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LABORATORY METHODS

AIR POLLUTION CONTROL DISTRICT • COUNTY OF LOS ANGELES


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Laboratory Methods

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AIR POLLUTION CONTROL DISTRICT
COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

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Laboratory Methods

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INTRODUCTION

This looseleaf notebook has been prepared primarily as a means of unifying and maintaining an up-to-date account of the District's laboratory procedures. It should also prove of value for instructing new employees and as a guide for the regular laboratory personnel. Each procedure was made as complete in itself as possible with a minimum of referrals to other APCD methods. This was done to facilitate answering requests for individual methods. Only those procedures which are routinely used in air monitoring and source testing are described. Each method is assembled in such a manner as to enable the chemist to perform the analysis without unnecessary reading. Source testing techniques appear in the notebook only as an adjunct to a specific method.

The notebook is similar in many respects to the SHELL METHODS SERIES and FLUOR LABORATORY METHODS. The numbering of the methods follows the form of the A.S.T.M. STANDARD METHODS OF ANALYSIS. In order to explain this better, let us take as an example the test number APCD 5-46. The 5 identifies the method and its position in the notebook (fifth method). The 46 refers to the year of its adoption by the District. If a tentative change is made to a method, it will bear the same first number as the old method, with its individual date, followed by an X(APCD 5-57X). After the new method has been found analytically sound, the X will be dropped.

Unless otherwise specified, the best grades of chemicals available are to be used. All reagents should conform to or exceed specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications exist. By general usage the term percentage means weight of solute diluted to 100 ml. of solution volume, or in the case of a liquid such as alcohol, it denotes the number of milliliters per 100 ml. of solution. References to water shall be understood to mean ordinary laboratory distilled water. When acids, ammonium hydroxide, and hydrogen peroxide are mentioned, concentrated reagents of the following specifications are intended:

		PERCENT BY WEIGHT	
	SPECIFIC GRAVITY	Minimum	Maximum
Acetic Acid	1.05	99.5	-
Formic Acid	1.20	87	-
Hydrochloric Acid	1.19	35	38
Nitric Acid	1.42	69	71
Perchloric Acid	1.67	70	72
Sulfuric Acid	1.84	95	98
Ammonium Hydroxide	0.90	27 (NH_3)	30 (NH_3)
Hydrogen Peroxide	1.10	28	30

The apparatus sections are limited to special equipment only, since it is assumed that the ordinary industrial hygiene laboratory is equipped with beakers, centrifuges, ring stands, etc. Many of the procedures employ a pump to draw a gas sample through impingers or freezeout traps at 0.04 to 1 cubic foot per minute. The pump may be a Willson No. 3A (Willson Products Co., Reading, Pa.) or Gast Model 0211 (Gast Manufacturing Co., Benton Harbor, Mich.) or their equivalent.

Standard conditions for source testing are those defined by Rule 3 of Regulation I in the Rules and Regulations of the Air Pollution Control District. These are taken to be 60° F. and 1 atmosphere.

It should be noted that some of the laboratory wet methods presented herein have been augmented or superseded for air monitoring purposes by automatic recording instruments developed and manufactured to specifications of the Los Angeles County Air Pollution Control District. A manual "Automatic Air Monitoring" is in progress which describes the devices developed to provide a continuous record of aerial contaminant concentrations.

ACETYLENE APCD 1-54

Laboratory Methods

AIR POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

ACETYLENE

APCD 1-54

SCOPE

The following method is used for the determination of acetylenic hydrocarbons, acetylene, and mono-substituted acetylenes of the type RC≡CH, but not di-substituted derivatives, RC≡CR. The lower limit of the method is about 15 p.p.m. of acetylene. Therefore, its use is limited to tests of specific sources. About 10,000 p.p.m. can be measured when 25 ml. of precipitating reagent is used, but there is no upper limit since a larger quantity of reagent can be employed.

METHOD SUMMARY

A sample is collected in an evacuated 2-liter flask, and is reacted with an ammoniacal solution of cuprous nitrate. Cuprous acetylide is precipitated, and the copper oxidized to cupric ion. The concentration of acetylene is related to the cupric ion. The latter is determined colorimetrically by developing the intense blue color of the cupric-ammonia ion.

SPECIAL APPARATUS

COLLECTION:

Two-liter, round-bottomed flask with a stopcock and standard-taper joint instead of the usual neck. The joint, a ♮ 14/35 outer part, is sealed to a 3-mm. diameter bore straight stopcock, which is in turn sealed to the flask.

ANALYTICAL:

Beckman Model DU spectrophotometer.

REAGENTS

COLLECTION: None.

ANALYTICAL:

Concentrated Ammonium Hydroxide.

Ammoniacal Cuprous Nitrate. Dissolve 1.7 grams of $Cu(NO_3)_2 \cdot 3H_2O$ in 30 ml. of water in a 100-ml. volumetric flask. Add 8 ml. of concentrated ammonium hydroxide and 6 grams of hydroxylamine hydrochloride. Shake until the mixture is colorless and then make up to volume. It is best to use freshly prepared reagent, but the solution will remain colorless for several days if a piece of metallic copper is added.

1N (approximate) Ammonium Hydroxide. Dilute 67 ml. of concentrated ammonium hydroxide to 1 liter with water.

Concentrated Nitric Acid.

6N (approximate) Nitric Acid. Dilute 390 ml. of concentrated nitric acid to 1 liter with water.

Standard Cupric Solution. Weigh accurately 1 gram of clean copper foil (99.9% weight assay) to the nearest milligram into a 100-ml. Erlenmeyer flask using forceps to handle the foil. Add 15 ml. of 6N nitric acid to dissolve the copper. Heat gently to expel the oxides of nitrogen. Transfer the solution quantitatively to a 1-liter volumetric flask and make up to volume with water. Pipet 0.5, 1.0, 2.0, 3.0, and 4.0 ml. of the final solution into a series of 10-ml. volumetric flasks. To each flask add 0.5 ml. of concentrated nitric acid and 1 ml. of concentrated ammonium hydroxide. Make up to volume with water and shake to mix the contents. The concentration of cupric ion in milligrams per milliliter in each 10-ml. volumetric flask is:

$$VW \times 10^{-4} \qquad (1)$$

where

V = milliliters of cupric solution pipetted into the 10-ml. volumetric flask

W = milligrams copper foil in 1-liter volumetric flask

Measure the absorbance of the solutions at 620 mμ against a blank of water, using a Beckman Model DU spectrophotometer with a slit width of 0.08 mm., tungsten lamp, and 1-cm. Corex cells. Prepare a calibration curve by plotting milligrams of cupric ion per milliliter vs. the absorbance of the solution on rectangular-coordinate graph paper.

COLLECTION OF THE SAMPLE

Clean and dry the special 2-liter sample flask, and then evacuate to a pressure of 1 to 2 mm. of mercury. Introduce the sample by opening the stopcock of the flask at the gas source for about 10 seconds.

SAMPLE PREPARATION

After the sample is returned to the laboratory, allow it to stand for at least 1 hour to attain thermal equilibrium with the room. Any significant amounts of moisture collected will condense. Determine the pressure in the flask by connecting it to an open-end mercury manometer. Open the stopcock and measure the difference, in millimeters, between the levels of mercury. Close the stopcock and disconnect from the manometer. Note the room temperature and atmospheric pressure.

ANALYTICAL PROCEDURE

Introduce 10 ml. of the ammoniacal cuprous nitrate reagent into the 2-liter sample flask as follows: If the pressure in the flask is close to atmospheric, place it in the refrigerator for 30 to 60 minutes in order to obtain a greater differential. Then, pour about 5 ml. of ammoniacal cuprous nitrate reagent into the ♕14/35 joint (stopcock is still closed), open the stopcock slightly and let the reagent run into the flask slowly. Close the stopcock before all of the reagent has run into the flask. Repeat with another 5-ml. portion of reagent.

Shake the flask for 10 minutes with frequent rotation to wet the surface. If acetylenic hydrocarbons are present, a brick-red precipitate of cuprous acetylide will form immediately. Pour the contents of the flask into a medium porosity, fritted-glass, filter funnel which has been wetted with 1N ammonium hydroxide. Maintain an atmosphere of dry nitrogen over the material in the funnel during all of the procedure by directing a slow stream of nitrogen from a cylinder into the funnel through a glass nozzle (Figure 1). This precaution avoids the possibility of oxidative decomposition of the unstable acetylide.

Wash the flask three times with 15-ml. portions of 1N ammonium hydroxide. Transfer the washings to the funnel and draw off the filtrate into a 100-ml. filter flask by applying gentle suction. Discard the washings. Finally, wash the precipitate with 10 ml. of 1N ammonium hydroxide and discard the washings. Do not allow the solid acetylides to become dry, as they are explosive.

Place the funnel over a 25-ml. filter flask and add 5 ml. of 6N nitric acid. Then add concentrated nitric acid dropwise until reaction begins (3 to 4 drops). Allow to stand until the precipitate dissolves completely. Draw the solution through the funnel by applying gentle suction. Pour the filtered solution into a 25-ml. casserole.

Add 5 ml. of 6N nitric acid to the original 2-liter sample flask. Then add 0.5 ml. concentrated nitric acid. Rotate the flask so that the entire inside surface is washed with acid. Allow to stand until all the residual cuprous acetylide adhering to the walls has dissolved. Transfer this solution to the funnel and draw it into the 25-ml. filter flask by means of gentle suction.

Wash the flask once more with 5 ml. of 6N nitric acid and transfer to the funnel. Add the contents of the 25-ml. filter flask to the solution in the casserole. Wash the funnel and filter flask with 3 to 5 ml. of water and pour this into the casserole.

The casserole contains about 20 ml. of solution in which is dissolved cupric nitrate equivalent to the acetylenic hydrocarbons present in the sample. Evaporate the contents to dryness on a hot plate at low heat. Ignite the dry residue in a muffle furnace at 500-600°C.

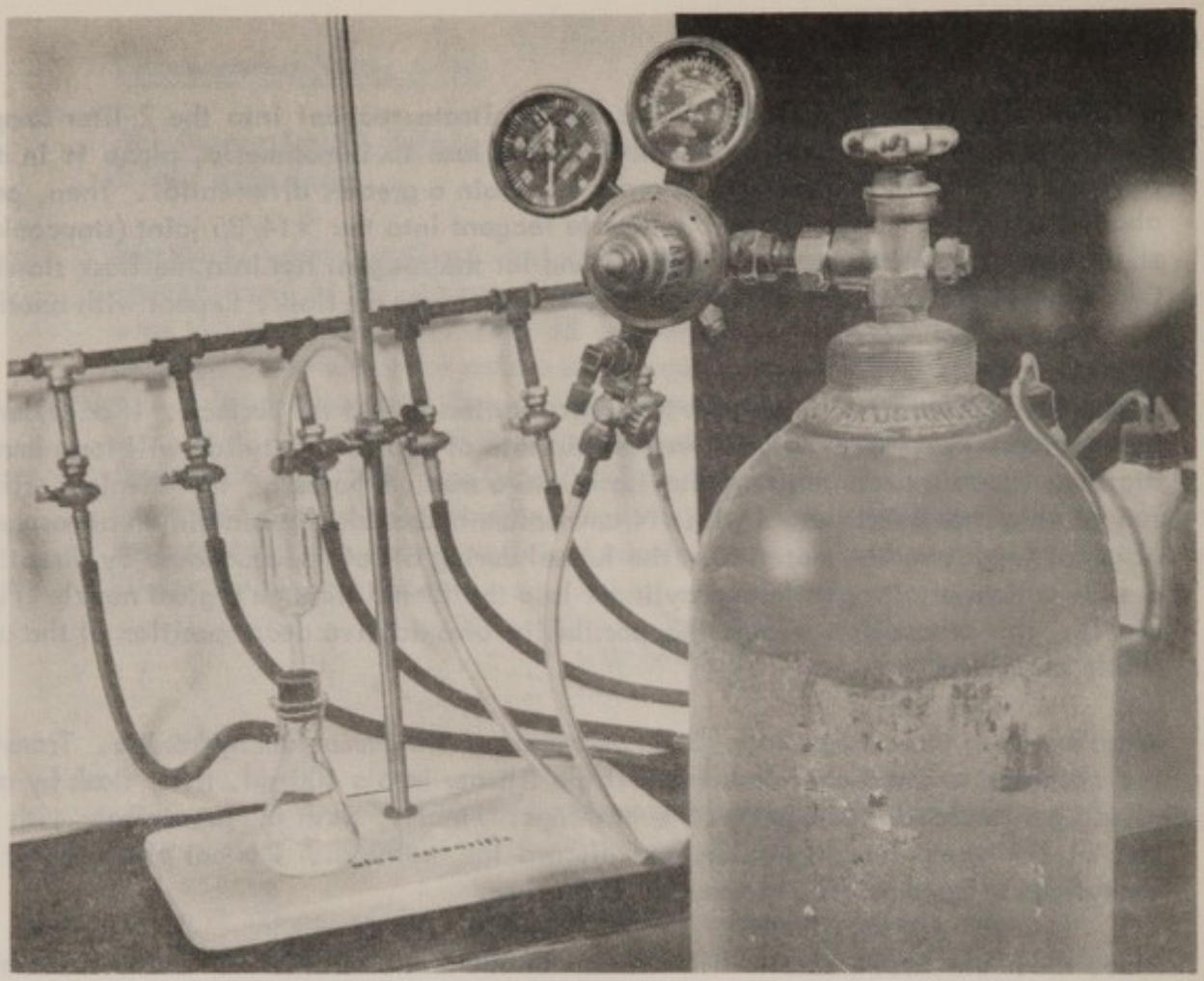


Figure 1. Purging with nitrogen during the filtration of cuprous acetylide.

Dissolve the residue, now cupric oxide, in 0.5 ml. of concentrated nitric acid with gentle heating. Transfer the solution quantitatively to a 10-ml. volumetric flask using a small amount of wash water. Add 1 ml. of concentrated ammonium hydroxide and swirl to mix the contents. Make the solution up to volume with water. If it is apparent that the copper content of the sample is high, dilute the solution to 50 ml., 100 ml., or 250 ml., with the inclusion of the following amounts of acid and base:

Ml. Final Volume	Ml. HNO_3	Ml. NH_4OH
10	0.5	1.0
50	2.5	5.0
100	5.0	10.0
250	12.5	25.0

It will be observed that these figures include the 0.5 ml. of acid used to dissolve the residue and the 1 ml. of base to develop the color.

An intense blue color is developed due to the formation of the cupric-ammonia ion. Measure the absorbance of the solution at 620 m μ against a blank of water using a Beckman Model DU spectrophotometer with a slit width of 0.08 mm., tungsten lamp, and 1-cm. Corex cells. Read the concentration of cupric ion in milligrams per milliliter from the previously prepared calibration chart.

REPORTING AND CALCULATIONS

Monoalkynes in parts per million by volume (dry basis) are:

$$\frac{490\ W_m T}{v_m(P_r + \Delta P)} \qquad (2)$$

where

ΔP = sample flask differential pressure, millimeters of mercury (with respect to atmospheric pressure)

P_r = atmospheric pressure, millimeters of mercury (at the time of the ΔP measurement)

T = room temperature, degrees Kelvin (at the time of the ΔP measurement)

V_m = measured volume of sample flask, liters*

W_m = milligrams of copper (multiply milligrams cupric ion per milliliter, obtained from the calibration chart, by milliliters of the final solution volume)

If we assume as an approximation that acetylene is the only alkyne present, the concentration in grains per standard cubic foot (60°F., 1 atmosphere) is calculated by multiplying the parts per million by 4.79×10^{-4}.

REFERENCES

Jacobs, Morris B., "The Analytical Chemistry of Industrial Poisons, Hazards and Solvents," 2nd ed., Interscience, New York, 1949.

Nieuwland, J., and Vogt, R,, "The Chemistry of Acetylene," Reinhold, New York, 1945.

*Where moisture was present in the original sample and it is desired to put the sample volume on a stack-conditions basis, a correction must be made in the formula above. The moisture is usually determined in conjunction with some other test such as grain loading.

AEROSOLS, Ether Soluble APCD 2-54

Laboratory Methods

AIR POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

AEROSOLS, ETHER-SOLUBLE

APCD 2-54

SCOPE

This procedure is designed for atmospheric sampling. Although it can be applied to source testing with appropriate modifications, it is seldom used for this purpose.

METHOD SUMMARY

The sample is collected on a glass-fiber filter using a Staplex high-volume blower. The filter is extracted with ether and the solvent evaporated. The weight of the dry residue is expressed as micrograms of aerosols per cubic meter of air.

SPECIAL APPARATUS

COLLECTION:

Staplex high-volume blower with special filter head (Figure 1), 8 × 10 inch glass-fiber flash-fired filter-paper sheets (Mine Safety Appliances Co., No. 1106-B).

CALIBRATION:

Duct 4 inches inside diameter by 40 inches in length, standard Pitot tube and draft gage, Fahrenheit thermometer (Figure 2).

ANALYTICAL:

Soxhlet extraction apparatus.

REAGENTS

COLLECTION: None.

ANALYTICAL:

Ether. Reagent grade, no special pretreatment.

Ferrous Sulfate. Crystalline $FeSO_4 \cdot 7H_2O$.

CALIBRATION OF THE STAPLEX BLOWER

Attach a duct, 4 inches inside diameter by 40 inches long, to the exhaust of the blower with masking tape. Place a thermometer in the duct, and a glass-fiber filter in the special head. Turn the blower on and determine the velocity head of the air stream with a standard Pitot tube (hold the Pitot tube in the center of the 4-inch duct as shown in Figure 2). Note the temperature inside the duct in degrees Fahrenheit. Measure the inside diameter of the duct and determine the cross-sectional area in square feet. Obtain the velocity in feet per second from velocity tables (distributed free by Re-

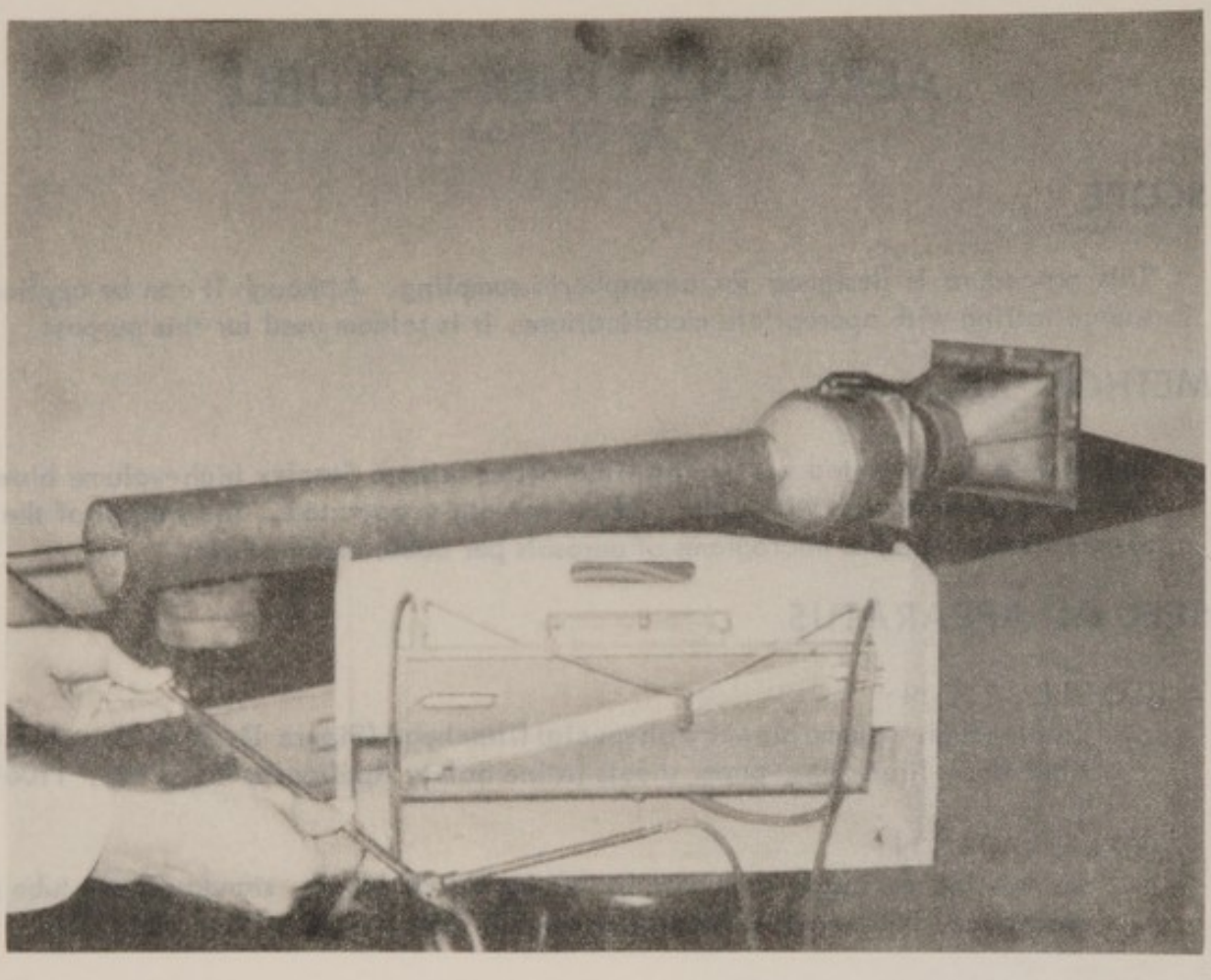


Figure 2. Staplex blower with duct attached and calibration being performed with a standard Pitot tube.

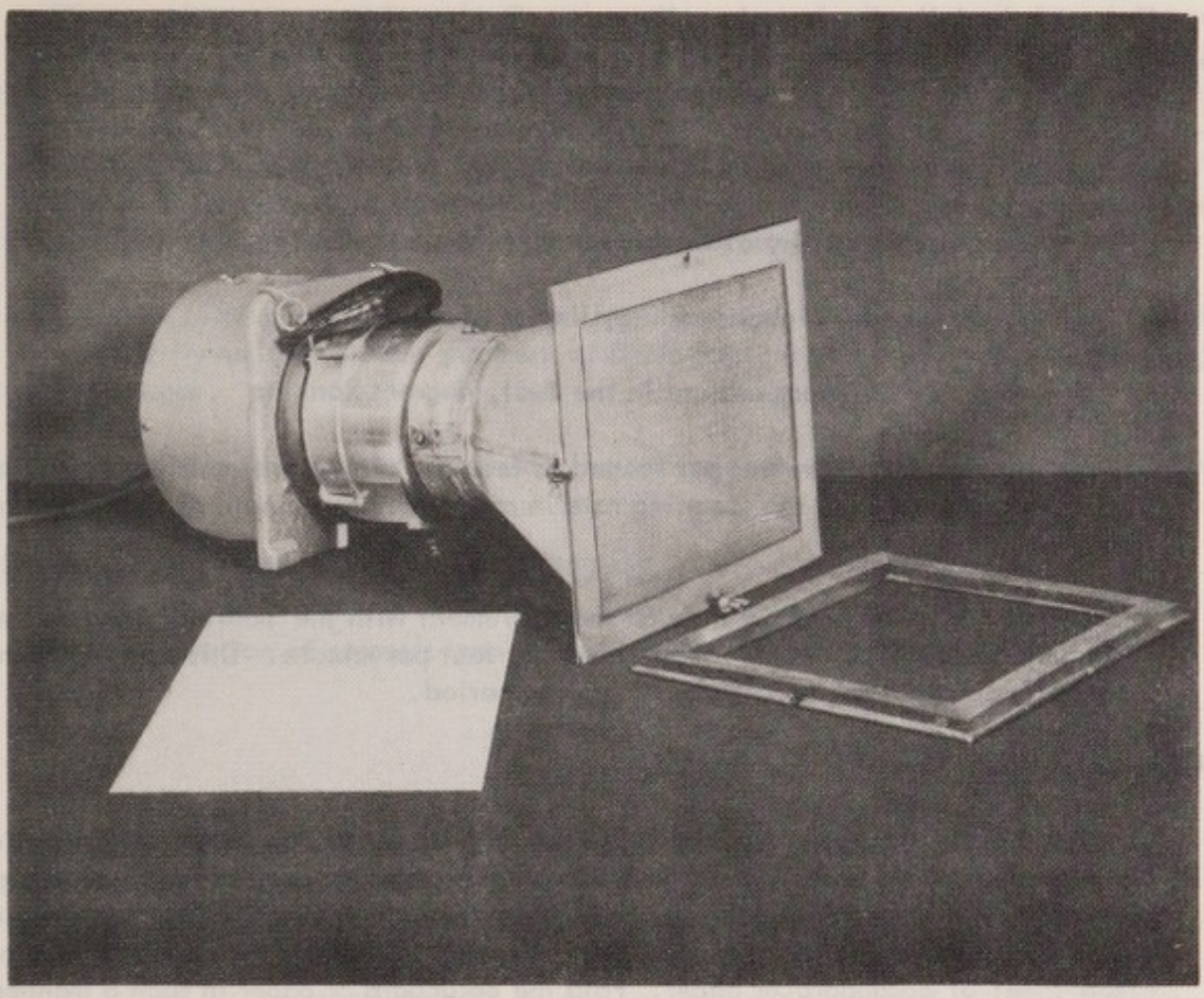


Figure 1. Staplex blower showing modified head for large glass-fiber filter papers.

search - Cottrell Inc., Boundbrook, N.J., and other sources), or calculate the velocity by the following equation:

$$u = 2.90\sqrt{H\,T} \qquad (1)$$

where

u = velocity of the air through the duct, feet per second

H = draft-gage reading, inches of water

T = air temperature in the duct, degrees Rankine

Convert the velocity from feet per second to feet per minute and multiply by the area of the duct to determine the sampling rate in cubic feet per minute at ambient conditions.

The average rate of air flow through the instrument with the modified head and with filter paper in place will be about 75 cubic feet per minute. This rate will remain essentially constant during a 1-hour sampling period.

COLLECTION OF THE SAMPLE

Collect the air samples by using two Staplex blowers simultaneously at one location. Place a sheet of the 8 x 10 inch glass-fiber filter paper in each blower, using a pair of forceps. Start the blowers on the hour and run for 56 minutes. After the sample is collected, remove the filter papers, using forceps, and place them face to face on a clean sheet of cardboard or paper. Fold the cardboard or paper in such a manner as to envelop the filter paper. Note the time, place, and date of the sample on the outside of the folded packet. Transport the packets to the laboratory in sealed envelopes or other suitable containers.

SAMPLE PREPARATION

Cut the two filter papers, obtained simultaneously, into pieces of about 1 square inch, using clean scissors while holding the filter paper with forceps. Allow the cut pieces to fall onto a piece of clean wrapping paper.

ANALYTICAL PROCEDURE

Place the cut filter papers in the 38-mm. Soxhlet extractor tube, using forceps. Pour 125 ml. of ether into the Soxhlet extraction flask and add a pinch of ferrous sulfate to prevent the build-up of peroxides. Start the extraction process by heating the flask in a water bath. Adjust the temperature of the water bath to maintain reflux cycles of 8 to 10 minutes. Continue the extraction for a period of 2 hours. Distill off the ether to a volume of about 35 ml. The distillate may be collected in a 250-ml. Erlenmeyer flask set in an ice bath and reused. Place a piece of Whatman No. 4 filter paper in

a 35-mm. short-stemmed funnel. Pour a small amount of ether through it and discard the filtrate. Filter the extracted material through the ether-washed filter paper collecting it in a tared 50-ml. Erlenmeyer flask. Rinse the filter with a small quantity of ether into the flask. Concentrate the extract to about 5 ml. on a water bath. Remove the last traces of ether by placing the flask in a vacuum drying oven for 1/2 hour, at 15 inches of vacuum and 60°C. Cool the flask in a desiccator and weigh. Repeat the vacuum drying procedure until constant weight is obtained.

Run a blank in the same manner, using two fresh sheets of filter paper and ether. Blanks are ordinarily run whenever a shipment of filter paper is received, but not on individual packages.

Subtract the blank from the sample determination and calculate the results according to Formula 2.

