10.0 µg/ml respectively.

2. With pipettes add 0.1, 0.3, 0.5, 0.7, 1.0, 3.0, 5.0, 7.0, and 10.0 ml of the 100 µg/ml HCHO Stock Solution respectively, to the 100 ml volumetric flasks.

3. Dilute to the mark with 1% aqueous bisulfite solution, stopper and mix well. Save these standard solutions.

4. Label ten 25 ml volumetric flasks blank, 0.1, 0.3, 0.5, 0.7, 1.0, 3.0, 5.0, 7.0 and 10.0 µg/ml respectively.

5. Pipette 5 ml aliquots of the standard solutions to their respective 25 ml volumetrics. Use 5 ml of bisulfite solution for the blank.

6. From a 1 ml pipette add 0.5 ml of the chromotropic salt solution to the 25 ml volumetric flasks. Swirl to mix.

7. From a 50 ml burette add 12.5 ml of concentrated sulfuric acid while swirling the 25 ml flask in an ice bath. Remove the flask from the bath and stopper. Swirl again to ensure complete mixing.

8. Place the 25 ml flasks in a boiling water bath for 15 minutes. Time required for the water to resume boiling should be included in the 15 minutes.

9. Cool the 25 ml flasks in an ice bath; dilute to volume with water and mix. After cooling to room temperature add more water if necessary.

10. Record the absorbance at 580 mμ against the blank using 1 cm silica cells.

11. Plot absorbances versus μg/ml as in Figures I and II.

Procedure:

1. To each of two gas scrub bottles add 10 ml of bisulfite solution. Close openings until ready to sample.

2. Calibrate the Mine Safety pump to deliver 1 SCFH with impingers attached.

3. At sampling site set up the collector as shown in Figure III. Note: If paraformaldehyde, trioxane, Celcon and sugars (PE and TMP) are suspected to be present as particulates place the filter assembly before the sample unit.

4. Start airflow and continue scrubbing for at least 15 minutes. If the HCHO concentration is low, a longer scrub time will be required.

5. After sampling is complete disconnect the assembly and close the openings of the scrub bottles.

6. Pipette a 5 ml aliquot of the solution from the scrub bottle into a 25 ml volumetric flask and proceed as in Steps 6-10 under Standard Curve Preparation.

7. From the standard curve determine the concentration in μg/ml.

8. Calculate the ppm HCHO in Air from the following formula.

$$\text{ppm HCHO}^{*} = \frac{\mu g/Ml \times 10\ Ml}{1ft^3/hr \times \text{Scrub Time in hrs} \times 0.02595\ M^3/ft^3 \times 1293\ g/M}$$

ppm HCHO x 1293 = μg HCHO/cubic meter of air

* Adjusted to 25°C

References:

1. Sanders, F. D., "The Determination of Formaldehyde in Air", FDS 2-71, April 2, 1971, Chemcel Lab File 261.0.

2. Walker, J. F., Formaldehyde, Reinhold, 1964 pp 470-1.

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TABLE I

Effect of Interference on Formaldehyde Analyses

	ppm as HCHO	% Increase as HCHO
3 ppm HCHO (HCHO Std.)	3.00	- - -
3 ppm DAA + HCHO Std.	3.00	0.0
3 ppm DMK + HCHO Std.	3.05	1.7
3 ppm AcH + HCHO Std.	3.20	6.7
3 ppm Acrolein + HCHO Std.	3.70	23.3
3 ppm Meal + HCHO Std.	3.85	28.3
3 ppm MeOH + HCHO Std.	5.00	66.7 [1]
A mixture of 3 ppm each of HCHO, DAA, DMK, AcH, Acrolein, Meal, and MeOH	3.65	20.7