REPORTING AND CALCULATIONS

The concentration of aerosols in micrograms per cubic meter of air is:

$$\frac{35.3\ W}{rt} \qquad (2)$$

where

W = micrograms of residue from the two filters (blank subtracted)

r = sampling rate, cubic feet per minute (sum of the two blowers)

t = sampling period, minutes (usually 56 minutes)

Note that no temperature corrections are applied to the air sample.

AEROSOLS, Km Values APCD 3-54

Laboratory Methods

R POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

AEROSOLS

K_m VALUES

APCD 3-54

SCOPE

This procedure provides a measure of the amount of smoke, soot, and tarry matter in atmospheric samples. (N. B.)

METHOD SUMMARY

A filter sample is taken and the albedo of the deposit is measured using a reflectometer. Results are expressed in K_m units. This unit is defined as the deposit which produces an absorbance of 0.1 when the deposit area is 1 square centimeter and the volume of air sampled is 1 cubic meter. Since the method is based upon the deposition of heterogeneous black material on a white background and the material collected is not completely black, K_m is an arbitrary unit of measurement.

SPECIAL APPARATUS

COLLECTION:

Auto-Sampler manufactured by Albert L. Chaney Laboratories, Glendale, Calif., as shown in Figure 1. It is equipped with the following controls:

Strip-Belt Switch. Located to the right of and below the filter-clamp jaws. Set the dial to Strip when the filter-paper roll is being used. Set at Belt when filter-carrying plastic belt is being used.

Clock. Front set, 117 volts, 60 cycles. Located in the upper left corner of the control panel. In case of current interruption, the clock will stop. The Auto-Sampler will restart when the current is restored, but the clock will remain off to indicate the time of the current failure.

Clock Start Switch. Located below the clock in the lower left corner of the control panel. Push and release to start the clock when putting the sampler into service or after current interruption.

Panel Light. A pilot light is located in the upper center of the control panel. The light indicates when a cycle change is in progress.

Running-Time Meter. Located on the upper right corner of the panel. It indicates hours and tenths, and totalizes only the time that the vacuum pump is in actual

N. B.: This laboratory method has been augmented since Sept. 1957 for air monitoring purposes by an automatic recording instrument, Auto-Sampler Model 106, manufactured to District specifications by Albert L. Chaney Chemical Laboratory, Inc., Glendale, California, and later modified by the Los Angeles County Air Pollution Control District.

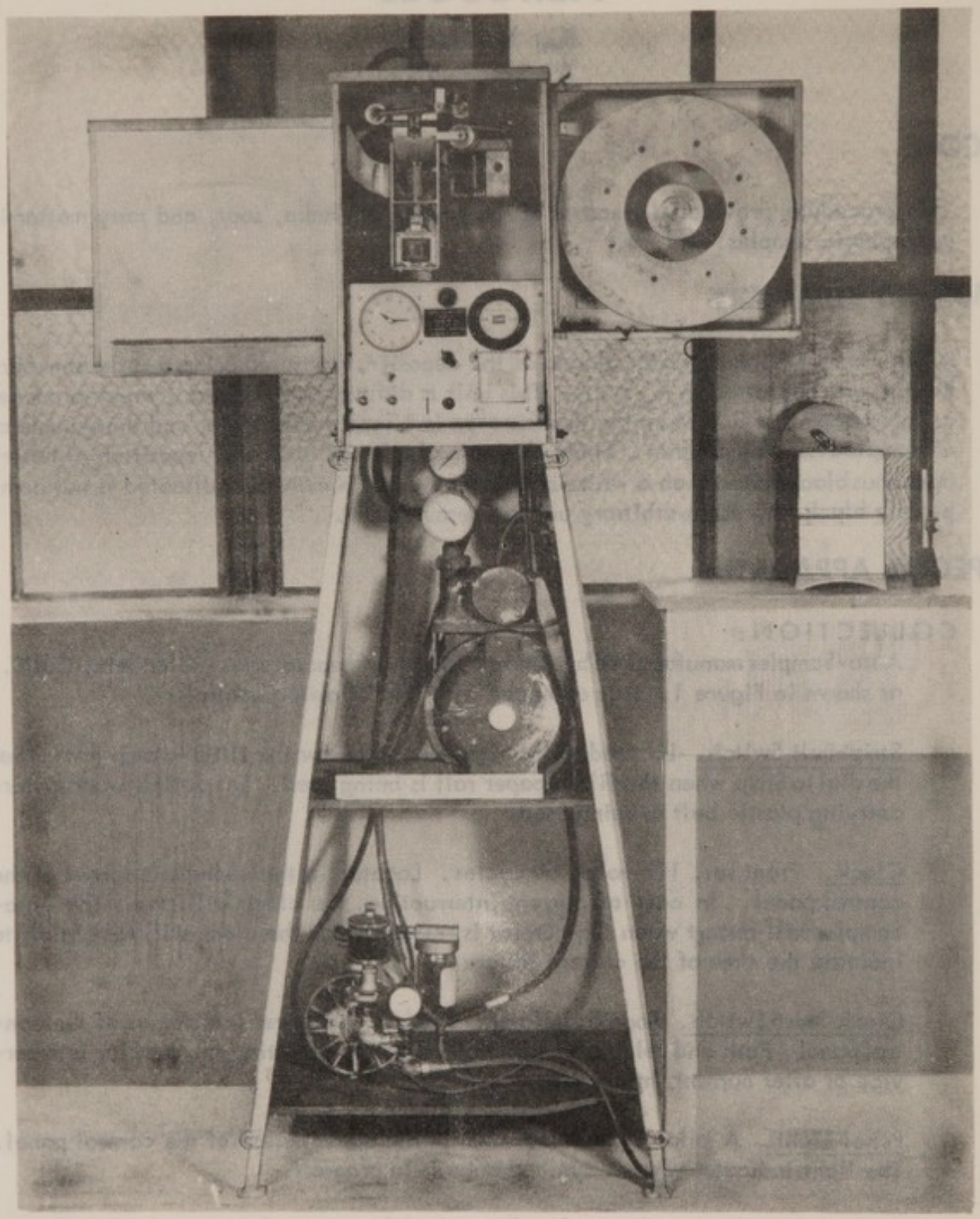


Figure 1. Chaney Auto-Sampler.

operation. The value should be recorded in pencil on each belt or roll when it is changed. The length of any single shut-down may be computed from the running time meter reading. The time that this occurred is shown by the clock.

On-Off Switch. Located immediately below the clock. In the Off position it shuts down the entire machine except the clock.

Hold Button. Located below the On-Off switch. This control can be used only when the Strip-Belt switch is in the Belt position. When the control switch is at the CO position and no belt is in the machine, the Hold button can be depressed to open the filter clamps.

Reset Overload Relay. Located to the right of the Hold button. Push the lever down to the bottom of the slot to reset. A short, low voltage, or any other abnormal current condition will cause the lever to move upward in the slot and shut down the entire machine. Never try to force this lever upward.

Control Timer. Located under the cover in the lower right of the control panel. This timer operates on a 1-hour cycle. When first putting the Auto-Sampler into operation, it is usually desirable to start up on the hour. The timer must be set at the beginning of a cycle if a complete sample is to be collected on the first filter. To reset the timer, remove the cover, grasp the edge of the cam between the thumb and finger and move the front edge downward until the panel light goes out. The timer is now properly set. Do not attempt to move the front edge upward or the timer will be ruined. Replace the cover.

Control Switch. Located in the center of the panel and has four positions: NO-normal operation, VO-vacuum off, CO-clamps open, and SO-sample out. This switch is for use in changing belts or rolls and making other inspections. The Auto-Sampler will function normally only in the NO position. In the VO position the vacuum pump will be shut down, but the timer will continue to run. A 10-second pause should be made at this point before going to the CO position in order to allow the vacuum to fall. This prevents the filter from rupturing. In the CO position the vacuum will remain off and the filter clamps will remain open as long as a belt is in the machine or the Strip-Belt switch is set at Strip. If a belt is not in the machine and the Strip-Belt switch is at Belt, place the switch in the CO position and depress the Hold button. The clamps can then be held open until a new belt has been inserted. If the Strip-Belt switch is at Strip, the clamps will remain open when the control switch is at the CO position. In the SO position, the vacuum remains off, clamps open, and the belt will be run forward to the shut down position, if the Strip-Belt switch is at Belt. By depressing the Hold button, the belt will be run completely out of the machine. If the Strip-Belt switch is at Strip and the control switch is at the SO position, the vacuum will remain off, clamps will remain open, and the roll will be run completely out of the machine. The sample belt or roll may be moved forward one position at a time by switching from CO to SO momentarily and back to CO.

ANALYTICAL:

Photovolt reflectometer Model 610 (Figure 2), Sola constant-voltage transformer, No. 30805.

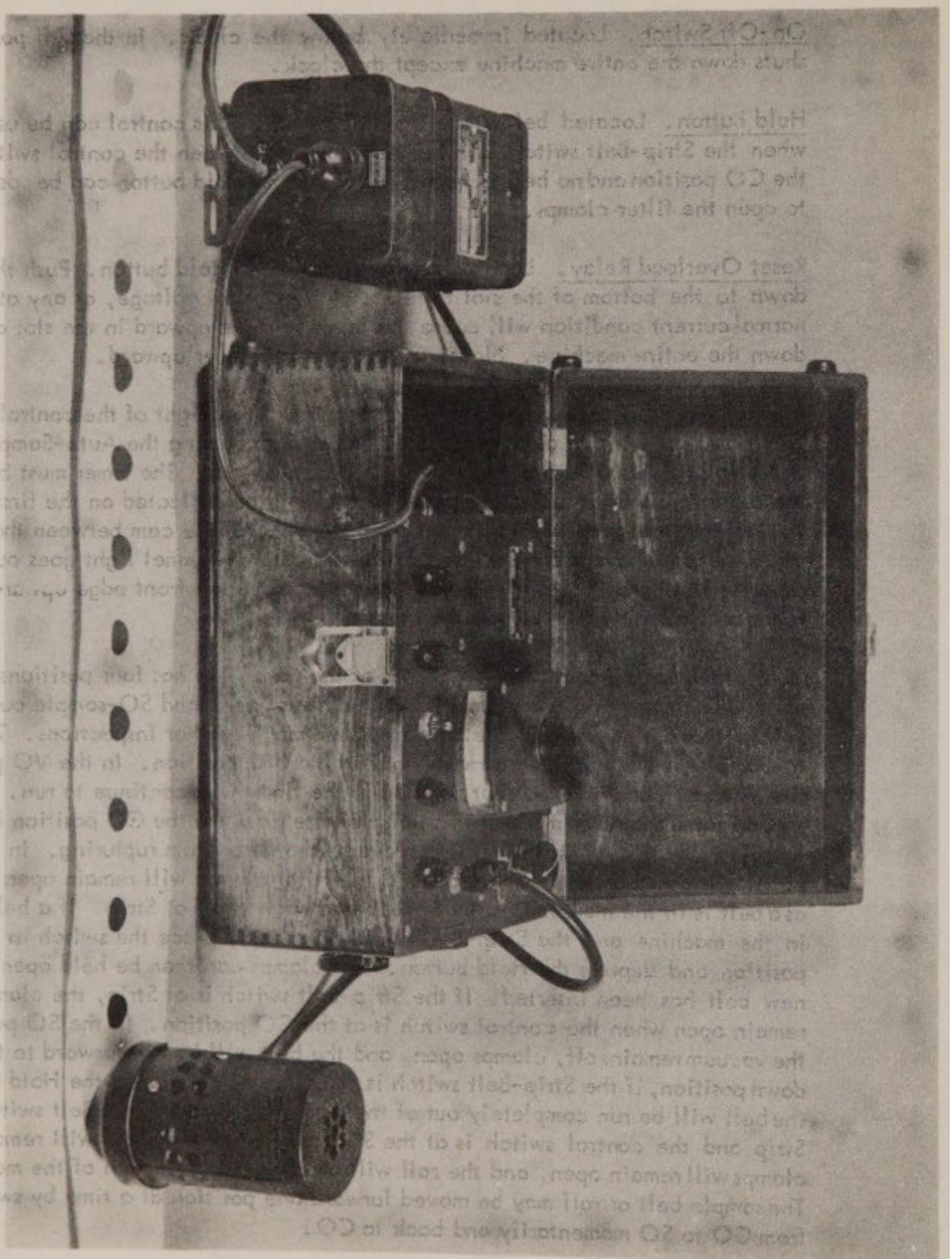


Figure 2. Photovolt reflectometer and scanning unit shown resting on a piece of white Precision Board which is used as a background for routine measurements.

REAGENTS

No reagents are necessary for this procedure.

COLLECTION OF THE SAMPLE

The samples are collected on Whatman No. 52 filter paper by means of the Chaney Auto-Sampler. Where plastic belts carrying individually glued filter-paper discs are fed through the machine, it will function without attention until the last sample on the belt has been taken. The sampler will then automatically shut down until reloaded and restarted. Where a roll of filter paper is fed through the machine continuously, the time consuming process of gluing filters to the plastic belt is eliminated. With the filter-paper roll, the machine will not shut down automatically; therefore, it must be serviced before all of the filter paper has been used.

In order to operate the Auto-Sampler with the plastic belt it is necessary to load the belt with filters. This is accomplished in the following manner: Lay the belt upside down on a clean flat surface with its leading end facing to the right. Place three 1/8-inch diameter spots of rubber cement around the periphery of each hole in the belt; one near the forward edge and one on each side. Do not place a spot at the rear edge. Lay a 5.5-cm. diameter filter paper (Whatman No. 52) over each hole and press down on the cement spots. Handle the filter papers only by the edges. Turn the belt over and number the filters just inside the opening with a medium pencil. Roll the belt around the plastic magazine support ring so that it will feed off the top from left to right. Index holes along the edge of the belt will be to the rear and filter papers will be on the underside of the belt. Place belt and support in the left magazine of the Auto-Sampler.

If a filter-paper roll is to be used, no special preparation of the filters is necessary. Place the roll of filter paper on the peg in the left magazine of the Auto-Sampler so that it will feed off the top from the left to right.

To load the Auto-Sampler with the belt, turn the Strip-Belt switch to Belt, the On-Off switch to On, the control switch to CO, depress the Hold button, slide the nose of the belt carefully under the hold-down roller, limit-switch rollers, and through the jaws up to the feed rolls. The position of these rollers and the filter clamps is shown in Figure 3. The Hold button may be released any time after the belt nose has entered the clamps. If an old belt is in the machine, the control switch should have been placed in the SO position rather than the CO position. On depressing the Hold button, the old belt would automatically move out of the way while the new one was being inserted. The old belt may be rapidly removed by lifting the top feed roll with the knob provided and sliding the belt forward with the control switch in the CO position. With the control switch at CO, enter the nose of the new belt between the feed rolls. The belt will feed up to and stop at the first filter position. Check for belt alignment in the feed rolls and adjust if required. Return the control switch to NO.

To load the Auto-Sampler with the filter-paper roll, turn the Strip-Belt switch to Strip, the On-Off switch to On, and the control switch to CO. Slide the leading end of the

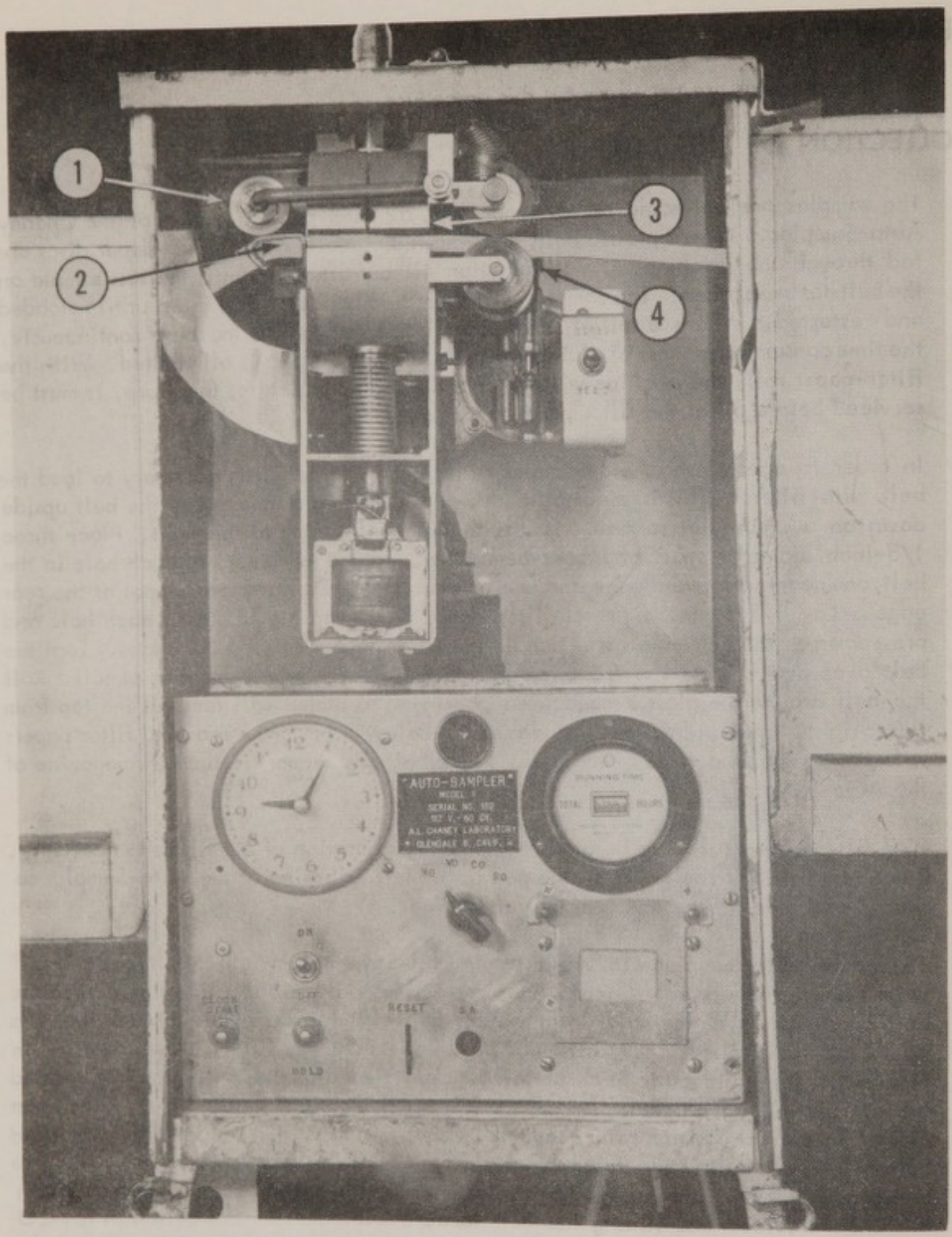


Figure 3. Close-up photograph showing the mechanism used for handling and clamping the filter-paper strip. (1) Hold-down roller. (2) Limit-switch rollers (not visible in the photograph since they are located toward the rear of the compartment and, therefore, are obscured by the hold-down roller and filter strip). (3) Filter clamps. (4) Feed rolls.

filter-paper strip under the hold-down roller, limit-switch rollers, and through the jaws up to the feed rolls. Turn the control switch to the SO position. The filter strip will then commence running through the machine. When enough paper has passed through for easy attachment in the right magazine, turn the control switch to CO and wait until the strip stops running. Then turn to NO and attach the end onto the support ring in the right magazine. If a roll is already in the machine and the finished samples are to be removed, turn the control switch to VO until the vacuum falls. Then turn to SO until the desired amount of paper runs through the machine. Turn the control switch to CO, wait until the strip stops and cut the previously used filter paper from the strip. Attach the unused end to the magazine support, and return the control switch to the NO position.

The air-flow system is shown in Figure 4. After the Auto-Sampler is loaded with either the belt or roll of filter paper and the control switch is at NO, adjust the air-flow rate by means of the stopcock to deliver 25 cubic feet of air per hour. A rotameter has been installed on the Auto-Sampler for rapid checks on the air-flow rate. When starting the machine, also check the rate by timing the Sprague meter. This meter is normally used to obtain the cumulative volume of air sampled during any period desired.

After collection, return the samples to the laboratory for analysis making certain that they are well protected during transit.

The following precautions should be exercised when operating this machine:

(a) Never allow the jaws of the filter clamp to snap together. Insert some material such as a filter paper or an ordinary 3 x 5 inch file card between them.

(b) Insert a cork or stopper between the centers of the feed rolls when the machine is to be out of service for some time. This will prevent flattening of the rubber feed roller.

(c) The critical-flow orifice must be between the vacuum pump and the Sprague meter in order to prevent damage to the meter. The meter should not operate over 10 inches of mercury vacuum.

(d) Never touch the filters with the fingers except at the edges.

(e) Keep all the parts free from excess oil and dirt. Place oil only at points designated by the manufacturer.

(f) Keep the covers closed as far as possible.

(g) Keep the vacuum-pump trap empty of water and oil.

(h) Keep the fingers and hands away from the machine during the change cycle when the control switch is in the NO position.

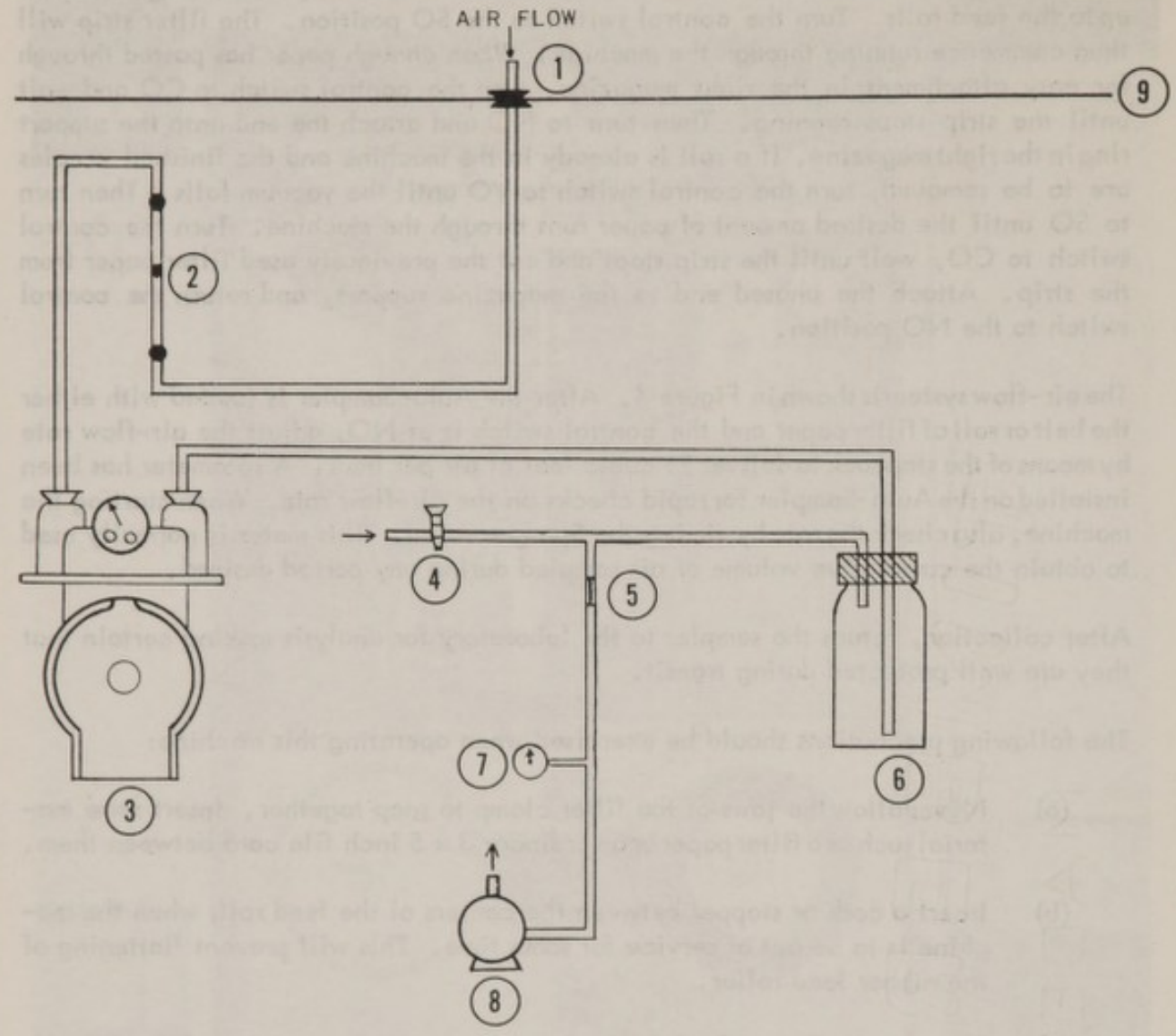


Figure 4. Air-flow system for the Auto-Sampler. ① Filter clamps. ② Rotameter. ③ Dry gas meter. ④ Stopcock for adjusting the flow rate. ⑤ 0.5-mm. orifice. ⑥ Surge bottle. ⑦ Vacuum gage. ⑧ Air pump. ⑨ Filter-paper strip.

SAMPLE PREPARATION

If the plastic belt carrying the filters is used, remove the filters from the belt for the reflectance measurements. If the roll of filter paper is used, the measurements can be made directly on the roll.

ANALYTICAL PROCEDURE

Although the District has used the Beckman DU spectrophotometer with a reflectance attachment for determining K_m values in the past, it was found that the values could be determined much faster by using the Photovolt reflectometer. The latter instrument is shown in Figure 2.

Plug the alternating-current line of the Photovolt reflectometer into the constant-voltage transformer and plug the transformer into a 115-volt, 60-cycle line. Set the toggle switch AC-Bat in the AC position and the ON-OFF switch to OFF. Adjust the mechanical zero of the instrument with the knob on top of the meter. Turn the two knobs on the lower left side of the instrument to the maximum clockwise position and leave them there. Set the ON-OFF switch to the ON position and allow the instrument to warm up for 1 hour. Lay the filter-paper strip on a background having a white surface (white Precision Board, single thickness). The search unit is placed over a clean spot on the filter paper and the two knobs on the lower right side of the instrument are adjusted until the meter reads 100 divisions (the knob on the left is for coarse adjustment and the knob on the right is for fine adjustment). Center the search unit over the sample to be tested and record the meter reading. Calculate the K_m value according to Equation 1.

Check the span of the instrument after each five readings on the clean filter paper. Checking and adjusting the span near the test readings periodically allows the operator to compensate for variations in the filter paper.

REPORTING AND CALCULATIONS

The K_m values are calculated according to the following equation:

$$K_m = 91 \log \frac{100}{R} \qquad (1)$$

where

R = percent reflectance with respect to clean filter paper as read on the reflectometer

K_m = that deposit which produces an absorbance of 0.1 when the deposit area is one square centimeter and the volume of air sampled is one cubic meter

REFERENCE

Hall, S.R., Anal. Chem., 24, 996-1000 (1952).

AEROSOLS, Metals, Spectographic APCD 4-57X

Laboratory Methods

AIR POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

AEROSOLS

METALS, SPECTROGRAPHIC *

APCD 4-57X

SCOPE

This method is used for the determination of metals in atmospheric aerosols.

METHOD SUMMARY

Aerosols are collected on filter paper using an Auto-Sampler. The filters are charred to concentrate the metals and a spectrographic analysis is performed on the char.

SPECIAL APPARATUS

COLLECTION:

Automatic filter sampler (Auto-Sampler, or Recording Auto-Sampler Model 106, Albert L. Chaney Chemical Laboratory Inc., Glendale, Calif.).

ANALYTICAL:

Arc-spectrograph (1.5-meter grating spectrograph, 7A./mm., Model 2060, with 35-mm. camera, Applied Research Laboratories, Glendale, Calif.) with Multi-source unit (Applied Research Laboratories, Model 22) (Figure 1), densitometer (Applied Research Laboratories Model 42), high purity spectrographic graphite electrodes (lower electrode, platform type; upper electrode, regular tip with undercut) (Figure 2), developing facilities for films.

REAGENTS

COLLECTION:

No reagents are necessary for the collection of the sample.

ANALYTICAL:

Film. 35-mm. Eastman Spectrum No. 2 film.

Developer. Kodak D-19.

5% Acetic Acid. Dilute 50 ml. of glacial acetic acid to 1 liter with water.

Rapid Liquid Fixer. Kodak rapid liquid fixer.

* This procedure was provided through the courtesy of H. W. Johnson, Pacific Spectrochemical Laboratories, Los Angeles, Calif.

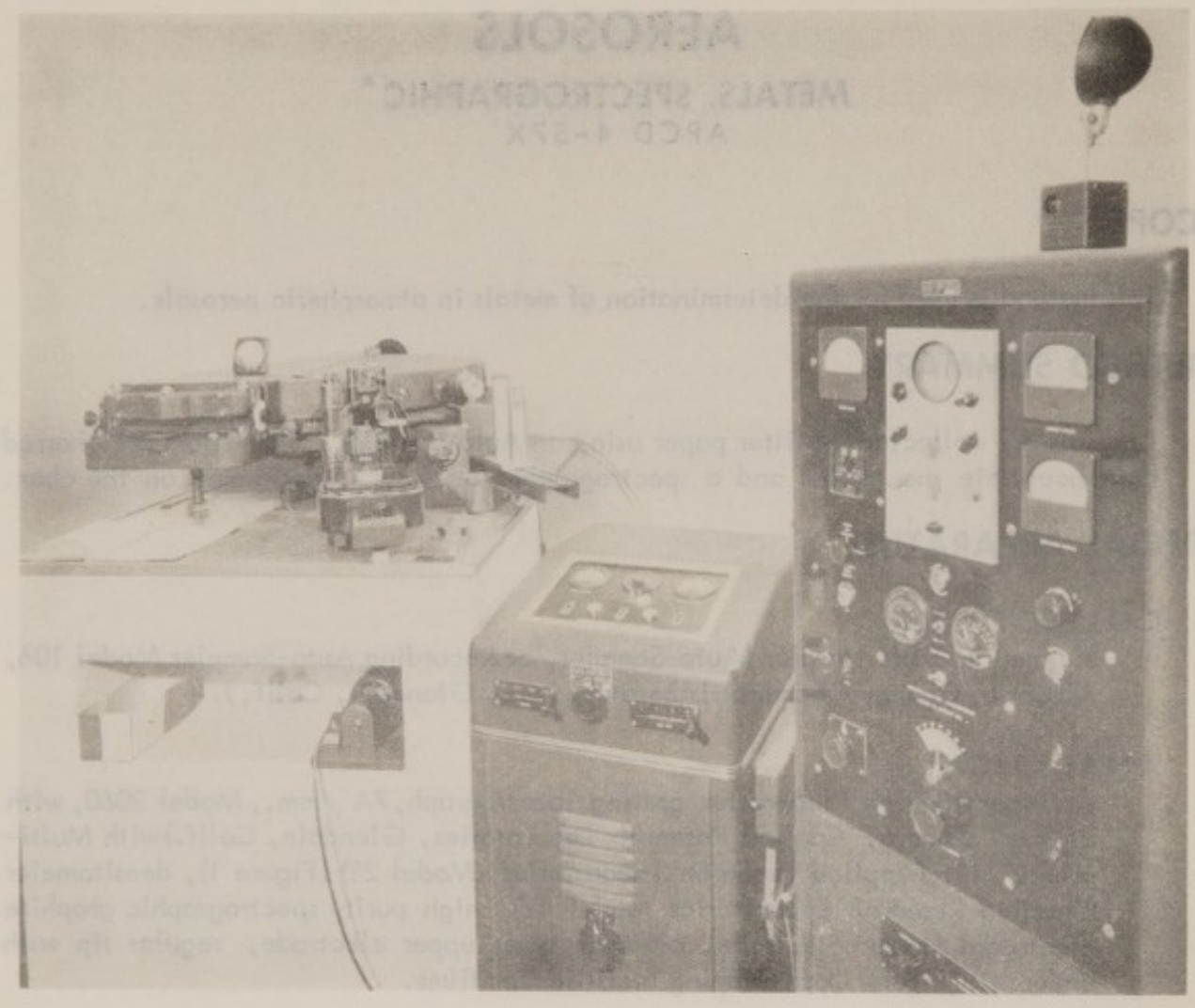


Figure 1. Arc-spectrograph and Multisource unit.

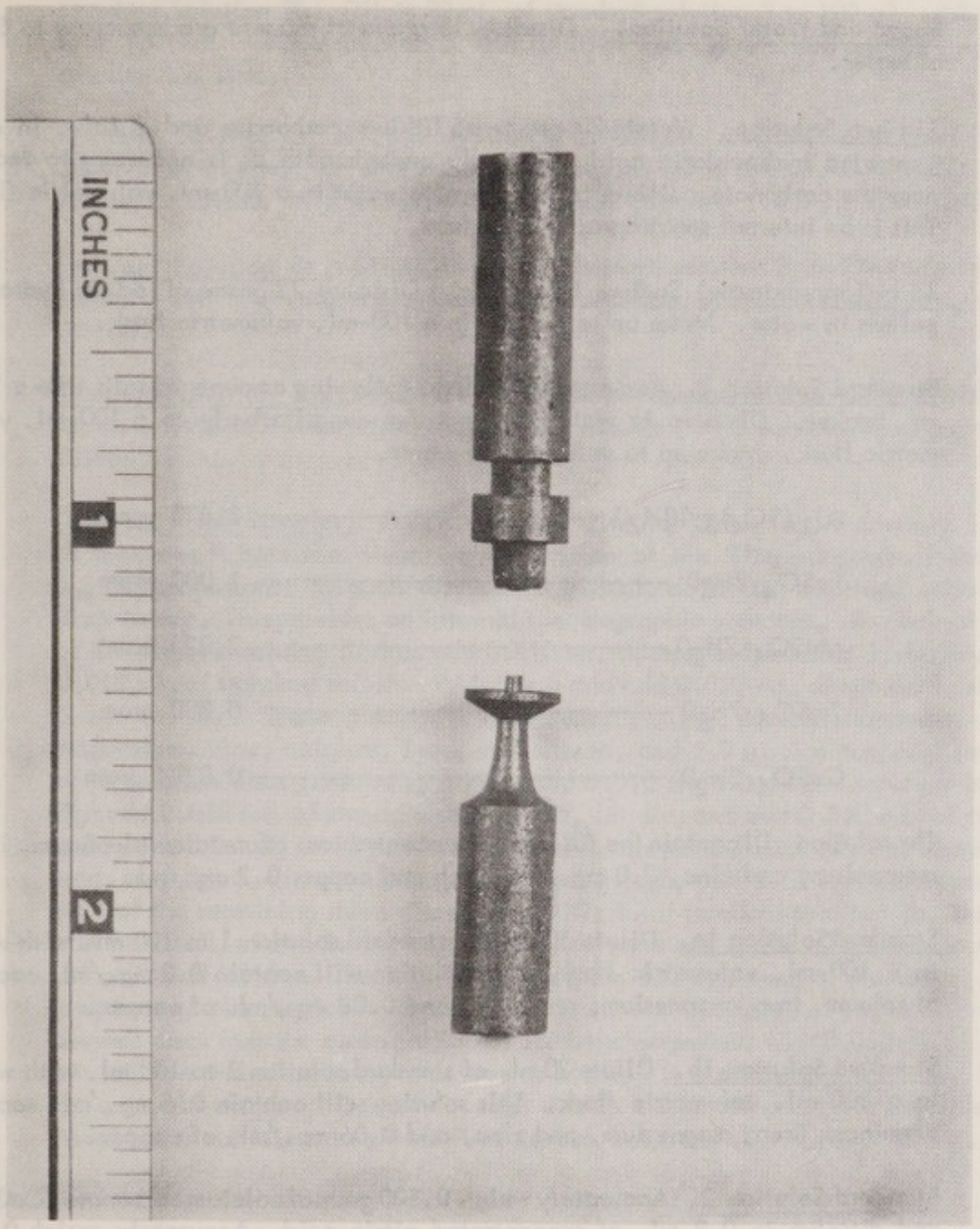


Figure 2. Spectrographic electrodes in respective positions. The upper electrode is a regular tip with undercut. The lower electrode is a platform type.

Sugar and Water Solution. Dissolve 15 grams of reagent grade sucrose in 60 ml. of water.

Lithium Solution. Weigh 20 grams of lithium carbonate and dissolve in concentrated hydrochloric acid using only enough acid as is necessary to decompose the carbonate. Dilute to volume with water in a 100-ml. volumetric flask. This is an internal spectrographic standard.

18 N (approximate) Sodium Hydroxide. Dissolve 72 grams of sodium hydroxide pellets in water. Make up to volume in a 100-ml. volumetric flask.

Standard Solution 1. Accurately weigh the following amounts of salts into a 250-ml. beaker. Dissolve in water and transfer quantitatively to a 100-ml. volumetric flask. Make up to volume with water.

$Al_2(SO_4)_3 \cdot 18H_2O$	2.470 grams
$FeSO_4 \cdot 7H_2O$	1.000 gram
$MgSO_4 \cdot 7H_2O$	2.026 grams
$ZnSO_4 \cdot 7H_2O$	0.880 gram
$CuSO_4 \cdot 5H_2O$	0.0794 gram

The solution will contain the following concentrations of metals: aluminum, iron, magnesium, and zinc, 2.0 mg./ml. each and copper 0.2 mg./ml.

Standard Solution 1a. Dilute 10 ml. of standard solution 1 to 100 ml. with water in a 100-ml. volumetric flask. This solution will contain 0.2 mg./ml. each of aluminum, iron, magnesium, and zinc, and 0.02 mg./ml. of copper.

Standard Solution 1b. Dilute 30 ml. of standard solution 1 to 100 ml. with water in a 100-ml. volumetric flask. This solution will contain 0.6 mg./ml. each of aluminum, iron, magnesium, and zinc, and 0.06 mg./ml. of copper.

Standard Solution 2. Accurately weigh 0.500 gram of calcium carbonate ($CaCO_3$) and dissolve in 0.8 ml. of concentrated nitric acid. Accurately weigh 0.320 gram of lead nitrate ($Pb(NO_3)_2$) and transfer with the calcium carbonate in nitric acid solution to a 100-ml. volumetric flask. Dilute to volume with water. This solution will contain 2.0 mg./ml. each of calcium and lead.

Standard Solution 2a. Dilute 10 ml. of standard solution 2 to 100 ml. with water in a 100-ml. volumetric flask. This solution will contain 0.2 mg./ml. each of calcium and lead.

Standard Solution 2b. Dilute 30 ml. of standard solution 2 to 100 ml. with water in a 100-ml. volumetric flask. This solution will contain 0.6 mg./ml. each of calcium and lead.

Standard Solution 3. Accurately weigh 0.300 gram of silicic acid (H_2SiO_3) and dissolve in 0.4 ml. of 18 N sodium hydroxide in a 100-ml. volumetric flask. Dilute to volume with water. This solution contains 1.0 mg./ml. of silicon.

Standard Solution 3a. Dilute 10 ml. of standard solution 3 to 100 ml. with water in a 100-ml. volumetric flask. This solution will contain 0.1 mg./ml. of silicon.

Standard Solution 3b. Dilute 30 ml. of standard solution 3 to 100 ml. with water in a 100-ml. volumetric flask. This solution will contain 0.3 mg./ml. of silicon.

Standard Filter Samples. Punch out nine circular disks, approximately 1 inch in diameter * from the clean unused portion of the filter-paper roll used for K_m determinations. To each disc add 0.010 ml. of lithium solution. Allow the discs to dry. This provides an internal spectrographic standard. To each of three of the discs containing lithium add 0.010 ml. of standard solution 1, let dry; add 0.010 ml. of standard solution 2, let dry; and add 0.020 ml. of standard solution 3 and let dry. These discs will then contain 20 µg. each of aluminum, iron, magnesium, zinc, calcium, lead, and silicon, and 2.0 µg. of copper. To each of three other discs containing lithium add 0.010 ml. of standard solution 1a, let dry; add 0.010 ml. of standard solution 2a, let dry; and add 0.020 ml. of standard solution 3a and let dry. These discs will contain 2.0 µg. each of aluminum, iron, magnesium, zinc, calcium, lead, and silicon, and 0.20 µg. of copper. To each of the remaining three discs add 0.010 ml. of standard solution 1b, let dry; add 0.010 ml. of standard solution 2b, let dry; and add 0.020 ml. of standard solution 3b and let dry. These discs will contain 6.0 µg. each of aluminum, iron, magnesium, zinc, calcium, lead, and silicon, and 0.60 µg. of copper. Prepare several discs from the clean portion of the filter-paper roll with 0.010 ml. of lithium solution and allow to dry to be used as blanks. It is customary to run one blank for every 10 samples. Carbonize each disc in a separate porcelain crucible at a temperature sufficient to give a final carbon weight of slightly over 10 mg.

CALIBRATION

It is necessary to calibrate the film to be used in subsequent analyses. By means of this calibration the operator will be able to convert percent transmission on the densitometer to relative intensity.

* The precise diameter for the discs is not critical, but they should be as large as is practicable, and it is essential that their exact area be known. The discs must be the same size for standards, blanks, and unknown samples.

With the spectrograph grating set so that well defined lines will appear in the 2950 to 3050A. region, expose the film to an iron spectrum (use iron electrodes) at two successive steps of the rotating sector. The sector steps are such that successive steps increase the transmitted light intensity by a factor of two. Selection of the steps is a matter of experience. Develop the film in Kodak D-19 for 3 minutes at 70°F. with agitation, stop in 5% acetic acid for 10 seconds, and fix with the rapid liquid fixer.

Call the step having the better transmission, the Clear Step, and the other the Absorbed Step. Adjust the densitometer so that the galvanometer reads percent transmission directly (100% for clear film). Then read 12 to 15 lines on the densitometer at both steps. Select the heaviest line on the clearer film which should have a reading of about 3 to 5% and the lightest line which should be 80 to 90%. Prepare a preliminary curve, similar to Figure 3, plotting on rectangular-coordinate graph paper the percent transmission of the Absorbed Step, T_A, vs. the percent transmission of the Clear Step, T_C, for each line.

Prepare a second graph on log-log paper with percent transmission as the ordinate and relative intensity as the abscissa. Choose a point (T_A', T_C') from the preliminary curve and plot T_C' at an intensity of 1.0 and T_A' at an intensity of 0.5 (a factor of two in intensity occurs between successive sector steps). From the preliminary curve, obtain the T_A of a point whose T_C is numerically the same as T_A', call this T_A'' and plot it at an intensity of 0.25. Also, from the preliminary curve, read the T_C of a point which has a T_A numerically the same as T_C', call this T_C''' and plot it at an intensity of 2.0. Read the T_C of another point from the preliminary curve which has a T_A numerically the same as T_C''', call this T_C'''' and plot it at an intensity of 4.0. Draw a curve connecting all the points. This is then called the calibration curve (Figure 4).

Prepare a calibration scale by projecting lines horizontally from the vertical axis to the calibration curve and then down to the horizontal axis for each value of percent transmission (Figure 5). This scale is then used to prepare the slide rule shown in Figure 6.

COLLECTION OF THE SAMPLE

The samples are collected by means of the Auto-Sampler discussed under "K_m Values" (Method No. APCD 3-54).

SAMPLE PREPARATION

Punch a circular disc out of the center of each filter spot. The area of each disc should be the same as those used for standards and blanks. To each disc add 0.010 ml. of lithium solution and allow the discs to dry. Carbonize each disc in a separate porcelain crucible at a temperature sufficient to give a final carbon weight of slightly over 10 mg. Mix each char well and weigh out 10 mg. of each mix. Carry the blanks and nine standards through the rest of the procedure along with the samples. Secure each 10 mg. char with sugar and water solution to separate platform electrodes.

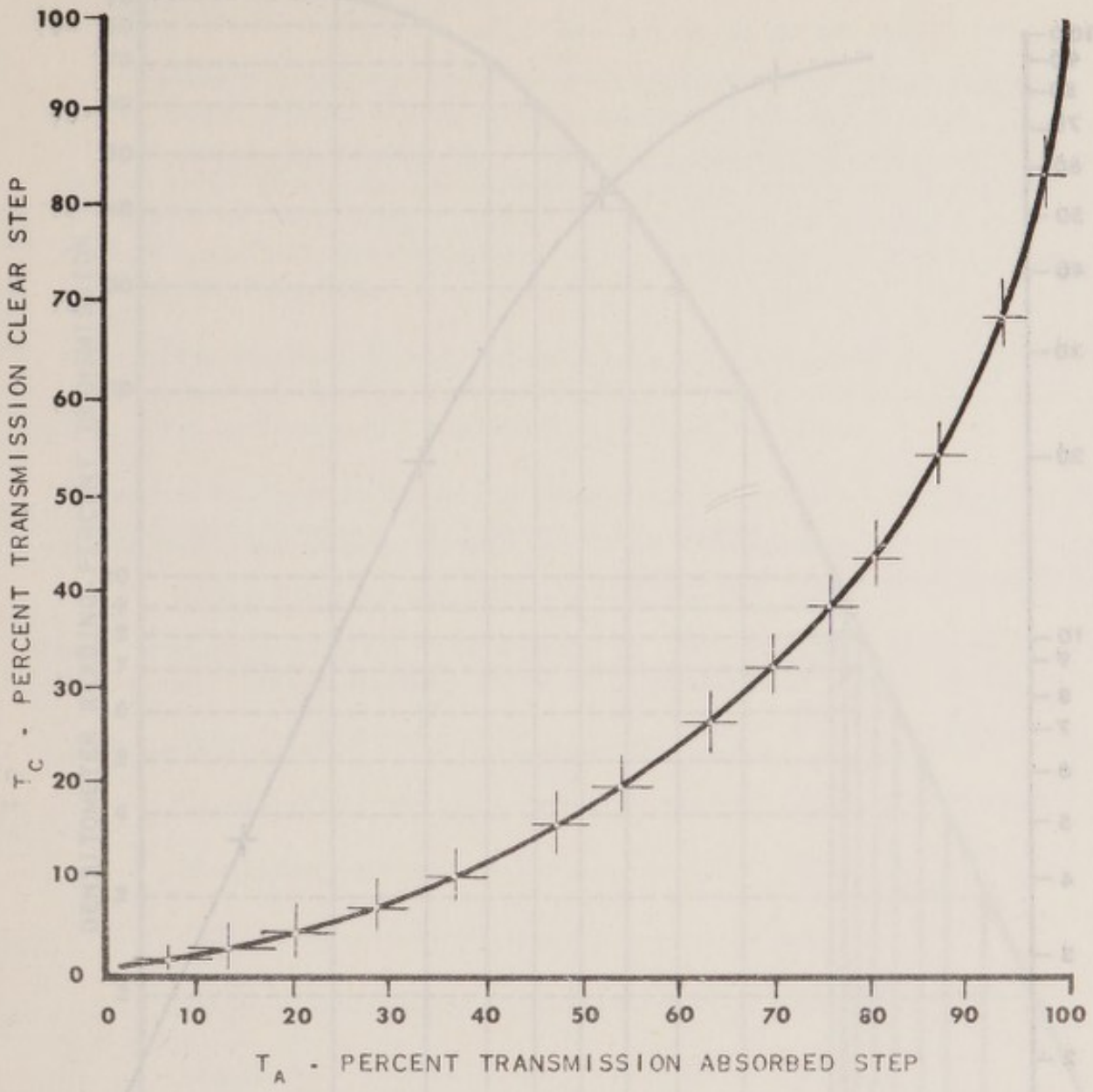


Figure 3. Preliminary calibration curve.

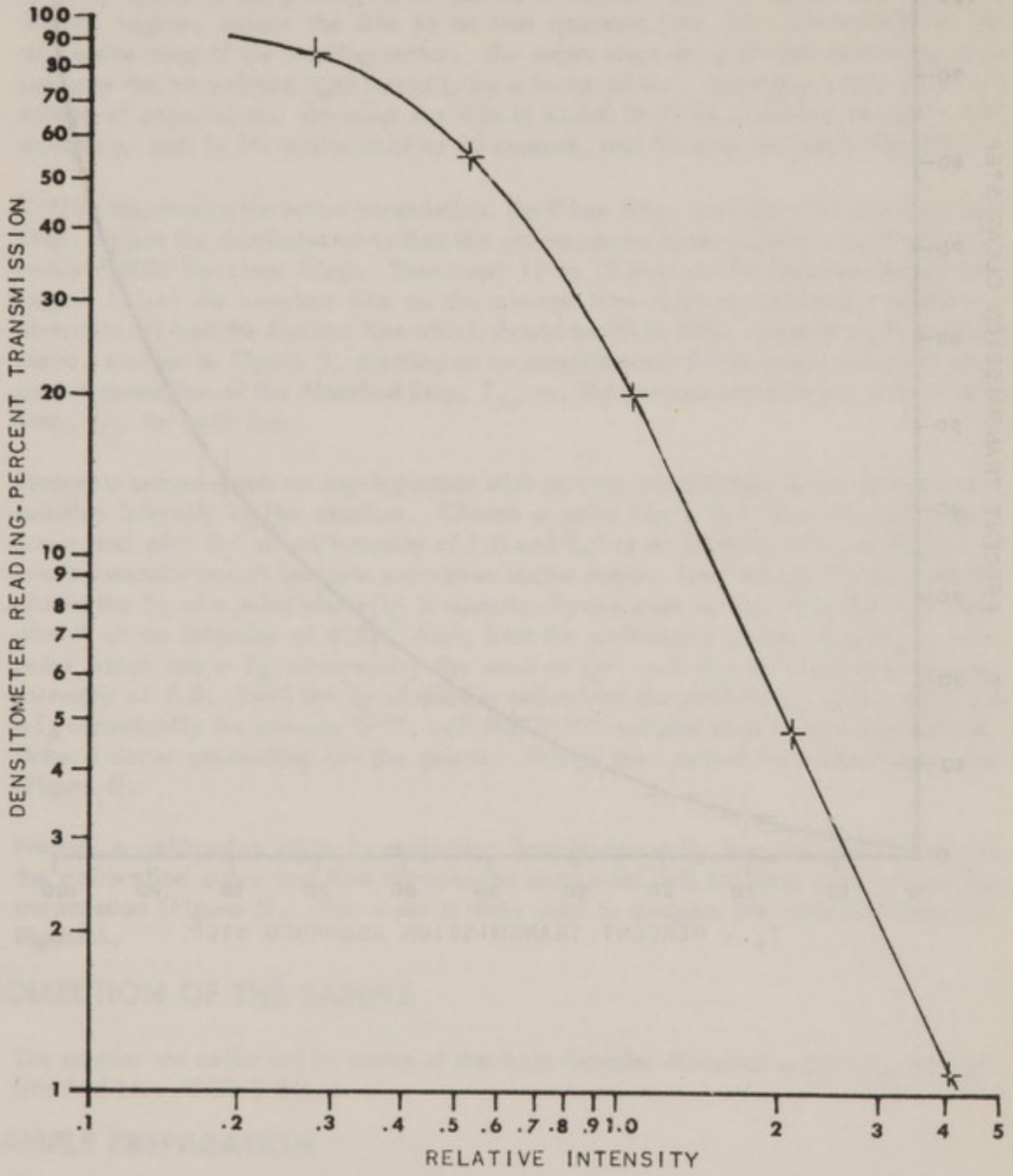


Figure 4. Calibration curve.

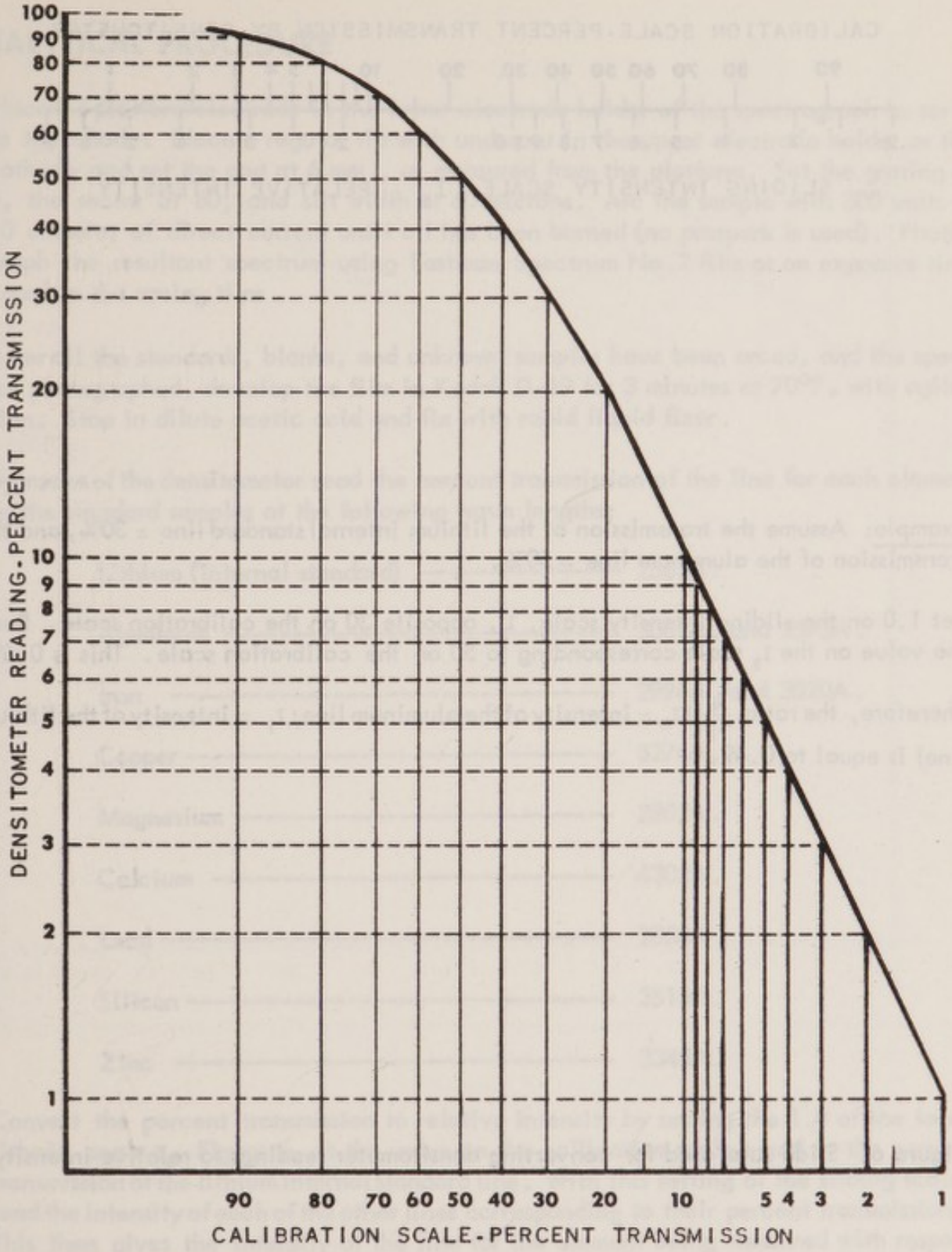
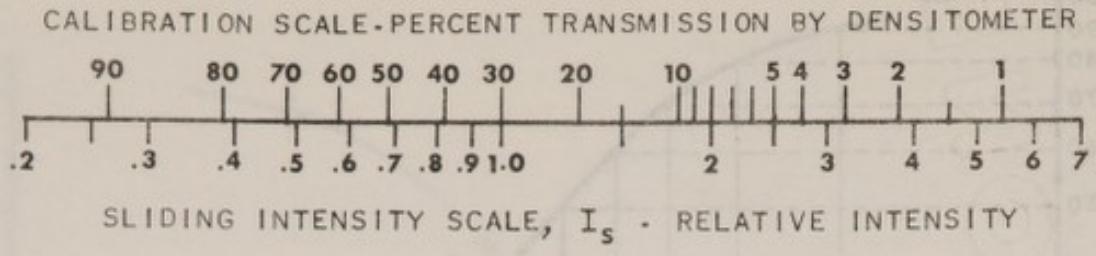


Figure 5. Calibration scale preparation.



Example: Assume the transmission of the lithium internal standard line = 30%, and the transmission of the aluminum line = 50%.

Set 1.0 on the sliding intensity scale, I_s, opposite 30 on the calibration scale. Read the value on the I_s scale corresponding to 50 on the calibration scale. This is 0.69.

Therefore, the ratio $\frac{I_e}{I_l}$ (I_e = intensity of the aluminum line; I_l = intensity of the lithium line) is equal to 0.69.