1. Scrubbing efficiency of MeOH in 1% bisulfite solution is negligible.

FIGURE 1

Calibration Curve for Chromotropic Acid and Formaldehyde

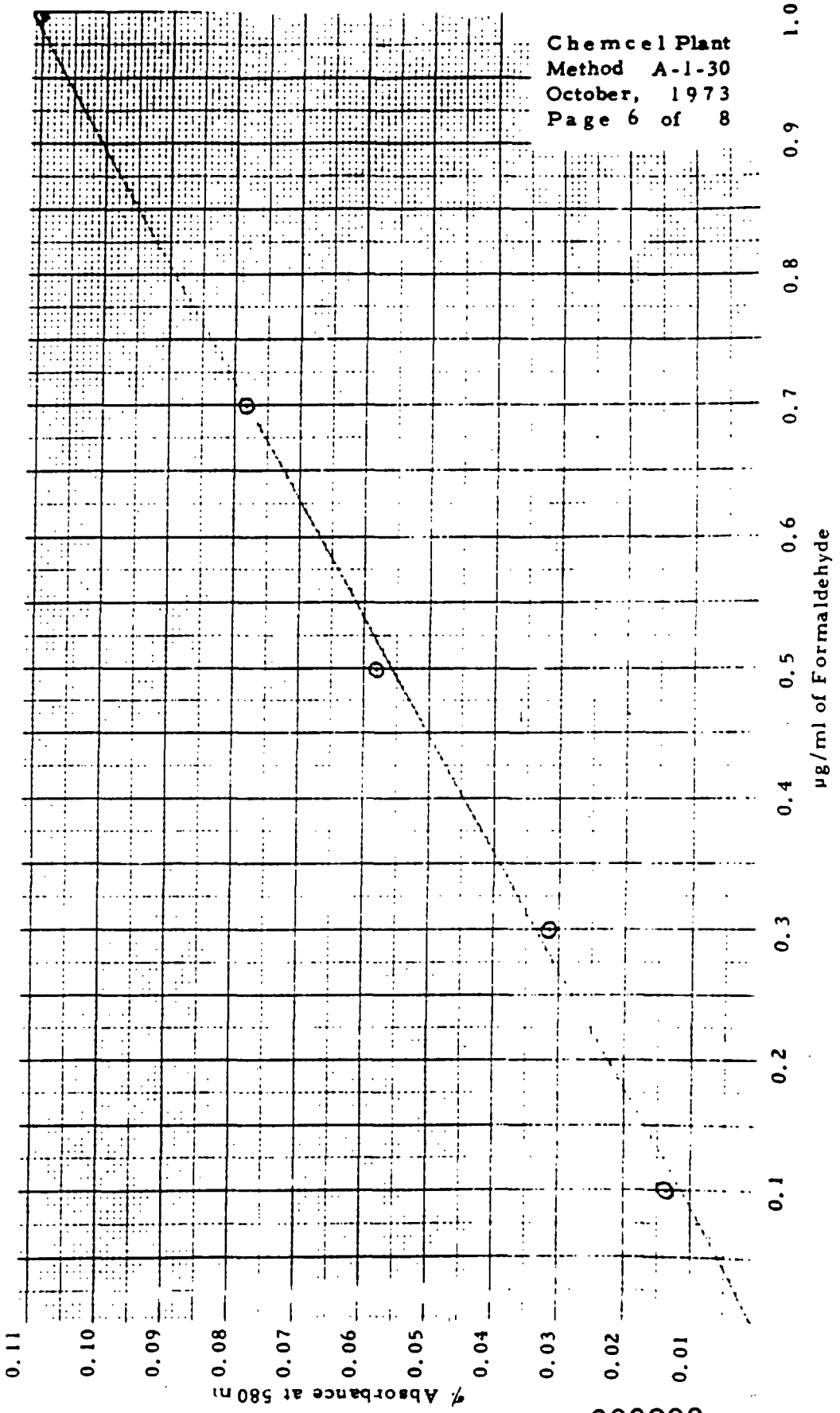

FIGURE II