Figure 6. Slide rule used for converting densitometer readings to relative intensity.

ANALYTICAL PROCEDURE

Place the platform electrode in the lower electrode holder of the spectrograph to serve as the anode. Place a regular tip with undercut in the upper electrode holder as the cathode and set the gap at 6 mm., as measured from the platform. Set the grating at 5, the sector at 60, and slit width at 60 microns. Arc the sample with 300 volts at 10 amperes of direct current until all has been burned (no prespark is used). Photograph the resultant spectrum using Eastman Spectrum No.2 film at an exposure time equal to the arcing time.

After all the standards, blanks, and unknown samples have been arced, and the spectra photographed, develop the film in Kodak D-19 for 3 minutes at 70°F. with agitation. Stop in dilute acetic acid and fix with rapid liquid fixer.

By means of the densitometer read the percent transmission of the line for each element in the standard samples at the following wave lengths:

Lithium (internal standard)	2563A.
Aluminum	3082A. and 2575A.
Iron	2994A. and 3020A.
Copper	3274A.
Magnesium	2802A.
Calcium	4302A.
Lead	2833A.
Silicon	2516A.
Zinc	3345A.

Convert the percent transmission to relative intensity by setting the 1.0 of the logarithmic scale I_s, Figure 6, at the value on the calibration scale equal to the percent transmission of the lithium internal standard line. With this setting of the sliding scale, read the intensity of each of the other lines corresponding to their percent transmissions. This then gives the intensity of the line for the element being measured with respect to the lithium standard as unity.

Prepare working curves, similar to Figures 7a and 7b for each of the above elements contained in the standards by plotting micrograms of each element vs $\frac{I_e}{I_l}$ on log-log paper.

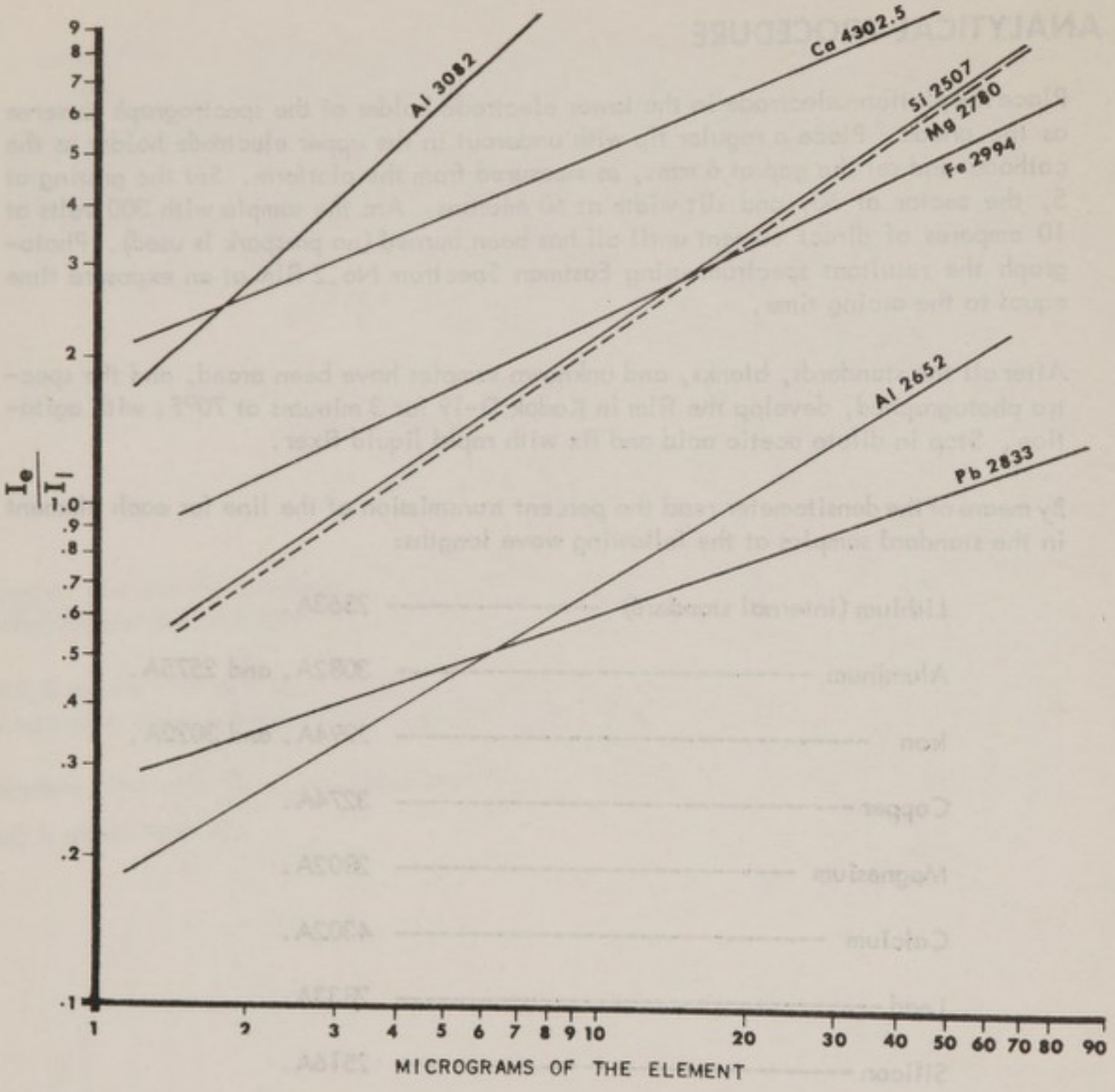


Figure 7a. Sample working curve for various metals to be analyzed.

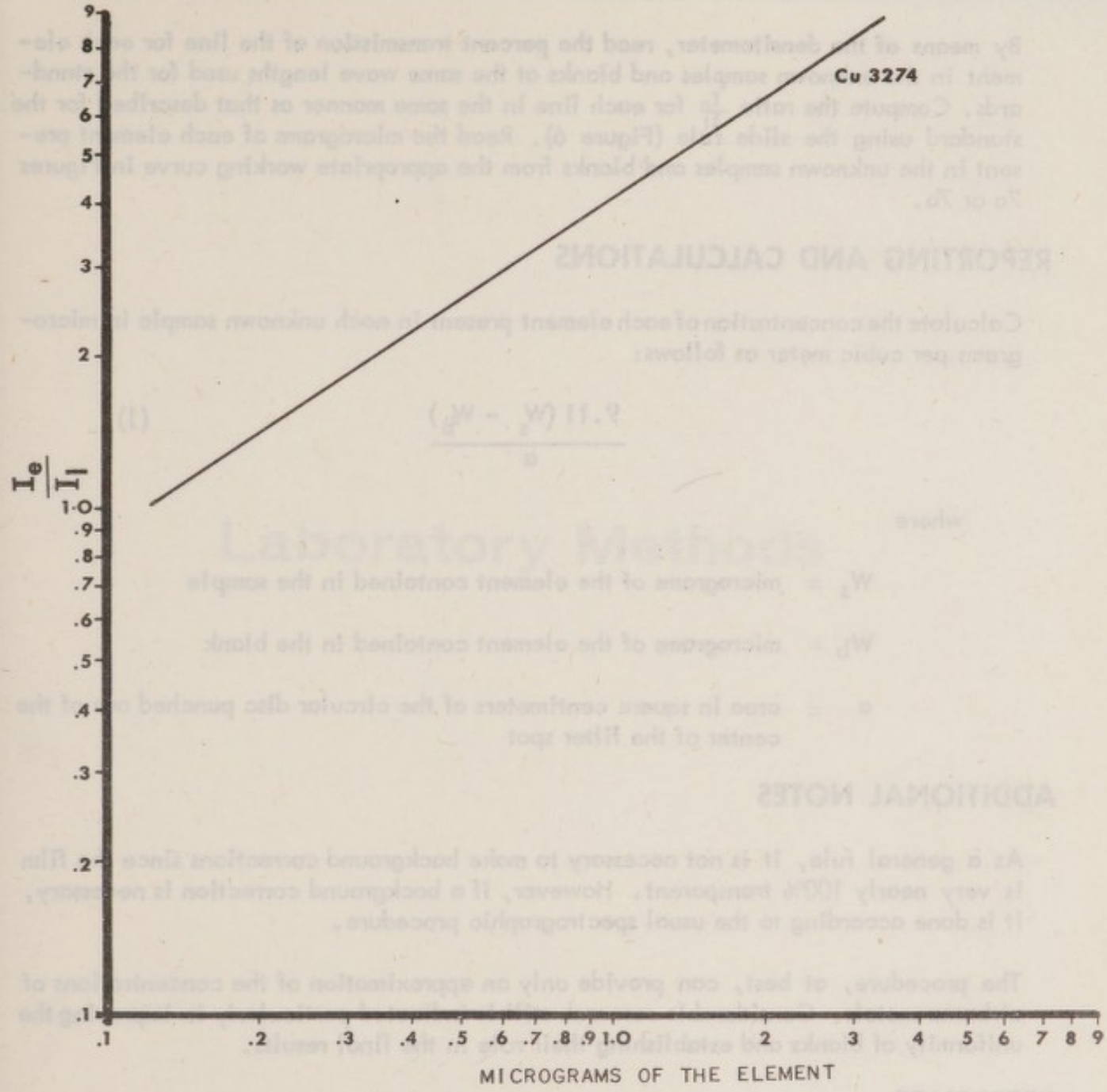


Figure 7b. Sample working curve for copper.

By means of the densitometer, read the percent transmission of the line for each element in the unknown samples and blanks at the same wave lengths used for the standards. Compute the ratio $\frac{I_e}{I_l}$ for each line in the same manner as that described for the standard using the slide rule (Figure 6). Read the micrograms of each element present in the unknown samples and blanks from the appropriate working curve in Figures 7a or 7b.

REPORTING AND CALCULATIONS

Calculate the concentration of each element present in each unknown sample in micrograms per cubic meter as follows:

$$\frac{9.11\,(W_s - W_b)}{a} \qquad (1)$$

where

W_s = micrograms of the element contained in the sample

W_b = micrograms of the element contained in the blank

a = area in square centimeters of the circular disc punched out of the center of the filter spot

ADDITIONAL NOTES

As a general rule, it is not necessary to make background corrections since the film is very nearly 100% transparent. However, if a background correction is necessary, it is done according to the usual spectrographic procedure.

The procedure, at best, can provide only an approximation of the concentrations of airborne metals. Considerable research still is indicated particularly in improving the uniformity of blanks and establishing their role in the final results.

REFERENCE

Harvey, C.E., "Spectrochemical Procedures," Applied Research Laboratories, Glendale, California, 1950.

ALDEHYDES, TOTAL APCD 5-46

Laboratory Methods

IR POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

ALDEHYDES, TOTAL

APCD 5-46

SCOPE

This procedure is used to determine total aldehydes in either the atmosphere or specific sources. It is independent of any change in bisulfite-ion concentration caused by atmospheric oxidation of the collection medium. However, ketones, if present in the sample, will be included in the results. The lower limit of the method is about 0.02 p.p.m. for a 168-liter air sample, and 1 p.p.m. for a 2-liter grab sample.

METHOD SUMMARY

The samples are reacted with a solution of sodium bisulfite to form addition compounds. The excess bisulfite ion is destroyed with iodine solution. By adjusting the pH of the solution, the addition compounds are decomposed freeing bisulfite ion equivalent to the aldehydes present in the sample. The liberated bisulfite ion is then titrated with standard iodine.

SPECIAL APPARATUS

COLLECTION:

For Air Sampling. Three midget impingers connected in series to a stopcock, orifice-type flowmeter, and air pump, assembled as shown in Figure 1.

For Source Testing. Two-liter round-bottomed flask with a short length of 8-mm. glass tubing connected to the neck, 3-inch length of heavy-wall gum-rubber tubing, screw clamp, and solid-glass plug.

REAGENTS

COLLECTION:

1% (approximate) Sodium Bisulfite. Dissolve 5 grams of sodium bisulfite ($NaHSO_3$) in 500 ml. of water.

ANALYTICAL:

1% Starch. Weigh 1 gram of soluble starch into a 150-ml. beaker. Add 1 to 2 ml. of water and stir to make a paste. In a separate beaker, heat 100 ml. of water to boiling and pour into the paste while stirring. For accurate work the starch solution should be made fresh daily.

0.05N Sodium Thiosulfate. Dissolve 12.5 grams of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 1 liter of freshly boiled and cooled water. Add 0.1 gram of sodium carbonate as a preservative. This will retard the slow change of titer

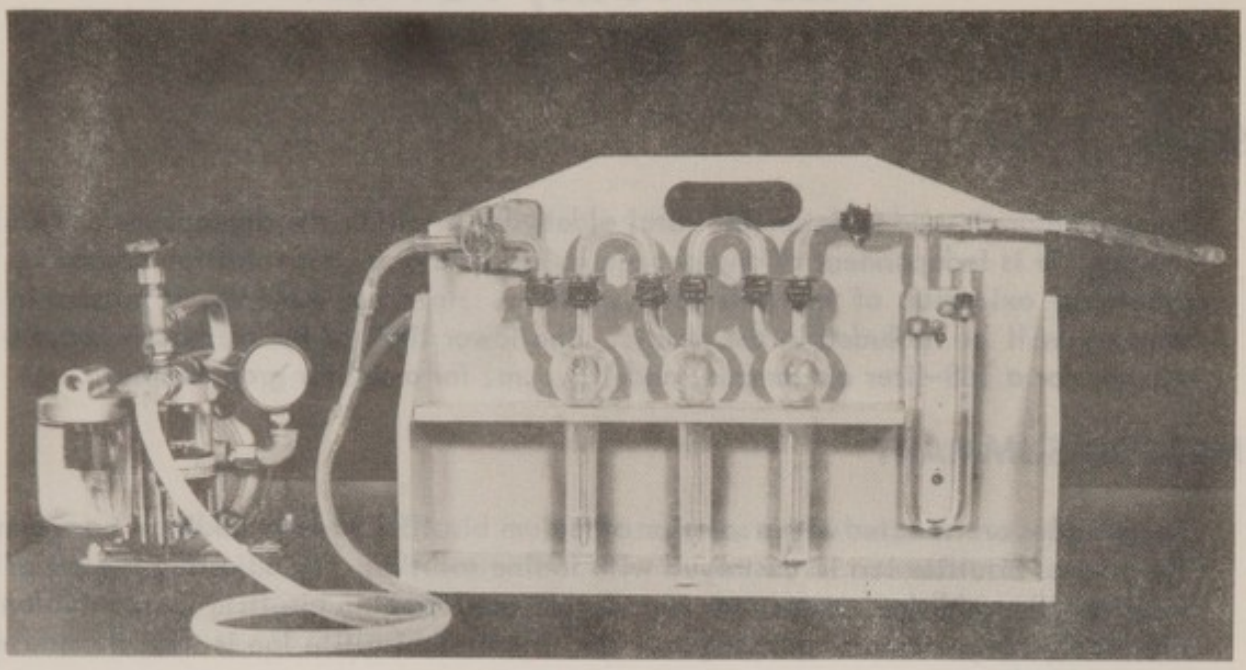


Figure 1. Midget impinger train used for air sampling.

which a solution of thiosulfate normally undergoes. Allow the solution to stand for 24 hours before use. To standardize the thiosulfate proceed as follows: Dry some potassium dichromate (primary-standard grade) in an oven at 110°C. for 1 hour. Cool in a desiccator. Weigh 2.452 grams of the dry dichromate into a 1-liter volumetric flask and dissolve in about 500 ml. of water. Make up to volume with water and mix thoroughly. Pipet exactly 25 ml. of the solution into a 500-ml. Erlenmeyer flask. Pour 25 ml. of water into another Erlenmeyer flask for a blank determination. Add 50 ml. of water, 10 ml. of concentrated hydrochloric acid, and 3 grams of solid potassium iodide to each flask. Swirl each flask once, cover, and place in the dark for 5 minutes. Dilute the solution in each flask with 200 ml. of water and titrate with the 0.05N sodium thiosulfate solution until the brown color is almost discharged. Add 3 ml. of starch indicator and titrate to colorless. Subtract the volume of sodium thiosulfate required for the blank titration from the sample titration. The normality of the sodium thiosulfate solution is:

$$\frac{1.25}{V_t} \qquad (1)$$

where

V_t = milliliters of sodium thiosulfate used for the titration (blank subtracted)

0.1N (approximate) Iodine. Dissolve 20 to 25 grams of potassium iodide in as little water as possible. Add 12.7 grams of iodine and stir. When dissolved, make up to 1 liter with water and store in a dark bottle. This reagent need not be standardized.

0.005N Iodine. Dilute 50 ml. of 0.1N iodine to 1 liter with water. Standardize daily with the 0.05N sodium thiosulfate as follows: Pipet 50 ml. of the iodine solution into a 250-ml. Erlenmeyer flask. Titrate with the 0.05N sodium thiosulfate until the brown color is almost discharged. Add 3 ml. of starch indicator and titrate to colorless. The normality of the iodine solution is:

$$0.02\ V_t N_t \qquad (2)$$

where

V_t = milliliters of sodium thiosulfate used for the titration

N_t = exact normality of sodium thiosulfate

Buffer Solution. Dissolve 80 grams of anhydrous sodium carbonate in 500 ml. of water. Add 20 ml. of glacial acetic acid slowly to avoid excessive frothing. Dilute to 1 liter. Adjust the pH to 9.6 ($\pm$0.1) with sodium carbonate or acetic acid as required using a pH meter.

COLLECTION OF THE SAMPLE

For Air Sampling. Pipet 10 ml. of 1% sodium bisulfite into each of the three midget impingers. A pipet is used for convenience rather than for accuracy. Assemble the sampling apparatus as shown in Figure 1. Draw the air sample through the impingers for 1 hour at a rate of 2.8 liters per minute (0.1 cubic foot per minute). Regulate the flow with the stopcock between the last impinger and the pump. Ordinarily, the temperature correction for the volume of gas may be neglected, unless the temperature goes above about 100°F. or below about 50°F. The moisture in the air sample can also be neglected. Pour the contents of all three impingers into a screw-cap bottle for transport back to the laboratory. Rinse each impinger with a small amount of water and add the rinsings to the bottle. For continuous hourly sampling, two sets of impingers are used, one on each side of the holder in Figure 1. While one sample is being taken, the other set of impingers are prepared. At the end of the hour the operating impinger train is turned off and the other is immediately turned on.

For Source Testing. To a clean 2-liter sample flask add 10 ml. of 1% sodium bisulfite solution. Connect the flask to a vacuum source and evacuate to boiling (vapor pressure of the solution). Pinch off the rubber tubing with the screw clamp and disconnect from the source of vacuum. Insert the solid-glass plug into the open end of the rubber tubing. To collect the sample remove the glass plug and open the screw clamp for about 10 seconds at the source. Retighten the screw clamp and replace the glass plug.

SAMPLE PREPARATION

For Air Sampling. Pour the contents of the screw-cap bottle into a 250-ml. Erlenmeyer flask. Rinse the bottle two or three times with water and add the rinsings to the flask. Prepare a blank by adding 10 ml. of 1% sodium bisulfite solution and 40 ml. of water to a 250-ml. Erlenmeyer flask.

For Source Testing. Shake the sample flask for 15 minutes with frequent rotation to provide a thorough scrubbing action. Determine the pressure of the flask by connecting it to an open-end mercury manometer and measuring the difference, in millimeters, between the mercury levels. Note the room temperature and atmospheric pressure. Pour the contents into a 250-ml. Erlenmeyer flask. Rinse the sample flask two or three times with water and add the rinsings to the Erlenmeyer flask. Prepare a blank in the same manner as described above under air sampling.

ANALYTICAL PROCEDURE

Pour 2 ml. of 1% starch solution into each flask. Add 0.1N iodine dropwise until a dark blue color is produced. Care should be taken to see that all of the sulfur dioxide resulting from the decomposition of bisulfite is removed as it may cause the end point to fade. This can be conveniently accomplished by blowing a small jet of air into the flask while swirling the contents vigorously for several minutes. Decolorize each

solution by adding 0.05N sodium thiosulfate dropwise. Add 0.005N iodine to a faint blue end point. Cool thoroughly in an ice bath and add 50 ml. of chilled buffer to each flask. Allow to stand in the ice bath for 10 to 15 minutes after the buffer addition. Then titrate the liberated bisulfite in each flask with 0.005N iodine to the same faint blue end point present before addition of the buffer. Keep the sample chilled in order to avoid a fading end point.

REPORTING AND CALCULATIONS

For Air Sampling. The concentration of aldehydes (mono) in parts per million by volume is:

$$72\ VN \qquad (3)$$

where

V = milliliters of 0.005N iodine used for the titration following the addition of buffer (blank must be subtracted)

N = exact normality of 0.005N iodine

For Source Testing. Aldehydes (mono) in parts per million by volume (dry basis) is:

$$\frac{VNT \times 31.2 \times 10^3}{v_m (P_r + \Delta P)} \qquad (4)$$

where

V = milliliters of 0.005N iodine used for the titration following the addition of buffer (blank must be subtracted)

N = exact normality of the iodine used for the titration following the addition of buffer

ΔP = sample flask differential pressure, millimeters of mercury (with respect to atmospheric pressure)

P_r = atmospheric pressure, millimeters of mercury (at the time of the ΔP measurement)

T = room temperature, degrees Kelvin (at the time of the ΔP measurement)

V_m = measured volume of sample flask, liters *

To express the results in terms of grains per standard cubic foot (60°F., and 1 atmosphere) as formaldehyde, multiply the parts per million of aldehydes by 5.53×10^{-4}.

REFERENCE

Goldman, F. H., and Yagoda, H., Ind. Eng. Chem., Anal. Ed., 15, 377-8 (1943).

*Where moisture was present in the original sample and it is desired to put the sample volume on a stack-conditions basis, a correction must be applied to Formula 4. The moisture is usually determined in conjunction with some other test such as grain loading.

AMMONIA AND AMMONIUM ION APCD 6-56

Laboratory Methods

IR POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

AMMONIA AND AMMONIUM ION

APCD 6-56

SCOPE

Ammonia and ammonium ion are frequently encountered in tests of furnace stacks, catalytic cracking plant regenerator emissions, and other specific sources. Because extremely large samples would be required, the method is generally not practical for air monitoring. The lower limit of the method is about 0.5 p.p.m. in a 1680-liter sample.

METHOD SUMMARY

The sample is collected by passing the gas through impingers containing water and dilute hydrochloric acid. The impinger solutions are combined and analyzed for ammonia using the well-known Kjeldahl procedure.

SPECIAL APPARATUS

COLLECTION:

Three standard Greenburg-Smith impingers held in a combination ice bath and rack, connected in series to a mercury manometer, dry gas meter (Zephyr No. 1A, Sprague Meter Co., Los Angeles, Calif., or equivalent), and air pump, with a screw clamp to control the gas-flow rate. The apparatus is assembled as shown in Figure 1.

ANALYTICAL:

Kjeldahl distillation apparatus as shown in Figure 2.

REAGENTS

COLLECTION:

5% (by weight) Hydrochloric Acid. Dilute 116 ml. of concentrated hydrochloric acid to 1 liter with water.

ANALYTICAL:

30% Sodium Hydroxide. Dissolve 300 grams of sodium hydroxide in water and make up to 1 liter. The caustic should be guaranteed suitable for Kjeldahl determinations and contain less than 0.001% nitrogen.

0.1% Methyl Red Indicator. Dissolve 0.1 gram of methyl red in 100 ml. of 95% ethyl alcohol.

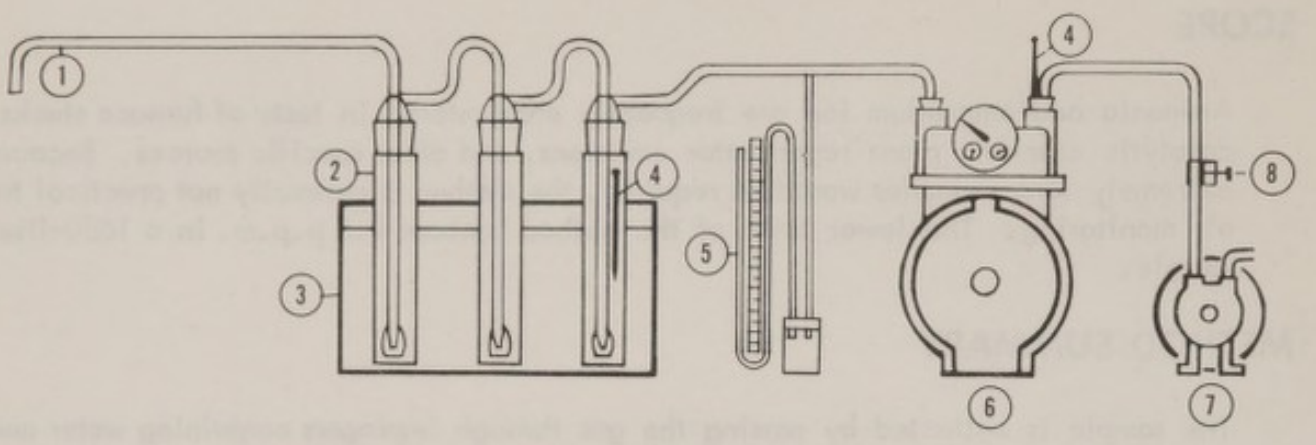


Figure 1. Sampling apparatus. (1) Sample probe. (2) Standard Greenburg-Smith impingers. (3) Ice-bath container. (4) Thermometer. (5) Mercury manometer. (6) Dry gas meter. (7) Air pump. (8) Screw clamp to control gas flow rate.

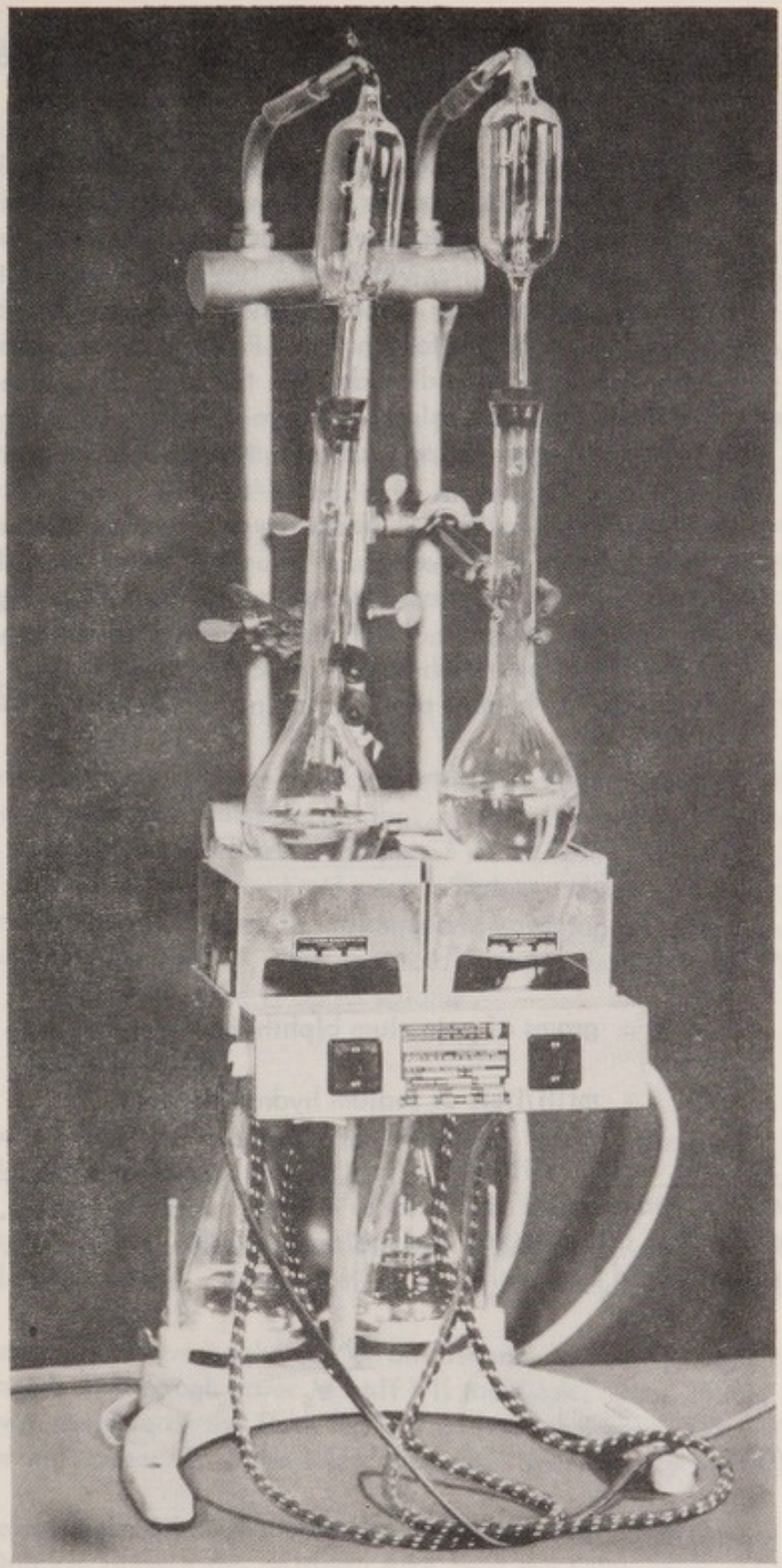


Figure 2. Two-unit Kjeldahl distillation apparatus showing Kjeldahl flask and trap in place.