Calibration Curve for Chromotropic Acid and Formaldehyde No. 2

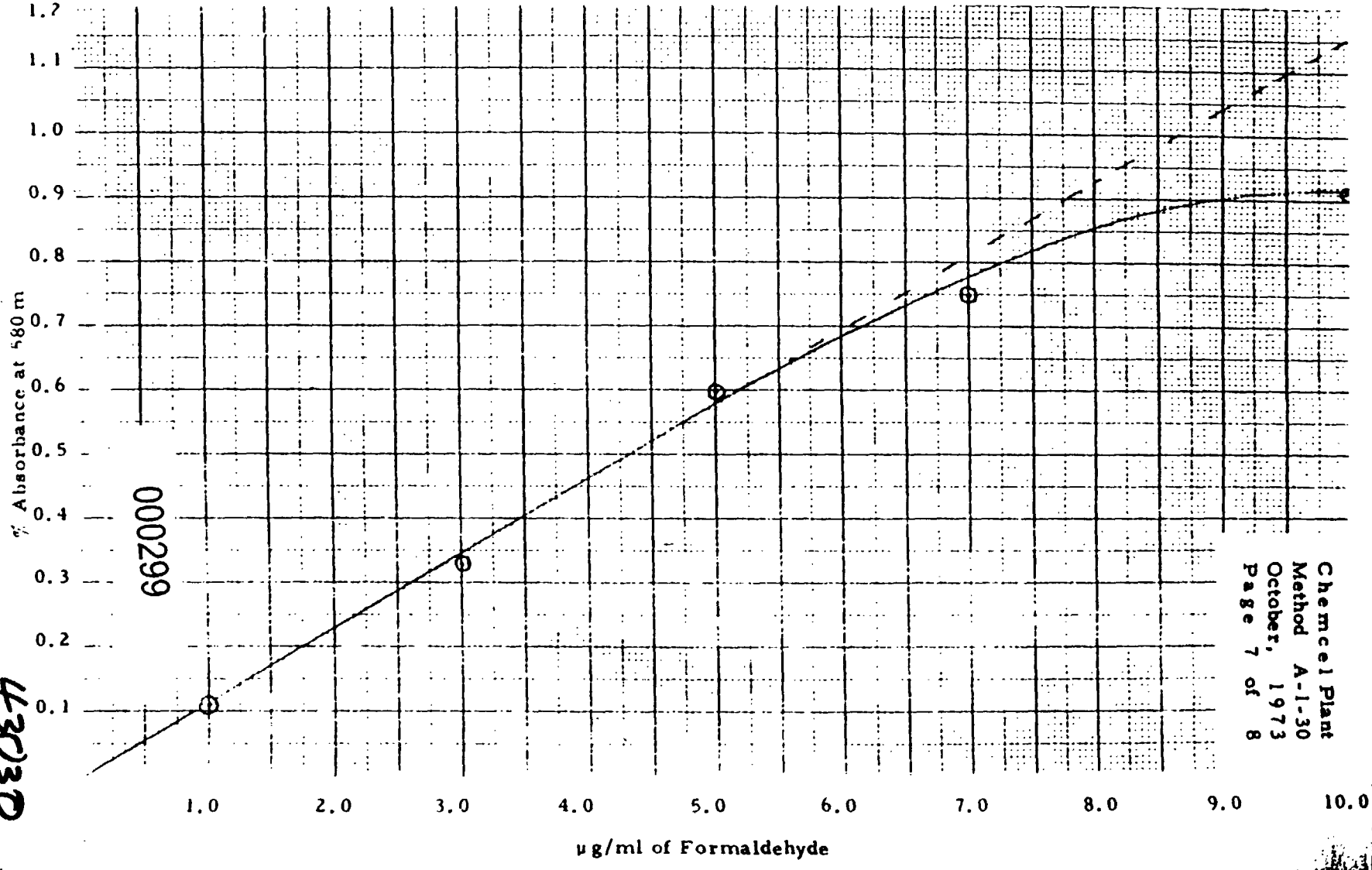

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FIGURE III

Formaldehyde Air Sampler