0.05% Phenolphthalein Indicator. Dissolve 0.05 gram of the solid in 50 ml. of 95% ethyl alcohol. Add 50 ml. of water.

0.1N Sodium Hydroxide. Dissolve 50 grams of sodium hydroxide pellets in 50 ml. of water in a polyethylene bottle. Allow to settle overnight or centrifuge. Weigh 8 grams of the clear supernatant liquid into a 100-ml. Erlenmeyer flask. Transfer the solution to a 1-liter volumetric flask and make up to the mark with freshly boiled and cooled water. Thoroughly mix the solution and transfer to a clean, dry polyethylene bottle for storage. Perform these operations quickly to avoid contamination by carbon dioxide from the air. If considerable quantities of standard sodium hydroxide solutions are to be handled, a large polyethylene bottle with siphon arrangement and Ascarite tube should be used.

Standardize the sodium hydroxide as follows: Dry some potassium biphthalate (primary-standard grade) in an oven at 110°C. for 1 hour. Cool in a desiccator. Accurately weigh, to the nearest tenth of a milligram, two 1-gram portions of the salt into separate 250-ml. Erlenmeyer flasks. Dissolve each in 25 ml. of water. Add 2 drops of phenolphthalein indicator to each flask and titrate with the sodium hydroxide to a faint pink end point.

Calculate the normality as follows:

$$\frac{4.90\ W}{V} \qquad (1)$$

where

W = grams of potassium biphthalate weighed into flask

V = milliliters of sodium hydroxide used

0.1N Sulfuric Acid. Dilute 2.7 ml. of concentrated sulfuric acid to 1 liter with water. Standardize the acid by titrating with standard 0.1N sodium hydroxide solution using methyl red indicator (yellow end point). The normality of the sulfuric acid is:

$$\frac{NV}{V_s} \qquad (2)$$

where

N = exact normality of sodium hydroxide used

V = milliliters of sodium hydroxide used

V_s = milliliters of sulfuric acid used

COLLECTION OF THE SAMPLE

Set up the apparatus so that the sample gas passes through the three impingers (connected in series), then through the dry gas meter, and out the vacuum pump. Place the mercury manometer between the last impinger and the gas meter, and the screw clamp between the gas meter and the air pump. Place a thermometer in the last impinger, and another in the gas meter (Figure 1). The former is used only in conjunction with other tests when the total moisture in the stack gases is to be determined. It is not pertinent to this procedure, and is left in place merely for convenience.

Add exactly 100 ml. of water to the first impinger and 100 ml. of 5% hydrochloric acid to the second impinger. Operate the third impinger dry to protect the meter and to catch any carryover. Place the impingers in an ice bath. Draw the sample through the impingers at 28.3 liters per minute (1 cubic foot per minute) for 1 hour. This will provide sufficient sample for measurements as low as 0.5 p.p.m. ammonia. Aliquots of the impinger solutions may be used where concentrations are higher. Record meter temperatures and pressures at 10-minute intervals during sampling and obtain an average.

SAMPLE PREPARATION

Pour the solutions from all three impingers into a clean, dry, 250-ml. graduate (or larger, depending on the moisture content of the gas) and note the volume. This is necessary to calculate the correct volume of the sample. Rinse the impingers twice with a small amount of water and make up to volume where an aliquot is to be taken later. In some tests, such as on an incinerator employing an afterburner, little or no ammonium ion may be present, and the total sample would be used. Therefore, it would not be necessary to make it up to volume.

ANALYTICAL PROCEDURE

Steam out the distillation apparatus for 1/2 hour by distilling over water from the Kjeldahl flask before each day's work.

Add exactly 100 ml. of 0.1N sulfuric acid and 2 to 4 drops of methyl red indicator to a 500-ml. Erlenmeyer flask. Immerse the end of the condenser in the solution.

Transfer the solution to be analyzed, or an aliquot, to the Kjeldahl flask. Add two or three glass beads and enough water to half fill the flask. Pour 25 ml. of 30% sodium hydroxide down the side of the flask rapidly without shaking. Place the flask on the electric heater and connect it to the Kjeldahl trap. Swirl gently to start the reaction.

Bring the contents of the Kjeldahl flask to a gentle boil and distill over about 150 ml. of liquid. Quickly remove the delivery tube from the Erlenmeyer flask after heating is stopped to prevent drawing back the sulfuric acid solution. Rinse the end of the tube into the Erlenmeyer flask and titrate with 0.1N sodium hydroxide to a yellow end point. Run a blank on 25 ml. of each new batch of 30% sodium hydroxide in the same manner and subtract it from the sample titration (see REPORTING AND CALCULATIONS).

REPORTING AND CALCULATIONS

The vapor equivalent of the condensate, v_w, in cubic feet at meter conditions is:

$$\frac{0.00267\ VT}{P} \qquad (3)$$

where

V = milliliters of water condensed in impingers (difference between initial and final volumes)

P = average meter pressure, inches of mercury absolute

T = average meter temperature, degrees Rankine

The corrected volume of the gas sample, v_c, in standard cubic feet (60°F., 1 atmosphere)is:

$$\frac{17.36\ P(v_m + v_w)}{T} \qquad (4)$$

where

v_m = volume of sample, cubic feet at meter conditions

v_w = vapor equivalent of condensate, cubic feet at meter conditions, from Formula 3

P = average meter pressure, inches of mercury absolute

T = average meter temperature, degrees Rankine

Calculate the ammonia in parts per million by volume as follows:

$$(V_a N_a - V_b N_b - V_c N_c + V_d N_d)\left(\frac{836\ A}{v_c}\right) \qquad (5)$$

where

V_a = milliliters of 0.1N sulfuric acid used for the sample

V_b = milliliters of 0.1N sodium hydroxide used for the sample titration

V_c = milliliters of 0.1N sulfuric acid used for the blank

V_d = milliliters of 0.1N sodium hydroxide used for the blank titration

N_a = exact normality of the 0.1N sulfuric acid used for the sample

N_b = exact normality of the 0.1N sodium hydroxide used for the sample titration

N_c = exact normality of the 0.1N sulfuric acid used for the blank

N_d = exact normality of the 0.1N sodium hydroxide used for the blank titration

$$A = \text{aliquot factor} = \frac{\left(\begin{array}{l}\text{volume to which absorbing solution}\\ \text{was diluted, milliliters}\end{array}\right)}{\left(\begin{array}{l}\text{aliquot used for the distillation,}\\ \text{milliliters}\end{array}\right)}$$

NOTE: Where the complete sample was used, A = 1

V_c = volume of the gas sample, corrected to 60°F. and 1 atmosphere, from Formula 4

In the usual case where the same sulfuric acid and sodium hydroxide are used for both the sample titration and blank titration, Formula 5 reduces to:

$$\frac{836\, AN_b\,(V_d - V_b)}{V_c} \qquad (6)$$

The symbols are the same as defined for Formula 5

To express the result in grains of ammonia per standard cubic foot (60°F., and 1 atmosphere) multiply the parts per million by 3.13×10^{-4}.

APCD

DUSTFALL APCD 7-53

Laboratory Methods

AIR POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

DUSTFALL

APCD 7-53

SCOPE

This procedure is used for measuring atmospheric dustfall. Airborne particulate matter settles into a jar containing water which is left out of doors for a month.

METHOD SUMMARY

The insoluble solids are measured by filtering and weighing a portion of the sample. The filtrate is evaporated and weighed to yield total soluble solids. Insoluble and soluble ashes are obtained on these samples after ignition in a muffle furnace. Another portion of the original sample is titrated to the methyl red end point with sodium hydroxide and the titer expressed as sulfur dioxide. Carbon dioxide is similarly determined by titrating to the phenolphthalein end point with sodium hydroxide. Chlorides are measured by titration with mercuric nitrate.

SPECIAL APPARATUS

COLLECTION:

3.5-liter square glass jar with screw-cap top (Anchor Hocking No. 274) (Figure 1).

REAGENTS

COLLECTION:

Distilled Water.

ANALYTICAL:

0.005N Potassium Chloride. Dissolve 0.373 gram of potassium chloride in about 500 ml. of water and dilute to 1 liter.

0.05N (approximate) Nitric Acid. Dilute 3.2 ml. of concentrated nitric acid to 1 liter with water.

0.05N (approximate) Sodium Hydroxide. Dissolve 2 grams of sodium hydroxide pellets in water and dilute to 1 liter.

Diphenylcarbazone-Bromophenol Blue Mixed Indicator. Dissolve 0.5 gram of diphenylcarbazone and 0.05 gram of bromophenol blue in 75 ml. of 95% ethyl alcohol and dilute to 100 ml. therewith. Store in a brown bottle.

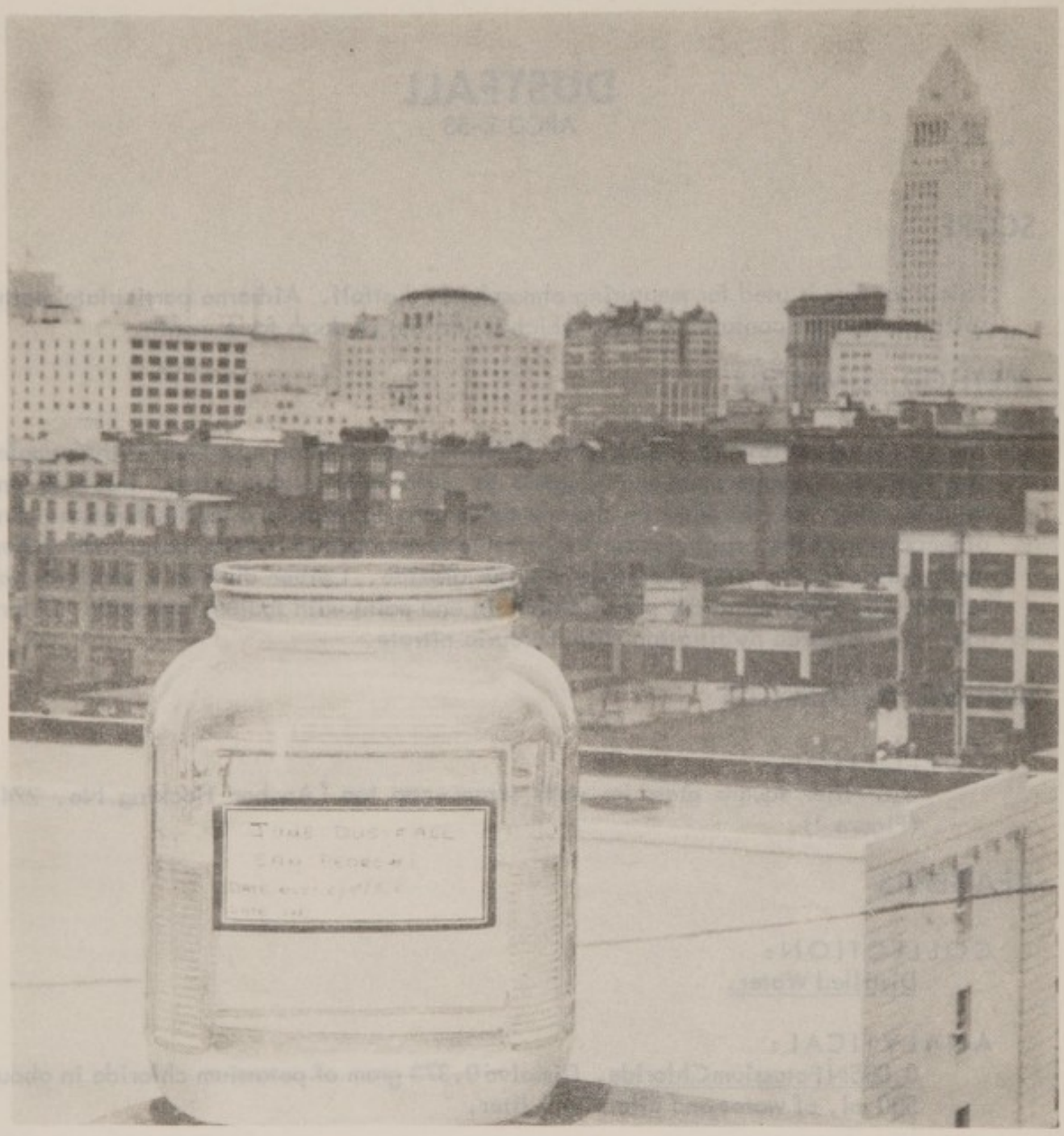


Figure 1. Dustfall jar shown in place at a station.

0.005N Mercuric Nitrate. Dissolve 0.4 gram of mercuric nitrate ($Hg(NO_3)_2 \cdot H_2O$) in water and dilute to 500 ml. Standardize the solution as follows: Dilute 10 ml. of 0.005N potassium chloride to 100 ml. with water in a 250-ml. Erlenmeyer flask. Place 100 ml. of water in another 250-ml. Erlenmeyer flask as a blank. Add 5 drops of the mixed indicator to each flask. If a blue-violet or red color develops, add 0.005N nitric acid dropwise until the color changes to yellow and add 1 ml. in excess. If a yellow or orange color forms on addition of the indicator, develop the blue-violet color by adding 0.05N sodium hydroxide dropwise, and then return to the yellow with nitric acid as above. The final solution should contain 1 ml. acid in excess.

Titrate the yellow acidified sample and blank with 0.005N mercuric nitrate to the first appearance of the blue-violet color. Subtract the volume of 0.005N mercuric nitrate needed for the blank titration from the sample titration. Calculate the normality of the mercuric nitrate as follows:

$$\frac{0.05}{V} \qquad (1)$$

where

V = milliliters of mercuric nitrate solution used for the titration (blank subtracted)

0.1N Sodium Hydroxide. Dissolve 50 grams of sodium hydroxide pellets in 50 ml. of water in a polyethylene bottle. Allow to settle overnight or centrifuge. Weigh 8 grams of the clear supernatant liquid into a 100-ml. Erlenmeyer flask. Transfer the solution quickly to a 1-liter volumetric flask and make up to the mark with freshly boiled and cooled water. After thorough mixing, transfer the solution to a clean, dry polyethylene bottle for storage. Perform these operations quickly to avoid contamination by carbon dioxide from the air. If large volumes of standard sodium hydroxide solutions are to be handled, a large polyethylene bottle with siphon arrangement and Ascarite tube should be used for storing and dispensing the solution.

Standardize the 0.1N sodium hydroxide as follows: Dry some potassium biphthalate (primary-standard grade) in an oven at 110°C. for 1 hour. Cool in a desiccator. Accurately weigh, to the nearest tenth of a milligram, two 1-gram portions of the salt into separate 250-ml. Erlenmeyer flasks. Dissolve each in 25 ml. of water. Add 2 drops of phenolphthalein indicator to each flask and titrate with the sodium hydroxide to a faint pink end point. Calculate the normality as follows:

$$\frac{4.90\ W}{V} \qquad (2)$$

where

W = grams of potassium biphthalate weighed into the flask

V = milliliters of sodium hydroxide used

0.002N Sodium Hydroxide. Pipet exactly 20 ml. of the standard 0.1N sodium hydroxide, just prepared, into a 1-liter volumetric flask. Dilute to 1 liter with freshly boiled and cooled water. The normality of this solution is:

$$0.02N \qquad (3)$$

where

N = exact normality of the 0.1N sodium hydroxide

0.1% Methyl Red. Dissolve 0.1 gram of methyl red in 100 ml. of 95% ethyl alcohol.

0.05% Phenolphthalein. Dissolve 0.05 gram of the solid in 50 ml. of 95% ethyl alcohol. Add 50 ml. of water.

COLLECTION OF THE SAMPLE

Fill the dustfall jar with 3.5 liters of water. This is volume V_1 (see REPORTING AND CALCULATIONS). Save some of the water, used to fill the jar, for blank determinations and makeup. At its station, place the jar on a clean, elevated support in order to avoid contamination from surrounding surfaces. The jar must be inspected on a regular schedule and more water added so that at least 500 ml. will be present in it when it is returned for analysis. Water used to replenish the jar is from the same batch of water used to fill it originally. Keep a record of the amount of water added. This is volume V_2. At the end of the month, return the jar for analysis.

SAMPLE PREPARATION

To remove insects and other large particles which cannot be classed as dust, pour the liquid remaining in the dustfall jar through a 20-mesh screen into a 1-liter graduate. Record this volume as V_8. Transfer the solution from the graduate to a 2-liter beaker. Carefully police and rinse the jar with a measured volume of the same batch of water used to fill the jars, and add it to the solution in the beaker. This is volume V_7.

Stir the sample in the beaker vigorously to insure uniform suspension of the solids and quickly pour into a 100-ml. graduate to the 100-ml. mark. Transfer to a 250-ml. Erlenmeyer flask. This is volume V_3. Similarly remove a 200-ml. aliquot to a 250-ml. Erlenmeyer flask. Make the latter sample smaller if the remainder in the beaker is under 400 ml. The water remaining in the beaker after the aliquots above have been removed is volume V_9.

ANALYTICAL PROCEDURE

ACIDITY:

Add 2 drops of methyl red indicator and 2 drops of phenolphthalein indicator to the 100-ml. aliquot (volume V_3) and to a blank consisting of a 100-ml. portion of water from the same batch used to fill the jar. The blank solution is volume V_4. Titrate the sample with 0.002N sodium hydroxide to the yellow end point of the methyl red indicator. This titer is volume V_c. Continue the titration rapidly to the first pink of the phenolphthalein indicator. The total amount of sodium hydroxide solution used is volume V_d. Titrate the blank with 0.002N sodium hydroxide rapidly to the first pink of the phenolphthalein indicator. This titer is volume V_e. In practice, the blank is always zero to the methyl red end point. Refer to REPORTING AND CALCULATIONS to calculate acidity as sulfur dioxide and carbon dioxide.

CHLORIDES:

When the suspended solids present in the 200-ml. aliquot have settled, transfer a 100-ml. aliquot of the supernatant liquid to a 250-ml. Erlenmeyer flask. This is volume V_5. Add 5 drops of diphenylcarbazone-bromophenol blue mixed indicator to the aliquot (volume V_5), and to a blank consisting of 100 ml. of water from the batch used to fill the jars. The blank solution is volume V_6. If a blue-violet or red color develops, add 0.05N nitric acid dropwise until the color changes to yellow and add 1 ml. in excess. If a yellow or orange color forms on the addition of the indicator, develop the blue-violet color by adding 0.05N sodium hydroxide dropwise, and then return to the yellow with nitric acid as above. The final solution should contain 1 ml. acid in excess.

Titrate the yellow acidified sample with 0.005N mercuric nitrate to the first appearance of the blue-violet color. This titer is volume V_b. Similarly titrate the blank. This titer is volume V_a.

SOLUBLE AND INSOLUBLE SOLIDS:

Boil the remainder of the dustfall water in the 2-liter beaker (volume V_9) down to a volume of 100 to 200 ml. and filter through a weighed Alundum crucible using gentle suction. Police the beaker and wash the contents through the filter with a measured volume of water. The measured amount of water added is recorded as volume V_{10}. Dry the crucible in an oven for 3 hours at 105°C. Cool in a desiccator, weigh, and subtract the weight of the empty crucible. The difference is weight W_5. Ignite the crucible at 800°C. in a muffle furnace for 20 to 30 minutes. Cool in a desiccator, weigh, and subtract the weight of the empty crucible. The difference is weight W_6. No blank is run, since distilled water normally contains no filterable solids. Transfer the filtrate in the suction flask to a beaker and evaporate to about 25 ml. Do not evaporate to dryness. Carefully transfer the solution to a weighed evaporating dish. Take to dryness in an oven at 105°C. Cool in a desiccator, weigh, and subtract the weight of the empty dish. The difference is weight W_1. Ignite the dish in a muffle furnace at 800°C. for 20 to 30 minutes. Cool in a desiccator, weigh, and subtract

the weight of the empty dish. The difference is weight W_2. Run a blank determination on 1 liter of the water used to fill the jars by carrying it through the same evaporation, drying, and igniting steps. The volume used for the blank determination is V_{11}; the weight of the blank solids is W_3; the weight of the blank-solids ash is W_4.

REPORTING AND CALCULATIONS

The symbols used in the calculations are as follows:

V_1 = milliliters of water used to fill the dustfall jar

V_2 = milliliters of makeup water used

V_3 = milliliters of water used for acidity titration

V_4 = milliliters of water used for acidity blank titration

V_5 = milliliters of water used for chloride titration

V_6 = milliliters of water used for chloride blank titration

V_7 = milliliters of water used for washing and policing of jar

V_8 = milliliters of water left in jar at end of month

V_9 = milliliters of water left in beaker after removing samples for acidity and chloride analyses

V_{10} = milliliters of water used to police beaker

V_{11} = milliliters of water used for soluble-solids blank determination

N_m = exact normality of 0.005N mercuric nitrate

N_s = exact normality of 0.002N sodium hydroxide

V_a = milliliters of 0.005N mercuric nitrate needed for chloride blank determination

V_b = milliliters of 0.005N mercuric nitrate needed for chloride sample determination

V_c = milliliters of 0.002N sodium hydroxide to titrate sample to the methyl red end point

V_d = milliliters of 0.002N sodium hydroxide to titrate sample to the phenolphthalein end point (includes titration to methyl red end point)

V_e = milliliters of 0.002N sodium hydroxide to titrate blank to the phenolphthalein end point

W_1 = milligrams of soluble solids in sample

W_2 = milligrams of soluble-solids ash in sample

W_3 = milligrams of soluble solids in blank determination

W_4 = milligrams of soluble-solids ash in blank determination

W_5 = milligrams of insoluble solids in sample

W_6 = milligrams of insoluble-solids ash in sample

ACIDITY:

Calculate the milligrams of sulfur dioxide as follows:

$$\frac{32\, V_c\, N_s\, (V_7 + V_8)}{V_3} \qquad (4)$$

Calculate the milligrams of carbon dioxide as follows:

$$\left[(V_d - V_c) - \frac{V_e\, V_3 (V_1 + V_2 + V_7)}{V_4 (V_7 + V_8)} \right] \left[\frac{44\, N_s (V_7 + V_8)}{V_3} \right] \qquad (5)$$

CHLORIDES:

Calculate chlorides in terms of milligrams of sodium chloride as follows:

$$\left[V_b - \frac{V_a\, V_5 (V_1 + V_2 + V_7)}{V_6 (V_7 + V_8)} \right] \left[\frac{58.5\, N_m (V_7 + V_8)}{V_5} \right] \qquad (6)$$

INSOLUBLE SOLIDS:

Calculate milligrams of insoluble solids as follows:

$$\frac{W_5\, V_8}{V_9} \qquad (7)$$

INSOLUBLE-SOLIDS ASH:

Calculate milligrams of insoluble-solids ash as follows:

$$\frac{W_6\, V_8}{V_9} \qquad (8)$$

SOLUBLE SOLIDS:

Calculate milligrams of soluble solids as follows:

$$\left[W_1 - \frac{W_3 V_9 (V_1 + V_2 + V_7 + V_{10})}{V_{11} (V_7 + V_8)}\right] \left[\frac{V_7 + V_8}{V_9}\right] \qquad (9)$$

SOLUBLE-SOLIDS ASH:

Calculate milligrams of soluble-solids ash as follows:

$$\left[W_2 - \frac{W_4 V_9 (V_1 + V_2 + V_7 + V_{10})}{V_{11} (V_7 + V_8)}\right] \left[\frac{V_7 + V_8}{V_9}\right] \qquad (10)$$

Convert the data from milligrams SO_2, CO_2, NaCl, solubles, and insolubles, to tons per square mile per month with the following factors (based on a mouth diameter for the jar of 4 5/16 inches):

Days Jar Exposed	Multiplying Factor
28	0.334
29	0.322
30	0.312
31	0.302
32	0.293
33	0.283

Enter the results on a report sheet as illustrated in Figure 2. The total dustfall on the report sheet is the sum of the insolubles and solubles. Similarly, the solids equal the sum of the ash and loss on ignition.

REFERENCES

Clarke, Frank E., Anal. Chem., 22, 553-5(1950).

Dept. of Scientific and Industrial Research, "Atmospheric Pollution in Leicester," Atmospheric Pollution Research Paper No. 1, His Majesty's Stationery Office, London (1945).

AIR POLLUTION CONTROL DISTRICT---COUNTY OF LOS ANGELES

DUSTFALL FOR FEBRUARY 1956

LOCATION	CODE NO.	TOTAL DUST FALL T/Mi^2		WATER INSOLUBLES T/Mi^2/Mo.			WATER SOLUBLES T/Mi^2/Mo.			CHLORIDES as NaCl	SO_2	CO_2
		MO.	YEAR	SOLIDS	LOSS ON IGN.	ASH	SOLIDS	LOSS ON IGN.	ASH	T/Mi^2/Mo.	T/Mi^2/Mo.	T/Mi^2/Mo.
Burbank	7	55.4	665.3	47.2	9.0	38.2	8.2	7.2	1.0	0.3	1.3	3.1
Branford Ave.	13	32.2	386.6	22.1	0.9	21.2	10.2	2.4	7.8	0.3	0.0	0.8
Sheldon Ave.	14	64.0	768.4	57.8	30.6	27.2	6.2	3.3	2.9	0.6	0.0	1.0
Whipple St.	15	29.8	357.0	21.6	7.6	14.0	8.2	8.2	0.0	1.0	0.8	4.7
Sylvan St.	16	27.9	334.9	22.6	7.6	15.0	5.3	5.3	0.0	2.5	0.5	1.8
Averages		41.9	502.4	34.3	11.1	23.1	7.6	5.3	2.3	0.9	0.5	2.3

Calculations By: A. Lyles
Checked By: Gliksman

APCD 7-53
P. 9 of 9

Figure 2. Typical dustfall report sheet.

FORMALDEHYDE APCD 8-53

Laboratory Methods

POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

FORMALDEHYDE

APCD 8-53

SCOPE

This method may be applied to samples from both air sampling and source testing. The lower limit of the method is about 0.03 p.p.m. in a 168-liter air sample, and 1 p.p.m. in a 2-liter grab sample.

METHOD SUMMARY

The samples are collected in a dilute solution of sodium bisulfite. Any aldehydes present form the bisulfite-addition compounds. An aliquot of the resultant solution is then treated with chromotropic acid in strong sulfuric acid. Formaldehyde forms a unique colored compound the exact nature of which is unknown but which appears to be of a quinoidal type. The intensity of the colored compound is then determined in a colorimeter and the corresponding concentration of formaldehyde read from a calibration curve.

SPECIAL APPARATUS

COLLECTION:

For Air Sampling. Three midget impingers connected in series to a stopcock, flow-meter, and air pump, assembled as shown in Figure 1.

For Source Testing. Two-liter round-bottomed flask with neck consisting of a short length of 8-mm. glass tubing, 3-inch length of heavy-wall gum-rubber tubing, screw clamp, and solid-glass plug.

ANALYTICAL:

Klett-Summerson industrial colorimeter, 500- to 560-mμ green filter (Klett-Summerson No. 54 or equivalent).

REAGENTS

COLLECTION:

1% Sodium Bisulfite. Dissolve 1 gram of sodium bisulfite ($NaHSO_3$) in 100 ml. of water.

ANALYTICAL:

1% Starch. Weigh 1 gram of soluble starch into a 150-ml. beaker. Add 1 to 2 ml. of water, and stir to make a paste. In a separate beaker, heat 100 ml. of water to boiling and pour into the paste while stirring. Allow to cool. For accurate work the starch solution should be made fresh daily.

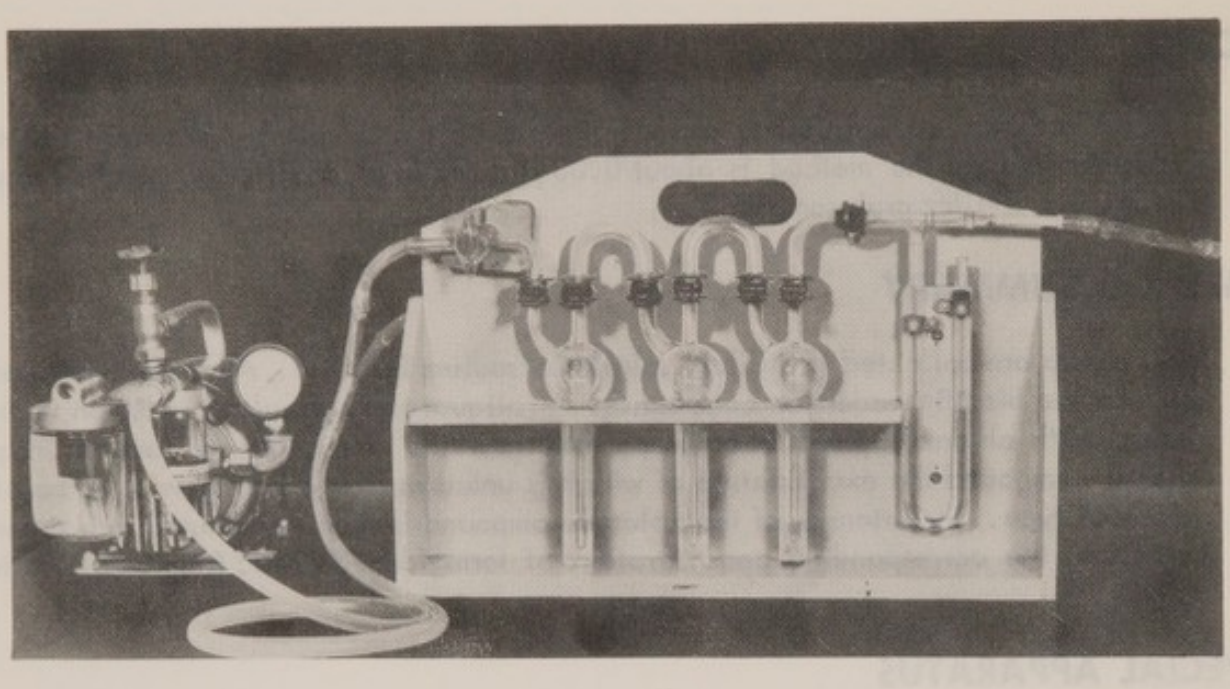


Figure 1. Midget impinger sampling train.

0.05N Sodium Thiosulfate. Dissolve 12.5 grams of $Na_2S_2O_3 \cdot 5H_2O$ in 1 liter of freshly boiled and cooled water. Add 0.1 gram of sodium carbonate as a preservative. This will retard the slow change of titer which a solution of thiosulfate normally undergoes. Allow the solution to stand for 24 hours before use.

To standardize the thiosulfate proceed as follows: Dry some potassium dichromate (primary-standard grade) in an oven at 110°C. for 1 hour. Cool in a desiccator. Weigh 2.452 grams of the dry dichromate into a 1-liter volumetric flask and dissolve in about 500 ml. of water. Make up to volume with water and mix thoroughly. Pipet exactly 25 ml. of the solution into a 500-ml. Erlenmeyer flask. Pour 25 ml. of water into another 500-ml. Erlenmeyer flask for a blank determination. Add 50 ml. of water, 10 ml. of concentrated hydrochloric acid, and 3 grams of solid potassium iodide to each flask. Swirl each flask once, cover, and place in the dark for 5 minutes. Dilute the solution in each flask with 200 ml. of water and titrate with the 0.05N sodium thiosulfate until the brown color is almost discharged. Add 3 ml. of starch indicator and titrate to colorless. Subtract the volume of sodium thiosulfate required for the blank titration from the volume required for the sample titration.

The normality of the sodium thiosulfate is:

$$\frac{1.25}{V_t} \qquad (1)$$

where

V_t = milliliters of sodium thiosulfate used (blank subtracted)

0.1N (approximate) Iodine. Dissolve 20 to 25 grams of potassium iodide in as little water as possible. Add 12.7 grams of iodine and stir. When dissolved, make up to 1 liter with water and store in a dark bottle.

0.005N Iodine. Dilute 50 ml. of 0.1N iodine to 1 liter with water. Standardize daily with the 0.05N thiosulfate as follows: Pipet 50 ml. of the iodine solution into a 250-ml. Erlenmeyer flask. Titrate with 0.05N sodium thiosulfate until the brown color is almost discharged. Add 3 ml. of starch indicator and titrate to colorless. The normality of the iodine is:

$$0.02\, V_t N_t \qquad (2)$$

where

V_t = milliliters of sodium thiosulfate used

N_t = exact normality of sodium thiosulfate

Buffer Solution. Dissolve 80 grams of anhydrous sodium carbonate in 500 ml. of water. Add 20 ml. of glacial acetic acid slowly and dilute to 1 liter. Adjust the pH to 9.6 (±0.1) with sodium carbonate or acetic acid as required, using a pH meter.

Standard Formaldehyde Solution. Dilute 3 ml. of formalin (approximately 37%) to 1 liter in a volumetric flask. To standardize, pipet 1 ml. of the solution into a 250-ml. Erlenmeyer flask, and 1 ml. of water into another flask as a blank. Add 30 ml. of 1% sodium bisulfite, and 2 ml. of 1% starch to each flask. Add 0.1N iodine dropwise to each flask until a dark blue color results. Decolorize each flask with 0.05N sodium thiosulfate and then return to a faint blue with 0.005N iodine. Chill each flask in an ice bath and add 50 ml. of chilled buffer. After addition of the buffer, allow to stand in the ice bath for 10 to 15 minutes, then titrate the liberated bisulfite in each flask to the same faint blue end point with 0.005N iodine. Subtract the volume of 0.005N iodine used for the blank determination from the volume used for the sample determination. The strength of the standard in micrograms per milliliter is:

$$VN \times 1.5 \times 10^4 \qquad (3)$$

where

V = milliliters of 0.005N iodine used for titration following the addition of buffer (blank subtracted)

N = exact normality of the 0.005N iodine

Dilute 1 ml. of this standard formaldehyde solution to 1 liter. The diluted solution contains approximately 1.2 μg. formaldehyde per milliliter.

76% (by weight) Sulfuric Acid. Slowly add 725 ml. of concentrated sulfuric acid to 350 ml. of water. It is advisable to place the container in which the dilution is to be made in a water bath to absorb some of the heat generated.

Chromotropic Acid Reagent. Weigh 0.875 gram of 4,5-dihydroxy-2,7-naphthalenedisulfonic acid, disodium salt (Eastman No. P230 or equivalent) into a 100-ml. beaker and add 4.25 ml. of water. Rapidly add 45.75 ml. of 76% sulfuric acid and stir to dissolve. Prepare fresh for each day's analyses as it decomposes on standing. The final mixture contains approximately 71% weight sulfuric acid.

Prepare a calibration curve for each new bottle of chromotropic acid as follows: Transfer 50 ml. of 76% sulfuric acid, by means of a graduate, to each of a series of six 150-ml. beakers. Warm the solutions in a water bath to 60 ± 2°C. Add 2 ml. of chromotropic acid to each beaker. Pipet 1 ml. of the 1.2 μg. per ml.

standard formaldehyde solution and 4 ml. of water into the first beaker, 2 ml. of the 1.2 μg. per ml. standard and 3 ml. of water into the second, 3 ml. of the 1.2 μg. per ml. standard and 2 ml. of water into the third, 4 ml. of the 1.2 μg. per ml. standard and 1 ml. of water into the fourth, 5 ml. of the 1.2 μg. per ml. standard to the fifth. The beakers will then contain approximately 1.2, 2.4, 3.6, 4.8, and 6.0 μg. formaldehyde per 5-ml. aliquot, respectively. Run a blank by adding 5 ml. of water to the sixth beaker containing chromotropic acid. Stir the solutions frequently and maintain at the specified temperature for 20 minutes. The color reaction is, in part, dependent upon the time in the bath, and, to a lesser extent, the time required before making the colorimeter reading. Hence, the sequence of events is critical. Likewise the solution temperature must be closely controlled. At the end of 20 minutes in the water bath, immerse the beakers in ice water. This procedure impedes the color development somewhat. Rapidly transfer to the colorimeter cell for reading. Measure the light absorption of the solutions in the photoelectric colorimeter with a 500- to 560-mμ green filter and a 20-mm. light path. Use the blank solution for zeroing the colorimeter. Prepare a calibration curve by plotting the colorimeter readings vs. micrograms of formaldehyde per 5-ml. aliquot on rectangular-coordinate graph paper.

COLLECTION OF THE SAMPLE

For Air Sampling. Add 10 ml. of 1% sodium bisulfite solution to each of the three midget impingers. Assemble the sampling apparatus as shown in Figure 1.

Draw air through the impingers at the rate of 2.8 liters per minute for 1 hour. The moisture content of the air may be neglected in any final calculations since it will not perceptibly influence the results. For ordinary atmospheric sampling the gas pressure and temperature are considered to be 760 mm. of mercury and 25°C.

For Source Testing. Pipet 10 ml. of 1% sodium bisulfite solution into a clean 2-liter sample flask. Connect the flask to a vacuum source and evacuate to the vapor pressure of the solution (boiling). Tighten the screw clamp on the rubber tubing and disconnect the flask from the vacuum source. Insert the solid-glass plug into the open end of the rubber tubing.

To collect the sample, remove the glass plug and open the screw clamp for about 10 seconds. Retighten the screw clamp and replace the glass plug.

SAMPLE PREPARATION

For Air Sampling. Transfer the contents of the three impingers to a single 50-ml. volumetric flask. Rinse each impinger twice with a small amount of water and add the rinsings to the 50-ml. volumetric flask. Make up to volume with water.

For Source Testing. Shake the 2-liter round-bottomed flask for 15 minutes, with frequent rotation, to provide a thorough scrubbing action. Determine the pressure of the flask by connecting it to an open-end mercury manometer and measuring the difference, in millimeters, between the mercury levels. Note the temperature and atmospheric pressure. Pour the contents into a 25-ml. beaker.

ANALYTICAL PROCEDURE

Pour 50 ml. of 76% sulfuric acid into each of two 150-ml. beakers. Warm the solutions in a water bath to 60±2°C. Add 2 ml. of chromotropic acid to each. Transfer a 5-ml. aliquot of the sample by pipet to one beaker, and 5 ml. of water to the other for a blank determination. Stir the solutions frequently and maintain at the specified temperature for 20 minutes. At the end of 20 minutes remove the beakers from the water bath, and immerse them in ice water. Rapidly transfer to the colorimeter cells for reading. Measure the light absorption of the solutions in the photoelectric colorimeter with a 500- to 560-m μ green filter and a 20-mm. light path. Use the blank for zeroing the colorimeter. Read the concentration of formaldehyde in micrograms per 5-ml. aliquot from the previously prepared calibration curve.

REPORTING AND CALCULATIONS

For Air Sampling. Calculate the parts per million of formaldehyde as follows:

$$W_A A \times 4.85 \times 10^{-3} \qquad (5)$$

where

W_A = micrograms of formaldehyde per 5-ml. aliquot of the collection solution

A = aliquot factor = $\frac{\text{milliliters of diluted absorbing solution}}{5}$

(this factor is usually "10")

For Source Testing. Calculate the parts per million of formaldehyde (dry basis) as follows:

$$\frac{2.078\, W_A A T}{v_m (P_r + \Delta P)} \qquad (4)$$

where

W_A = micrograms of formaldehyde per 5-ml. aliquot of the collection solution

$$A = \text{aliquot factor} = \frac{\left(\begin{array}{c}\text{milliliters of absorbing solu-}\\ \text{tion added to sample flask}\end{array}\right)}{5}$$

(this factor is usually "2")

V_m = measured volume of sample flask, liters*

ΔP = sample flask differential pressure, millimeters of mercury (with respect to atmospheric pressure)

P_r = atmospheric pressure, millimeters of mercury (at the time of the Δ P measurement)

T = room temperature, degrees Kelvin (at the time of the ΔP measure - ment)

To express the results in terms of grains per standard cubic foot (60°F. and 1 atmosphere), multiply the parts per million by 5.53×10^{-4}.

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*Where moisture was present in the original sample and it is desired to put the sample volume on a stack-conditions basis, a correction must be applied to Formula 4. The moisture is usually determined in conjunction with some other test such as grain loading.

FORMIC ACID APCD 9-53

Laboratory Methods

POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

FORMIC ACID
APCD 9-53

SCOPE

This laboratory procedure is designed for air sampling only. However, formic acid in stack gases can be determined by applying the same analytical procedure, as described herein, to a sample (or an aliquot) collected in dilute sodium hydroxide using impingers. Occasionally an aliquot from stack samples taken for total organic acids (APCD 16-57) is analyzed in this manner. The lower limit of the method is about 0.03 p.p.m. in a 680-liter air sample.

METHOD SUMMARY

The sample is collected by drawing air through three midget impingers containing dilute sodium hydroxide. The resultant solution, or an aliquot, is acidified and stirred to remove carbon dioxide. The solution is then brought to a pH of 8 or 9, evaporated, and treated with Vorlander's reagent. This effectively removes formaldehyde from further reactions by forming methylene bis-methone. The mixture is then treated with nascent hydrogen generated in situ from magnesium ribbon and hydrochloric acid. Methone, being tautomeric, is changed to the keto form in the acid medium used for reduction, hence any excess does not react with the newly generated formaldehyde. Methylene bis-methone does not release formaldehyde under these conditions. The free formaldehyde produced from formic acid is then measured by treating the mixture with chromotropic acid in strong sulfuric acid. Formaldehyde forms a unique colored compound, the exact nature of which is unknown, but which appears to be of a quinoidal type. The intensity of the colored compound is then determined in a colorimeter to give a measure of the formic acid present.

SPECIAL APPARATUS

COLLECTION:

Three midget impingers connected in series to a stopcock, flowmeter, and air pump, assembled as shown in Figure 1.

ANALYTICAL:

Beckman Model DU spectrophotometer.

REAGENTS

COLLECTION:

0.5N (approximate) Sodium Hydroxide. Dissolve 20 grams of sodium hydroxide pellets in water and dilute to 1 liter.

ANALYTICAL:

0.5N (approximate) Sodium Hydroxide. Same solution as used for collection.

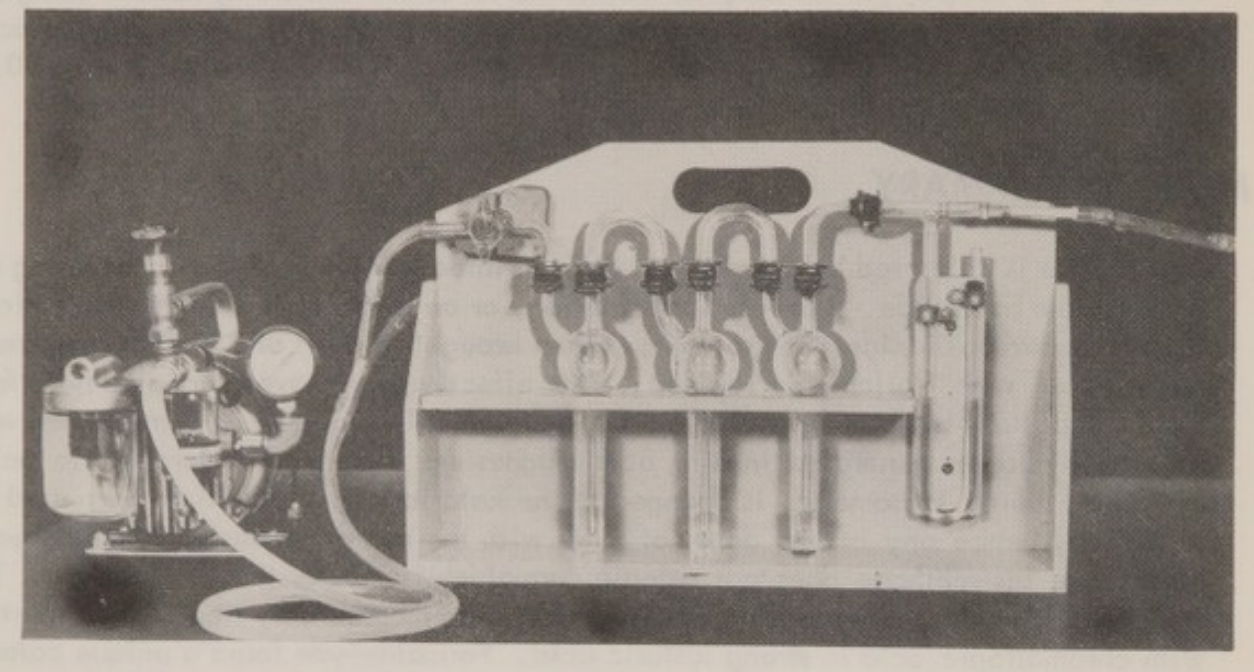

Figure 1. Midget impinger sampling train.

Buffer Solution (pH 7-8). Dissolve 1.7 grams of potassium dihydrogen phosphate (KH_2PO_4) and 6.7 grams of disodium monohydrogen phosphate ($Na_2HPO_4 \cdot 7H_2O$) in 1 liter of boiled water.

Vorlander's Reagent. Dissolve 0.2 gram of dimethyl dihydroresorcinol (5,5-dimethyl-1,3-cyclohexanedione, m.p. 147.5-149°C., Eastman No. 1259, or equivalent) in 100 ml. of buffer solution.

Magnesium Ribbon. Store the ribbon in a desiccator over sodium hydroxide pellets to minimize atmospheric attack.

76% (by weight) Sulfuric Acid. Slowly add 725 ml. of concentrated sulfuric acid to 350 ml. of water. It is advisable to place the container in which the dilution is to be made in a water bath to absorb some of the heat generated.

0.05% Phenolphthalein. Dissolve 0.05 gram of the solid in 50 ml. of 95% ethyl alcohol and add 50 ml. of water.

Chromotropic Acid. Weigh 0.875 gram of 4,5-dihydroxy-2,7-naphthalenedisulfonic acid, disodium salt (Eastman No. P230, or equivalent), into a 100-ml. beaker and add 5.0 ml. of water. Break up any lumps with a stirring rod. Rapidly add 45.0 ml. of concentrated sulfuric acid and stir to dissolve. Prepare fresh for each day's analyses as it decomposes on standing.

0.1N Sodium Hydroxide. Dissolve 50 grams of sodium hydroxide pellets in 50 ml. of water in a polyethylene bottle. Tightly stopper the bottle and allow the carbonate to settle overnight or centrifuge. This stock solution can be stored for future use. Weigh 8 grams of the clear supernatant liquid into a 100-ml. Erlenmeyer flask. Transfer the solution quickly to a 1-liter volumetric flask and make up to volume with freshly boiled and cooled water. After thorough mixing, transfer the solution to a clean, dry polyethylene bottle and keep tightly stoppered. Perform these operations quickly to avoid contamination by carbon dioxide in the air. If large volumes of standard sodium hydroxide solutions are to be handled, a 5-gallon polyethylene bottle with siphon arrangement and Ascarite tube should be used for storing and dispensing the solution. Standardize the 0.1N sodium hydroxide with primary-standard grade potassium biphthalate as follows: Dry the salt for 1 hour in an oven at 110°C. Accurately weigh two 1-gram portions of the salt, to the nearest milligram, into separate 250-ml. Erlenmeyer flasks and dissolve each in 25 ml. of water. Add 2 drops of phenolphthalein indicator to each flask and titrate with the sodium hydroxide solution. The end points should have a sharp change to pink and should persist for 5 minutes. The normality of the sodium hydroxide is:

$$\frac{4.90\,W}{V} \qquad (1)$$

where

W = grams of potassium biphthalate weighed into flask

V = milliliters of sodium hydroxide needed for the titration

Formic Acid Standards. Dilute 0.43 ml. of formic acid to 100 ml. with water in a volumetric flask. Determine the concentration of the formic acid solution by titrating a 10-ml. aliquot with 0.1N sodium hydroxide to the phenolphthalein end point. The concentration, in micrograms of formic acid per milliliter of solution, is:

$$VN \times 4.6 \times 10^{-3} \qquad (2)$$

where

V = milliliters of 0.1N sodium hydroxide solution used for the titration

N = exact normality of the sodium hydroxide solution

Prepare a spectrophotometer calibration curve for each new bottle of chromotropic acid as follows: Dilute 5, 10, and 15 ml. of the formic acid standard (prepared above) to 100 ml. with water in separate volumetric flasks. The final solutions contain approximately 230, 460, and 690 μg. of formic acid per milliliter respectively, depending on the original stock solution strength as determined by titration.

Pipet duplicate 0.5-ml. aliquots of the dilute standards into separate 10-ml. volumetric flasks. Into each flask, place about 80 mg. of magnesium ribbon cut into 1/4-inch pieces. Add 0.5 ml. of water to another 10-ml. flask containing magnesium ribbon as a blank. Immerse the flasks in an ice bath for several minutes. To each flask, add a total of 0.5 ml. of concentrated hydrochloric acid in 10 separate portions of 0.05 ml. The additions are made at intervals of not less than 1 minute. Wait at least 1 minute after the last addition of hydrochloric acid to allow for complete reduction of formic acid to formaldehyde. Cautiously add 5 ml. of chromotropic acid reagent to each flask in 0.25-ml. portions. After adding the first 0.25-ml. portion, remove the flasks from the ice bath. When the magnesium has dissolved, replace the flasks in the ice bath and continue the additions. After several milliliters have been added, violent foaming occurs. If it appears to be foaming too violently, cut down the portions used to 0.1 ml. and blow gently into the top of the flask. After the addition of the last portion of chromotropic acid, wait until the foaming has subsided. Remove the flasks from the ice bath and allow to warm at room temperature for a few minutes. If violent foaming again becomes evident, reimmerse the flasks in the ice bath. Continue this operation until no more foaming is

evident. Cautiously place the flasks in a water bath at 80 ± 2°C. If violent foaming again is evident, remove the flasks from the hot water bath until the foaming subsides. Reimmerse in the hot water bath. Continue this operation until violent foaming is no longer evident. Heat for 30 minutes in the hot water bath. A precipitate of unknown composition forms if it has not already appeared. Chill the flasks in an ice bath to slow the reaction, and make up to volume with 76% sulfuric acid. Mix thoroughly and allow to stand until the bulk of the suspended solids have settled. Transfer the supernatant liquid to a centrifuge tube and centrifuge for 5 minutes. The time for the events following introduction into the 80°C. bath is important and should be controlled within reasonable limits.

Determine the absorbance of each solution in a Beckman Model DU spectrophotometer at 570 mμ, using 1-cm. Corex cells and a slit width of 0.08 mm. Place the blank in the comparison cell of the spectrophotometer. Prepare a calibration curve by plotting absorbance vs. micrograms of formic acid per 0.5 ml. taken for reduction.

COLLECTION OF THE SAMPLE

Assemble the sampling apparatus as shown in Figure 1. Add 10 ml. of 0.5N sodium hydroxide to each of the three midget impingers. Draw the sample through the impingers at the rate of 2.8 liters per minute (0.1 cubic foot per minute) for 4 hours.

SAMPLE PREPARATION

For formic acid concentrations from 1 to 15 p.p.m. in a 680-liter gas sample: Pour the sample from each impinger into separate 10-ml. graduates and make up to volume with washings. Mix thoroughly and transfer a 2-ml. aliquot from each graduate to separate test tubes (marked at 4 ml.). To each test tube, add 0.02 ml. of 0.05% phenolphthalein and concentrated hydrochloric acid dropwise, while stirring, until the solutions become colorless. Use care to prevent frothing and loss of the sample during the liberation of carbon dioxide. Add a drop of concentrated hydrochloric acid in excess to each to give a pH of about 3, and stir the solutions rapidly for several minutes to liberate the last traces of carbon dioxide. Add 0.5N sodium hydroxide to bring the samples back to a pink color. The pH at this point is 8 to 9. Make up to the 4-ml. mark with buffered Vorlander's reagent. Heat in a water bath at 37 ± 2°C. for 1/2 hour, to allow any free formaldehyde to condense with Vorlander's reagent.

For formic acid concentrations of less than 1 p.p.m. in a 680-liter gas sample: Pour the sample from each impinger into separate 30-ml. beakers. Rinse the impingers with a small amount of water and add the washings to the beakers. To each beaker, add 0.02 ml. of 0.05% phenolphthalein, and concentrated hydrochloric acid dropwise, while stirring, until the solutions become colorless. Use care to prevent frothing and loss of the sample during the liberation of carbon dioxide. Add a drop of concentrated hydrochloric acid in excess to each to give a pH of about 3. Stir the solutions

rapidly for several minutes to liberate the last traces of carbon dioxide. Add 0.5N sodium hydroxide to each to bring the samples back to a pink color. The pH at this point is 8 to 9. Evaporate the solutions on a hot plate to a volume of 1 or 2 ml. Any crystals which form here will dissolve when Vorlander's reagent is added. Add 2 ml. of Vorlander's reagent to each and transfer to separate test tubes marked at 4 ml. Make up to volume with rinsings from the beakers. Heat in a water bath at 37 ± 2°C. for 1/2 hour to allow any free formaldehyde to condense with Vorlander's reagent.

ANALYTICAL PROCEDURE

Into each of four 10-ml. volumetric flasks, place about 80 mg. of magnesium ribbon, cut into 1/4-inch pieces. Add 0.5 ml. of water to one volumetric flask, as a blank. Transfer a 0.5-ml. aliquot from the test tubes to separate volumetric flasks containing the magnesium ribbon. Immerse the flasks in an ice bath for several minutes. To each flask add a total of 0.5 ml. of concentrated hydrochloric acid in 10 separate portions of 0.05 ml. The additions are made at intervals of not less than 1 minute. Wait at least 1 minute after the last addition of hydrochloric acid, to allow for complete reduction of formic acid to formaldehyde. Cautiously add 5 ml. of chromotropic acid reagent to each flask in 0.25-ml. portions. After adding the first 0.25-ml. portion, remove the flasks from the ice bath. When the magnesium has dissolved, replace the flasks in the ice bath and continue the additions. After several milliliters have been added, violent foaming occurs. If it appears to be foaming too violently, cut down the portions used to 0.1 ml. and blow gently into the top of the flask. After the addition of the last portion of chromotropic acid, wait until the foaming has subsided. Remove the flasks from the ice bath and allow to warm at room temperature for a few minutes. If violent foaming again becomes evident, reimmerse the flasks in the ice bath. Continue this operation until no more foaming is evident. Cautiously place the flasks in a water bath at 80 ± 2°C. If violent foaming again is evident, remove the flasks from the hot water bath until the foaming subsides. Reimmerse in the hot water bath. Continue this operation until violent foaming is no longer evident. Heat for 30 minutes in the hot water bath. A precipitate of unknown composition forms if it has not already appeared. Chill the flasks in an ice bath to slow the reaction, and make up to volume with 76% sulfuric acid. Mix thoroughly and allow to stand until the bulk of the suspended solids have settled. Transfer the supernatant liquid to a centrifuge tube and centrifuge for 5 minutes. The time for the events following introduction into the 80°C. bath is important and should be controlled within reasonable limits. Place the blank in a 1-cm. Corex cell, and a sample, in another 1-cm. Corex cell. Measure the absorbance of the sample in the spectrophotometer, at a wave length of 570 mμ. and a slit width of 0.08 mm., against the blank.

REPORTING AND CALCULATIONS

The concentration of formic acid in parts per million is:

$$\frac{0.531\, W_A A}{V_c} \qquad (3)$$

where

W_A = total micrograms formic acid in the three 0.5-ml. aliquots taken for the reduction step. The value for each impinger solution is read from the calibration curve, and the values are added together.

A = aliquot factor = 8 in the case where the evaporation procedure is used, and 40 where 2-ml. aliquots are used

v_c = measured volume of gas sampled, liters*

To obtain grains of formic acid per standard cubic foot (60°F. and 1 atmosphere), multiply the parts per million by 8.45×10^{-4}.

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*The measured volume of gas sampled is used for v_c unless the sampling temperature is below about 50°F. or above about 100°F.

HYDROCARBONS, TOTAL APCD 10-54

Laboratory Methods

R POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

HYDROCARBONS, TOTAL

APCD 10-54

SCOPE

This procedure is used to determine hydrocarbons in the air as well as in specific sources. The lower limit of the method is about 0.05 p.p.m. for a 55-liter air sample, and 10 p.p.m. where a mine-sample tube is used for collection.

METHOD SUMMARY

Hydrocarbons in the atmosphere are collected in a modified Shepherd trap immersed in liquid oxygen. Methane and the C_2's are probably captured only in part, if at all, by this technique. For source testing, where concentrations are larger, mine-sample tubes can be used.

Analysis is based on the point of maximum absorption in the range of 3 to 4 microns using a Beckman Model IR-2A infrared spectrophotometer. The instrument is calibrated with n-hexane and the analyses of unknown samples are reported in terms of parts per million as hexane. Hexane was selected so that all results could be expressed in terms of a standard which was convenient to use and which would approximate the absorbancy index of gasoline. Aromatics are not effectively measured because of relatively poor absorbance at the wave length used.

SPECIAL APPARATUS

COLLECTION:

For Air Sampling. Modified Shepherd traps (Figure 1), 665-ml. Thermos bottles, drying tubes containing Ascarite, rotameter, and air pump, assembled as shown in Figure 2.

For Source Testing. Mine-sample tubes (Figure 3).

ANALYTICAL:

Beckman Model IR-2A infrared spectrophotometer equipped with a 1-meter cell (Figure 4), circulating constant-temperature water bath (Labline, Inc., Chicago, Ill., Model 3052 or equivalent), magnetic stirrer, 50-liter round-bottomed flask, aluminum rotor.

REAGENTS

COLLECTION:

Ascarite. 8 - 20 mesh.

Liquid Oxygen.

ANALYTICAL:

n-Hexane. Technical grade, 95% weight assay (Phillips Petroleum Co., Chemical Products Dept., Bartlesville, Okla.).

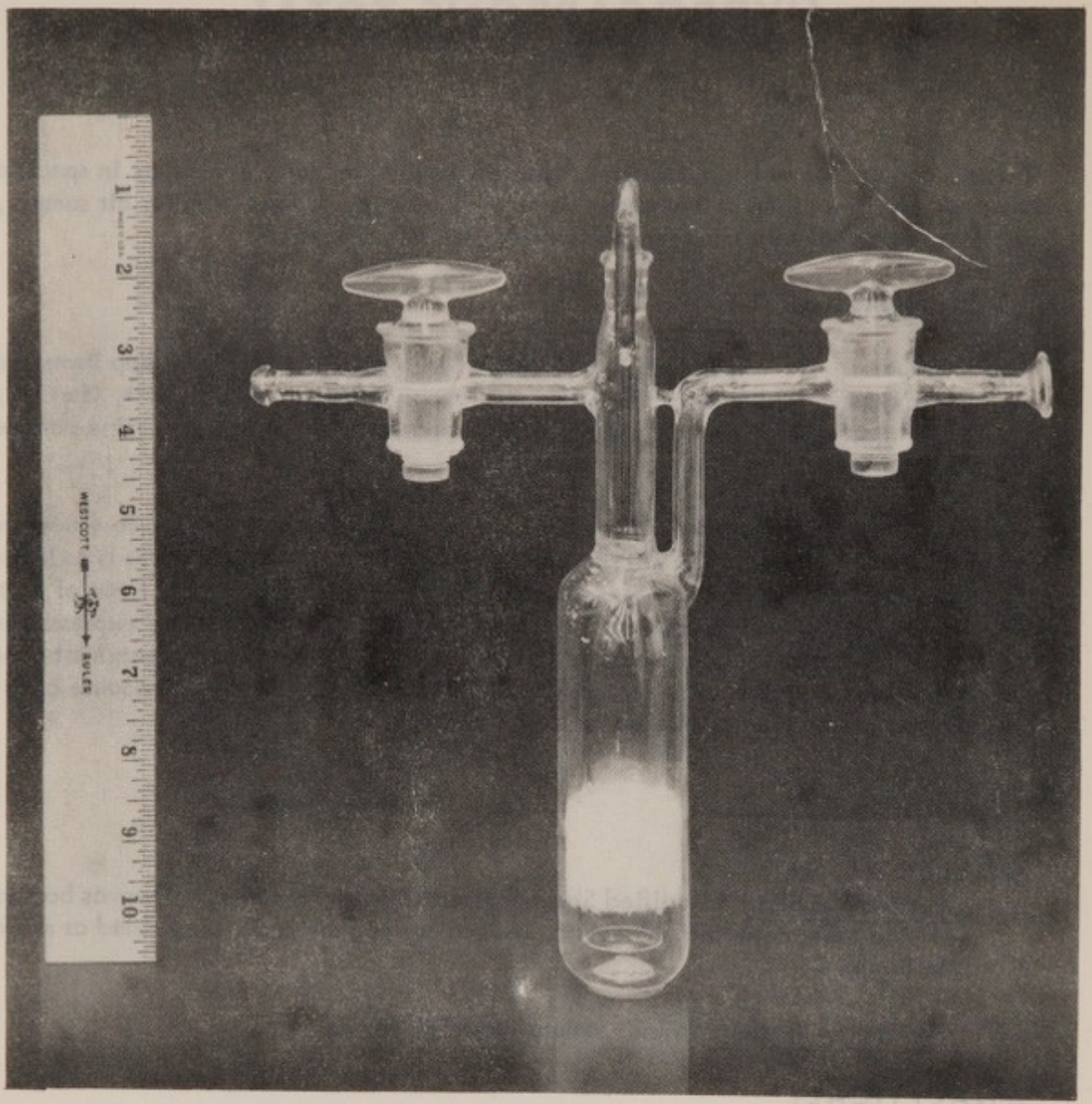

Figure 1. Modified Shepherd trap.

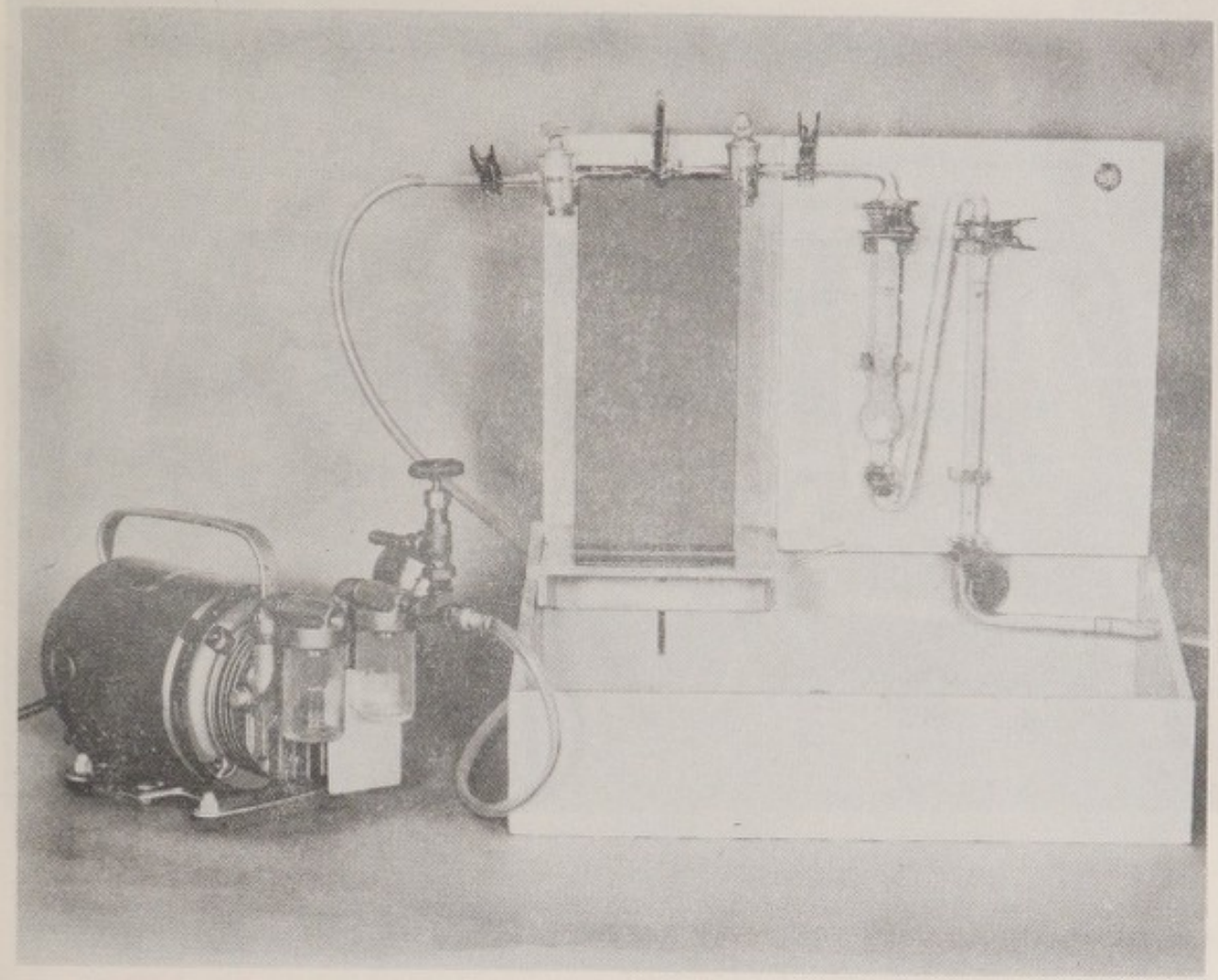

Figure 2. Air sampling train used for the collection of hydrocarbon samples.

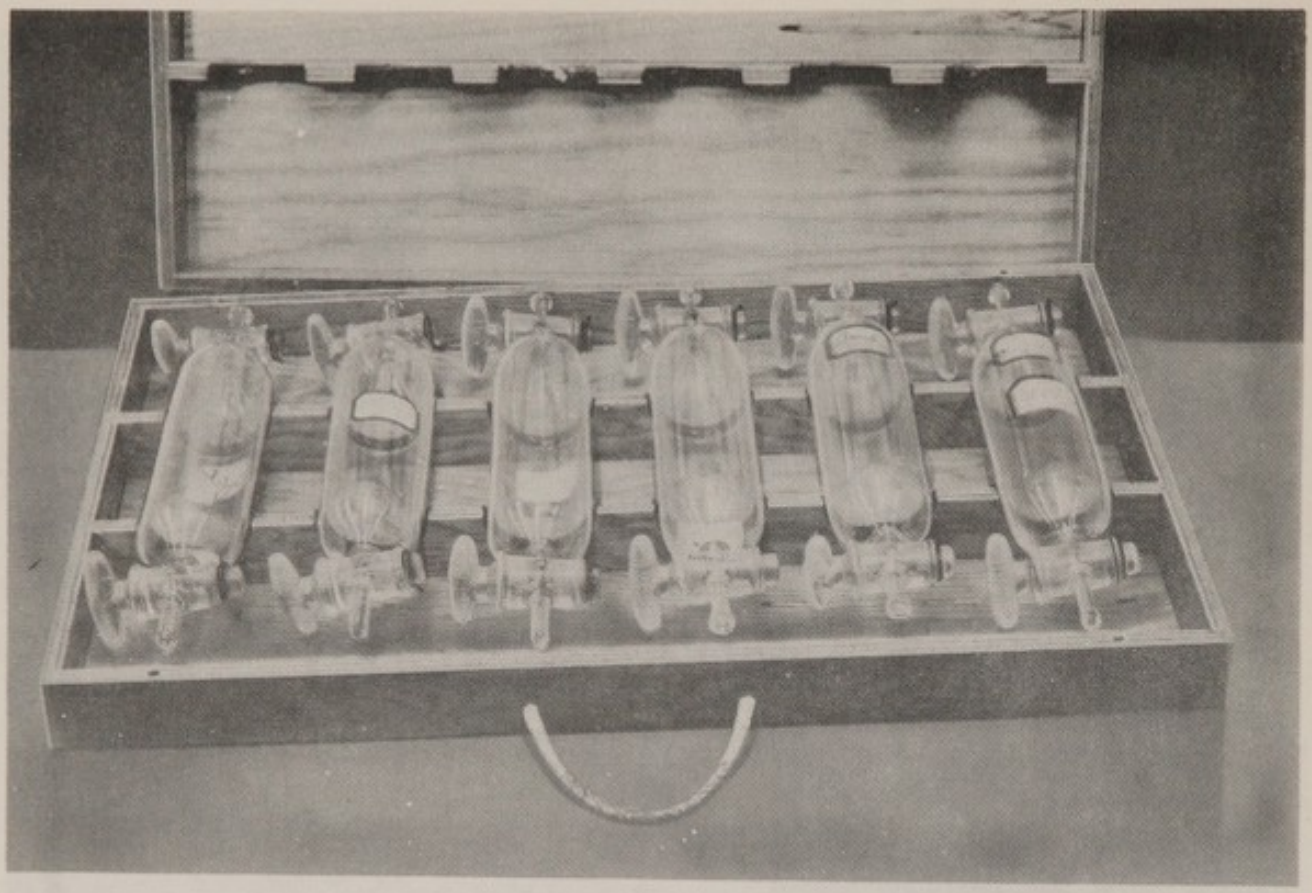

Figure 3. Mine-sample tubes.

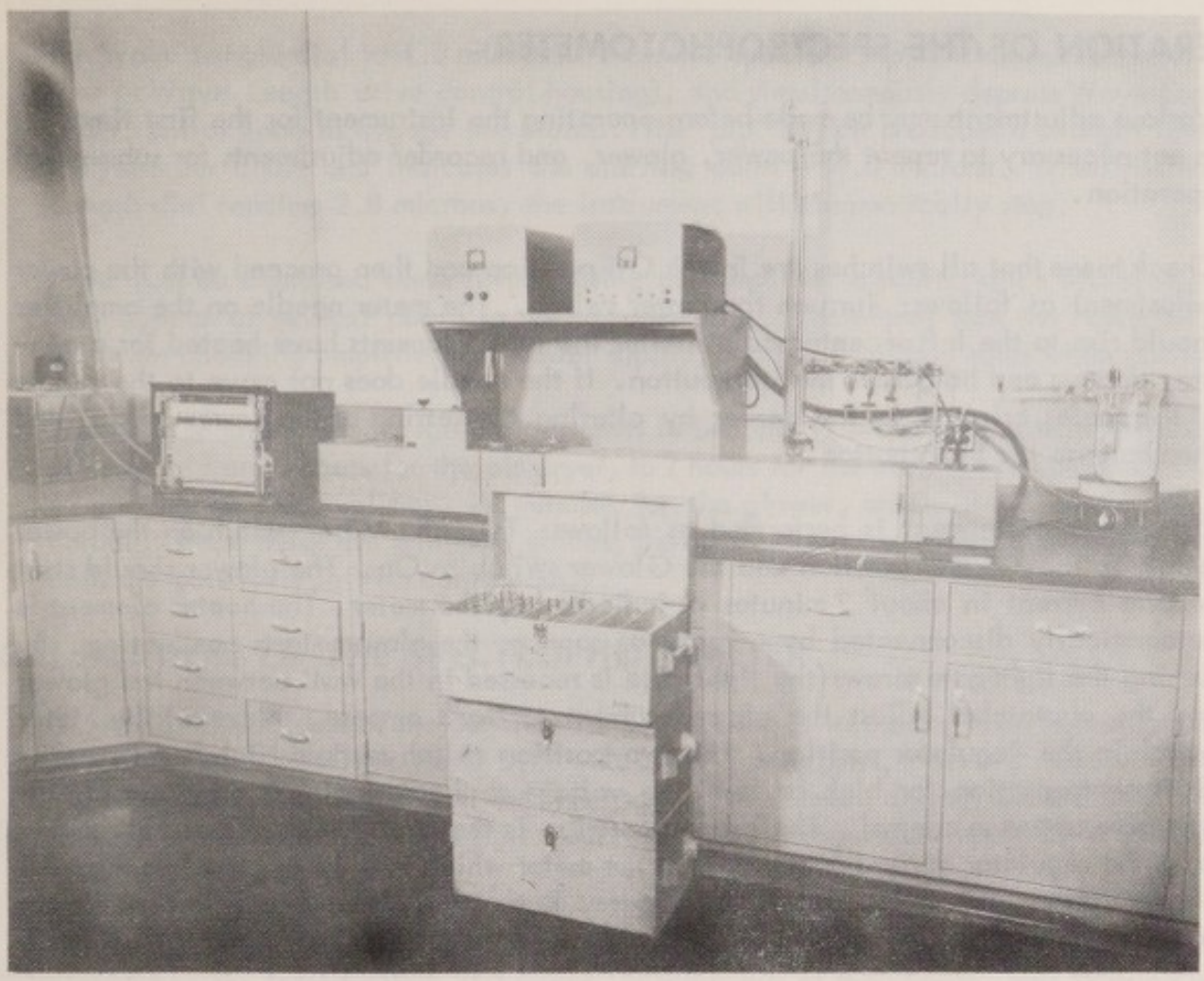

Figure 4. Beckman IR-2A spectrophotometer showing air dryer and thermostated water bath. A convenient carrier for Shepherd traps is shown in the foreground.

OPERATION OF THE SPECTROPHOTOMETER

Various adjustments must be made before operating the instrument for the first time. It is not necessary to repeat the power, glower, and recorder adjustments for subsequent operation.

Check to see that all switches are in the Off position and then proceed with the power adjustment as follows: Turn on the Power switch. The meter needle on the amplifier should rise to the left of center scale. After the tube filaments have heated for a minute, depress and hold down the Start button. If the needle does not move to the center of the scale, bring it to the center by altering the setting of the Power adjust, and then release the Start button.

The glower adjustment is performed as follows: Turn the Meter switch on the power supply to the Glower position and the Glower switch to On. The glower should start passing current in about 2 minutes as indicated by the meter. The heater element is automatically disconnected by a relay as soon as the glower starts conducting. By turning the light gate screws (the light gate is recessed in the wall between the glower and the phototube) adjust the glower current to 0.73 ampere. Next set the Meter switch in the Regulator position. The two-position switch marked High and Low provides compensation for high or low line voltage so that the glower regulator circuit will give optimum control. The proper position is the one which more closely maintains the regulator current at a value on the meter which is 0.17 ampere less than the glower current, or approximately 0.56 ampere. Return the Meter switch to the Glower position.

The recorder operation adjustment is performed as follows: Turn the Output switch to Linear, the Period control switch to 16, the Gain switch to 1, and the Gain control to full clockwise position. Pull the dark slide and filter control out to the MTL position and bring the pen on the zero line of the recorder by adjusting the zero control. The pen is now moved to indicate approximately 95 $\pm$ 2 on the recorder by pushing in the dark slide and filter control to position B, setting the slit width to 0.1 mm., and the Wave Length dial to some convenient setting so that the pen will reach 95. The degree of damping is indicated by the manner in which the pen reacts as it returns to zero when the dark slide and filter control is returned to the MTL position. When properly adjusted, the pen should move to zero on the chart, overshoot 1% or less, and return to rest at chart zero. If adjustment is indicated, very slight rotation of the slotted Damping control shaft will change the damping characteristics.

Blank and sample scans are performed in the following manner: Turn the Speed switch to 2 (special switch which has been installed to the right of the Wave Length drive control knob), the Shutter switch to Metal (special switch in back of Wave Length drive power switch), the Wave Length drive power switch to On, the Chopper switch to On, and pull the dark slide and filter control out to the MTL position. Check to see that the recorder pen is at zero on the chart; if not, adjust with the Zero control knob on the amplifier. Return the dark slide and filter control to position B, and set

the Wave Length dial to 4.0 microns. Press the special "pip" switch momentarily (on rear of Wave Length drive control housing), and simultaneously depress Wave Length drive control knob to engage the clutch. The "pip" switch produces a straight line on the recorder chart and indicates the starting point - 4.0 microns. When the Wave Length dial reaches 2.8 microns, the instrument will automatically stop.

Care must be exercised when investigating the amplifier circuits, since lethal voltage may appear at several points in normal operation. Therefore, turn the Power switch off when checking amplifier and power supply, and use insulated tools when possible.

Warm-up requirements for the various units to become stabilized for satisfactory operation vary from 6 hours for the air dryer, to 2 hours for the constant temperature bath, 30 minutes for the amplifier, 10 minutes for the glower, and to 3 minutes for the recorder. Since these are minimum values, the air dryer and constant temperature water bath are generally left on continuously.

CALIBRATION OF THE SPECTROPHOTOMETER

Determine the volume of the 50-liter flask by filling it to the top with known amounts of tap water. Clean the flask with a brush and detergent, rinse with copious quantities of water, and suspend it inverted to dry. To hasten drying, use infrared lamps to heat the external surface of the flask while aspirating clean laboratory air through it by means of a pump.

Fit the 50-liter flask with a rubber stopper covered with aluminum foil and several glass tubes for introduction of hexane, withdrawals of the sample, and flushing with air. The apparatus is shown in Figure 5. The glass tube at the rear reaches almost to the bottom of the flask, and is used to draw air through the flask. The tube that admits air to the flask (for flushing purposes) reaches just below the stopper and is connected to a drying tube containing Ascarite. This tube is also used to introduce the sample and is large enough in diameter to allow a 1-ml. pipet to pass through it. When the flask is flushed with air, the Ascarite tube is in place, otherwise a serological stopper is used to seal the tube. The sample withdrawal tube reaches to the middle of the flask and consists of capillary tubing. A rubber policeman or piece of rubber tubing with a pinch clamp is used to seal the end.

A magnetic stirrer is used to mix the air and hexane blends. The rotor is constructed of aluminum with a small Alnico magnet across the middle. The entire setup easily balances on the magnetic stirrer by use of a 5 1/2-inch O.D. cork ring containing nonmagnetic rods. Without these rods, the ring would slip down around the outside of the stirrer.

With the flask in place on the stirrer, draw air through it (using the Ascarite tube) for 15 minutes. Seal off the glass tubes with stoppers, and remove four 50-ml. (or more) samples with a syringe (as described below) and transfer to the spectrophotometer cell

Figure 5. Calibrating equipment used for preparing hexane standards. Note the spoked ring and special rotor.

for a blank determination. Run an infrared trace from 4 to 3 microns on the blank as described under blank and sample scan in the OPERATION OF THE SPECTROPHOTOMETER section. This will appear similar to Figure 6. At the time the scans in Figures 6 and 8 were run, the chart moved from 3 to 4 microns; hence, the pip at 3 microns. It has since been modified so that the wave length recorded is from 4 to 3 microns in order to take advantage of the automatic shut-off feature of the instrument. Obtain the transmittance of the blank by drawing a dotted curve fitting the shape of the hump, generally, as shown in Figure 6, using a flexible ruler. This is the base line for 100% transmission. Determine the actual transmittance of the blank by dividing the chart readings at the wave length of maximum absorption by the value from the base line at the same point. The blank transmittance will be subtracted later from that of the n-hexane to obtain the corrected transmittance for calibration. It is the practice to make several such blank determinations during the calibration and average the results for the final calculations.

With the rotor in place, add 1 ml. of n-hexane to the flask with a pipet through the inlet tube. Touch the pipet to the bottom of the inlet tube, but avoid getting any of the liquid anywhere else along the tube. Place the serological stopper on the tube, and start the stirrer. Allow the stirrer to run for 15 minutes. Remove 10 to 15 ml. of the mixture by poking the needle of the syringe through the rubber tubing connected to the capillary tube. This flushes the tube. Then transfer a 5-ml. sample to the spectrophotometer cell, which has previously been evacuated and sealed off, by poking the needle of the syringe through a rubber-tubing connection at the cell. The vacuum of the cell will pull the sample out of the syringe. Remove the syringe after the sample has been transferred. Run an infrared trace from 4 to 3 microns on the sample, as described under blank and sample scan in the OPERATION OF THE SPECTROPHOTOMETER section. Remove another 5-ml. sample from the flask and add it to the spectrophotometer cell, in the same manner. Repeat the procedure until a total of 20 to 30 ml. of sample have been added to the cell. Repeat the entire procedure by flushing the flask with air, as described above, and adding a fresh portion of n-hexane to the flask. This time remove 50-ml. portions of sample, adding a total of 300 ml. to the cell.

Calculate the transmittances of the n-hexane samples at the wave length of maximum absorption by using the curved base-line technique described for the blank.

Calculate the absorbance of each sample and blank as follows:

$$\log \frac{I}{T} \qquad (1)$$

where

T = transmittance of a sample or a blank

Then calculate the corrected absorbance by subtracting the average absorbance for the blanks from that of each sample.

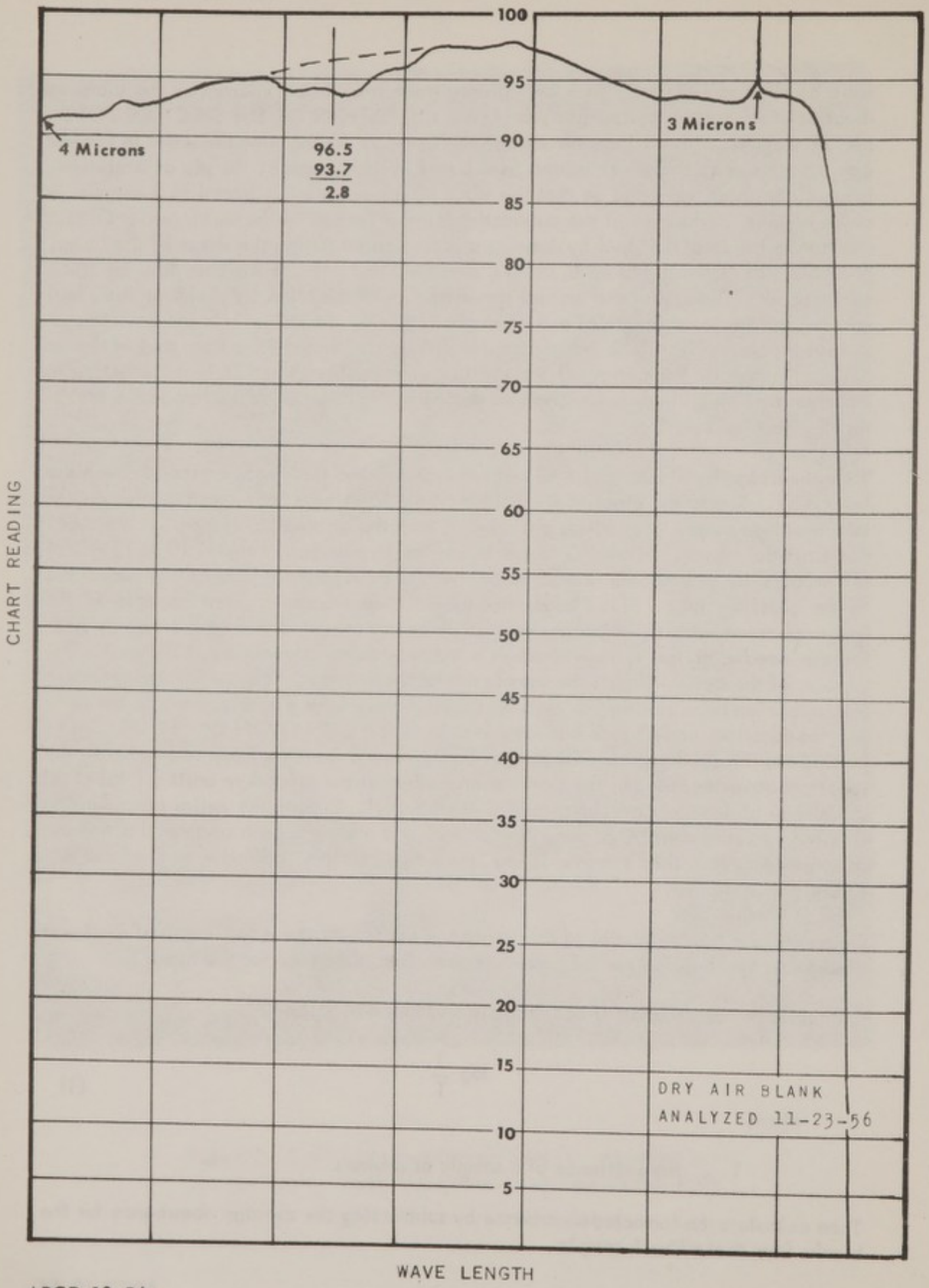

Figure 6. Blank trace by IR-2A for dry air.

Calculate the micrograms of n-hexane in each sample as follows:

$$\frac{DLA \times 10^3}{V_m} \qquad (2)$$

where

D = density of n-hexane, grams per milliliter

L = milliliters of n-hexane added to 50-liter flask

A = total milliliters of sample removed from 50-liter flask

V_m = measured volume of 50-liter flask, liters

Prepare a calibration curve by plotting the corrected absorbances of the samples vs. the micrograms of n-hexane on rectangular-coordinate graph paper. Draw the best line possible through the plotted points. Select several points on the curve. Divide the micrograms of n-hexane by the corresponding absorbance for each point and average the results. This average is called the calibration factor and is sued to calculate the micrograms of hydrocarbons, as hexane, in unknown samples (see REPORTING AND CALCULATIONS).

COLLECTION OF THE SAMPLE

For Air Sampling. Set up the apparatus as shown in Figure 2. Grease the stopcocks and ball joints lightly with a stopcock lubricant. Place a cardboard or metal tag on each Shepherd trap so that the location, date, and time of sampling can be recorded in pencil and readily erased after the analysis. Place a clean, dry Shepherd trap into the Thermos bottle. Check to see that the stopcocks are closed. Add liquid oxygen to the Thermos bottle slowly to within 1/2 inch of the top. Caution must be exercised to avoid excessive boiling over of the liquid oxygen. Make connections such that the flow of air is through the rotameter and Ascarite tube into the center barrel of the trap. Open the stopcock of the trap on the inlet side carefully to let air into the trap without abruptly hitting the float on the top of the rotameter. Start the pump, open the exit stopcock slowly, and adjust the rate to 1 liter per minute. Use the exit stopcock to control the flow. Where a series of samples are to be collected, the period of collection is 55 minutes, starting on the hour. This gives 5 minutes for changing traps and Ascarite tubes, if necessary. The Ascarite tubes may need to be changed after 2 or 3 runs if they begin to plug the system. Add liquid oxygen to the Thermos bottle during the sampling period to maintain the proper level. At the end of each sampling period, while the trap is still in the liquid oxygen, connect one arm to a vacuum pump and the other to a closed-end mercury manometer. Rapidly reduce the pressure in the system to approximately 75 mm. of mercury. Close the stopcocks, disconnect the trap, and remove it from the Thermos bottle. Place the trap in the carrying box for transport back to the laboratory.

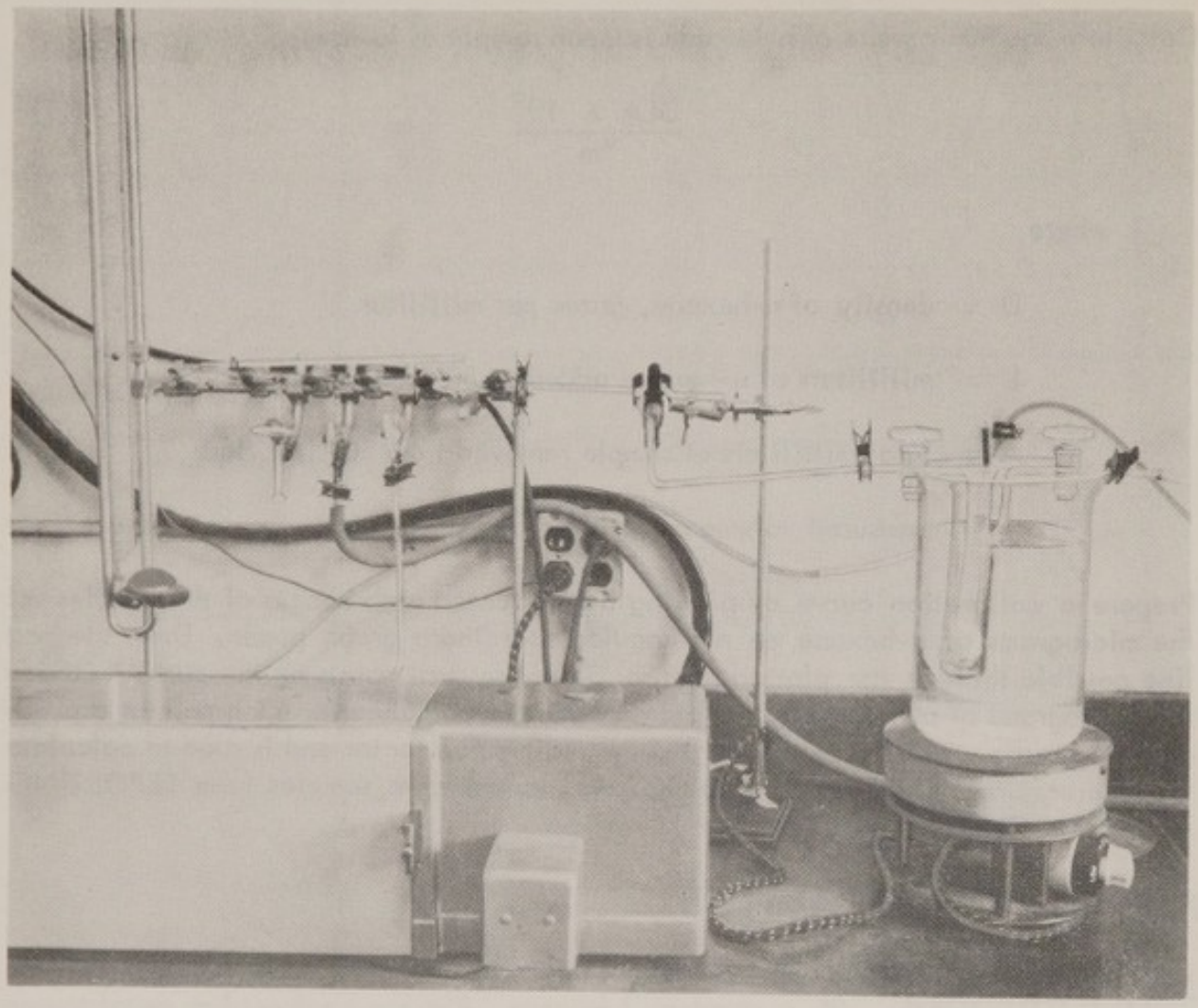

Figure 7. Simple manifold arrangement for evacuating the cell and making pressure measurements. The Shepherd trap is partially immersed in hot water during transfer to the spectrophotometer cell.

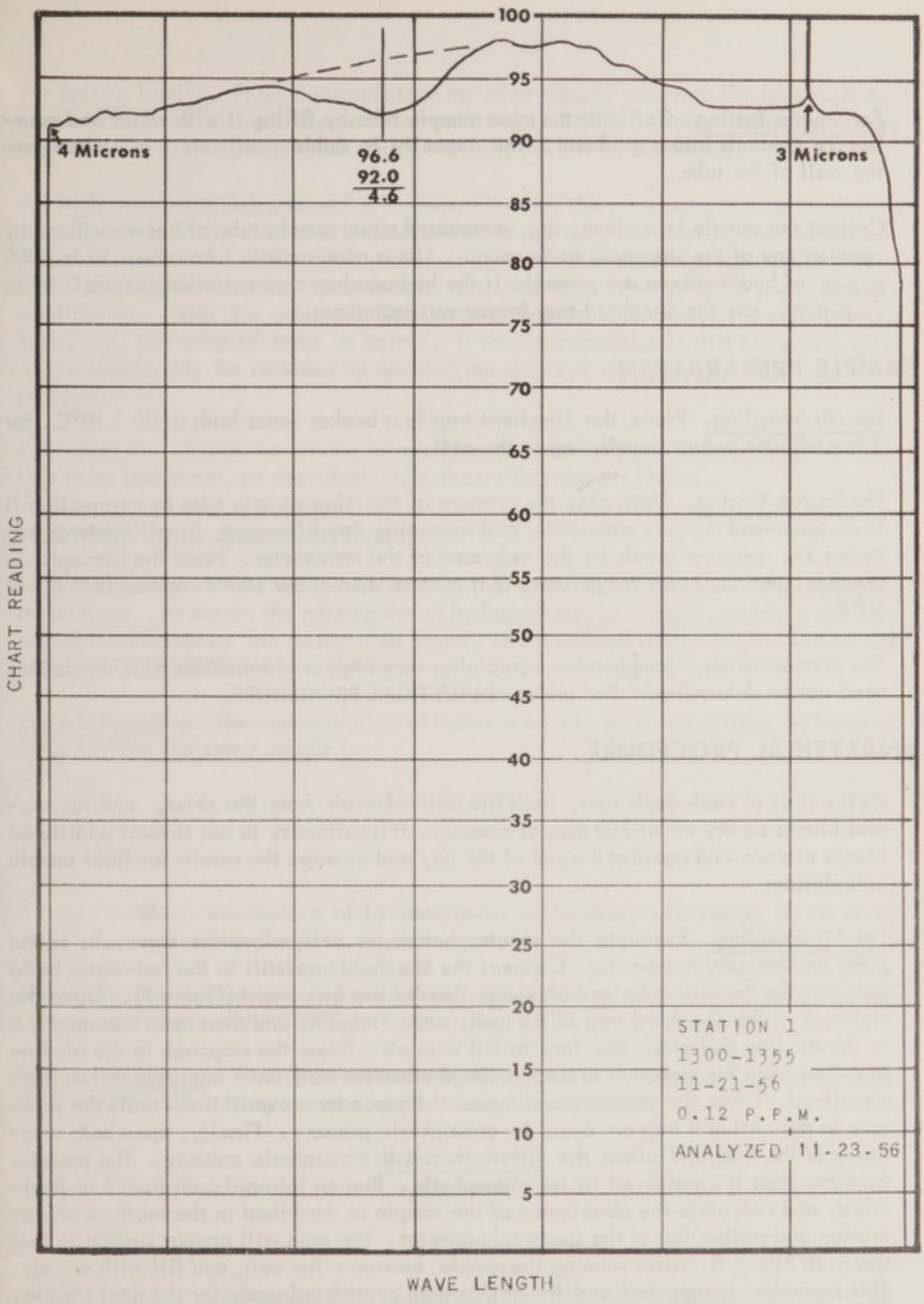

Figure 8. Typical IR-2A trace on freezeout of smoggy air.

For Source Testing. Calibrate the mine-sample tube by filling it with water and pouring the contents into a graduate. The capacity in cubic centimeters is etched onto the wall of the tube.

Collect the sample in a clean, dry, evacuated mine-sample tube of known volume by opening one of the stopcocks at the source. Use a mine-sample tube where 10 to 5000 p.p.m. of hydrocarbons are present. If the hydrocarbon concentration is from 0.05 to 25 p.p.m., use the Shepherd-trap freeze-out technique.

SAMPLE PREPARATION

For Air Sampling. Place the Shepherd trap in a beaker water bath at 80 $\pm$ 10°C. for a few minutes before transferring to the cell.

For Source Testing. Determine the pressure of the mine-sample tube by connecting it to an open-end mercury manometer and measuring the difference, in millimeters, between the mercury levels in the two arms of the manometer. Note the atmospheric pressure, and the room temperature if it is more than about 100°F. or less than about 50°F.

The pressure of mine-sample tubes containing very high concentrations of hydrocarbons need not be determined. See under ANALYTICAL PROCEDURE.

ANALYTICAL PROCEDURE

At the start of each day's runs, flush the cell with air from the drier, and run several blanks on dry air at 760 mm. of mercury. It is customary to run several additional blanks at noon and again at the end of the day and average the results for final sample calculations.

For Air Sampling. Evacuate the spectrophotometer cell, close the stopcocks to the pump and mercury manometer. Connect the Shepherd trap (still in the hot-water bath) between the Ascarite tube and air purge lines of the instrument (Figure 7). Open the stopcock of the Shepherd trap to the cell, close it again, and then open the stopcock to the air line and allow the trap to fill with air. Close the stopcock to the air line and then open the stopcock to the spectrophotometer cell until the pressure has been equalized. Close the stopcock and repeat the procedure several times until the pressure in the cell and trap are close to atmospheric pressure. Finally, open both stopcocks of the trap and allow the system to reach atmospheric pressure. The pressure from the drier is considered to be atmospheric. Run an infrared scan from 4 to 3 microns, and calculate the absorbance of the sample as described in the sections on operation and calibration of the spectrophotometer. The scan will appear similar to that shown in Figure 8. After running the sample, evacuate the cell, and fill with dry air. This procedure is repeated and the cell is then considered ready for the next sample.

For Source Testing. Flush the sample from the mine-sample tube into the spectrophotometer cell in the same manner as for air samples, except for samples containing a very high concentration (greater than about 1000 p.p.m.) of hydrocarbons.

For high concentrations proceed as follows: Connect the mine-sample tube (stopcocks closed) to the cell, open the stopcocks to the mercury manometer and the vacuum pump. Evacuate the spectrophotometer cell, and close the stopcock to the pump. Open the stopcock on the mine-sample tube and allow the system to reach pressure equilibrium. Note the pressure. Close the stopcocks and remove the mine-sample tube. Run the infrared trace as before. If the concentration is still too great, some of the sample may be removed by opening the stopcock to the pump. Again note the pressure.

Calculate the absorbance of the sample from the transmission values, using the flexible-ruler technique, as described under the calibration procedure.

REPORTING AND CALCULATIONS

Subtract the absorbance of the blank from that of the sample to obtain the corrected absorbance. To obtain the micrograms of hydrocarbons, as hexane, multiply the corrected absorbance by the calibration factor, as determined in the CALIBRATION OF THE SPECTROPHOTOMETER section.

For Air Sampling. The concentration of hydrocarbons in parts per million, as hexane, for a 55-liter freezeout sample is:

$$W \times 5.17 \times 10^{-3} \qquad (3)$$

where

W = micrograms of hydrocarbons, as hexane, calibration factor times absorbance

Generally, no temperature corrections are made on sample volumes unless the temperature goes above about 100°F. or below about 50°F.

For Source Testing. The concentration of hydrocarbons in parts per million, as hexane, for a sample collected by means of a mine-sample tube is:

$$\frac{W \times 2.16 \times 10^{5}}{v_s (P_r + \Delta P)} \qquad (4)$$

where

W = micrograms of hydrocarbons, as hexane, calibration factor times absorbance

v_s = measured volume of mine-sample tube, cubic centimeters

ΔP = differential pressure of the mine-sample tube, millimeters of mercury

P_r = atmospheric pressure (at the time of the ΔP measurement), millimeters of mercury

The parts per million of hydrocarbons, as hexane, for sample tubes containing high concentrations of hydrocarbons is:

$$\frac{W \times 2.16 \times 10^2}{v_c P_c} \qquad (5)$$

where

W = micrograms of hydrocarbons, as hexane, calibration factor times absorbance

v_c = volume of spectrophotometer cell, liters (in this laboratory $v_c = 0.495$)

P_c = pressure of the spectrophotometer cell, millimeters of mercury absolute

In cases where the moisture content of the original sample at the source exceeds 5% of the gas volume, a correction should be applied to Formulae 4 or 5. The moisture content is usually determined in conjunction with some other test such as grain loading.

To express the results in grains of hydrocarbons, as hexane, per standard cubic foot (60°F. and 1 atmosphere), multiply the parts per million by 1.58×10^{-3}.

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Beckman Instruments Inc., Fullerton, California, Bulletin 147-B (undated).

Mader, Paul P., Heddon, Merlyn W., Lofberg, Robert T., and Koehler, Ruth H., Anal. Chem., 24, 1899-1902(1952).

Shepherd, Martin, Rock, A.M., Howard, Royce, and Stormes, John, Anal. Chem., 23, 1431-40(1951).

OXIDES OF NITROGEN
Griess-Saltzmann Method APCD 11-56

Laboratory Methods

POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

OXIDES OF NITROGEN
GRIESS-SALTZMAN METHOD
APCD 11-56

SCOPE

This method is used to determine small concentrations of nitrogen dioxide found in the atmosphere. The lower limit of the method is about 0.1 p.p.m. in a 500-ml. sample bottle. By altering the volume of the sample, nitrogen dioxide in specific sources can also be measured. However, the phenoldisulfonic acid method is generally employed by this laboratory for source testing. (N. B.)

METHOD SUMMARY

The samples are collected in evacuated bottles containing the absorbing solution. The absorbing solution consists of a mixture of sulfanilic acid, acetic acid, and N-(1-naphthyl)-ethylenediamine dihydrochloride. After shaking, the nitrogen dioxide diazotizes the sulfanilic acid which then couples with N-(1-naphthyl)-ethylenediamine forming a dye. The intensity of the color is measured with a colorimeter and the concentration of nitrogen dioxide read from a calibration curve.

SPECIAL APPARATUS

COLLECTION:

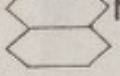
Chaney rotary sampler (Figure 1), 500-ml. bottles with narrow necks containing tabulated sidearms, 3-inch pieces of heavy-wall gum-rubber tubing, screw clamps, solid-glass plugs, and serological stoppers (Figure 2).

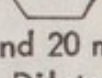
ANALYTICAL:

Spectrophotometer (Coleman Universal Model 14), microcuvettes (Coleman No. 14-315, minimum volume 2.5 ml.).

REAGENTS

COLLECTION:

0.1% N-(1-Naphthyl)-Ethylenediamine Dihydrochloride. Dissolve 0.1 gram of the solid  $\cdot 2HCl$ in 100 ml. of water.

Absorbing Reagent. Dissolve 5 grams of sulfanilic acid (HO_3S-  $\cdot H_2O$) in 800 ml. of water. Add 140 ml. of glacial acetic acid and 20 ml. of 0.1% N-(1-naphthyl)-ethylenediamine dihydrochloride solution. Dilute to 1 liter.

ANALYTICAL:

Standard Sodium Nitrite Solution. Accurately weigh 0.2755 gram of sodium

N. B.: This laboratory method has been superseded by the District since August 1956 for air monitoring purposes by an automatic recording instrument, Nitrogen Oxides Recorder, Model 3011, manufactured by Borman Engineering, Inc., North Hollywood, California, to District specifications and later modified by the Los Angeles County Air Pollution Control District.

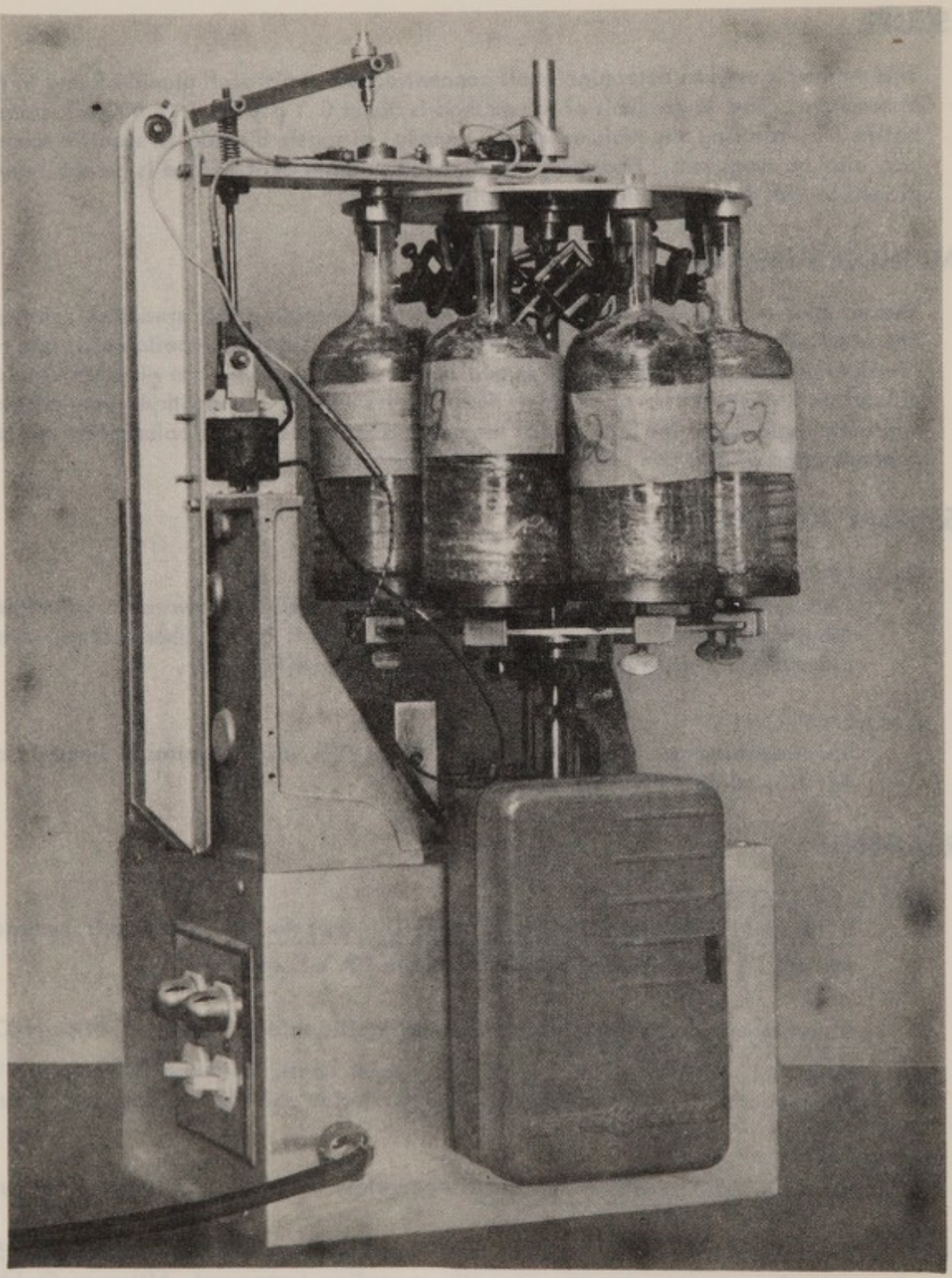


Figure 1. Chaney oxides of nitrogen sampler.

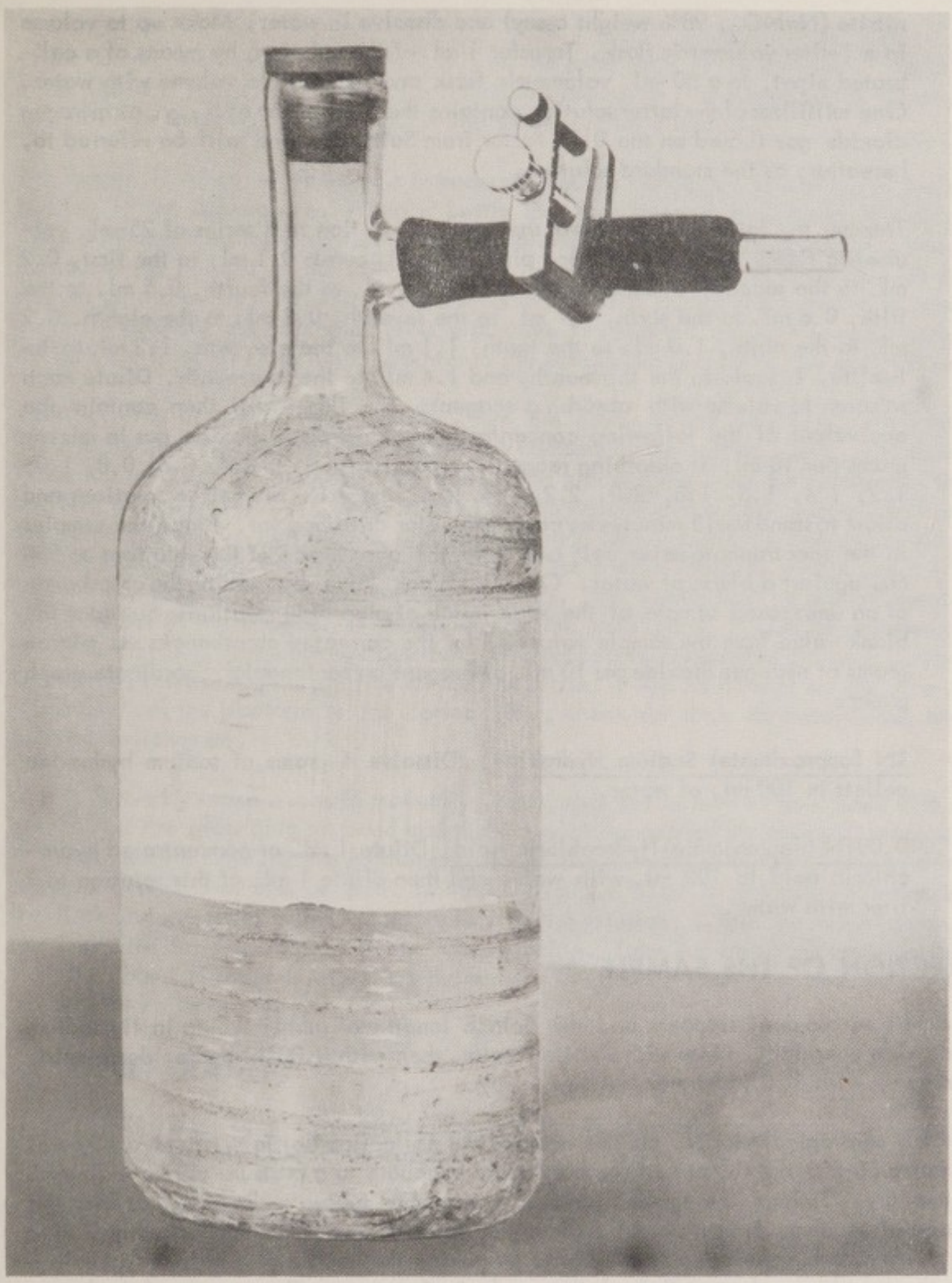


Figure 2. Sample bottle used with a Chaney rotary sampler.

nitrite ($NaNO_2$, 98% weight assay) and dissolve in water. Make up to volume in a 1-liter volumetric flask. Transfer 1 ml. of the solution, by means of a calibrated pipet, to a 50-ml. volumetric flask and make up to volume with water. One milliliter of the latter solution contains the equivalent of 5 μg. of nitrogen dioxide gas (based on the 0.72 factor from Saltzman) and will be referred to, hereafter, as the standard solution.

Transfer the following amounts of the standard solution to a series of 25-ml. volumetric flasks using a measuring pipet or 5-ml. buret: 0.1 ml. to the first, 0.2 ml. to the second, 0.3 ml. to the third, 0.4 ml. to the fourth, 0.5 ml. to the fifth, 0.6 ml. to the sixth, 0.7 ml. to the seventh, 0.8 ml. to the eighth, 0.9 ml. to the ninth, 1.0 ml. to the tenth, 1.1 ml. to the eleventh, 1.2 ml. to the twelfth, 1.3 ml. to the thirteenth, and 1.4 ml. to the fourteenth. Dilute each solution to volume with absorbing reagent. The flasks will then contain the equivalent of the following concentrations of nitrogen dioxide gas in micrograms per 10 ml. of absorbing reagent, respectively: 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, 2.0, 2.2, 2.4, 2.6, and 2.8. Shake the solutions and allow to stand for 15 minutes for complete color development. Place the samples in the spectrophotometer cell and read the absorbance of the solutions at 550 mμ against a blank of water. Obtain a blank value by reading the absorbance of an unexposed sample of the same batch of absorbing solution. Subtract the blank value from the sample values. Plot the corrected absorbances vs. micrograms of nitrogen dioxide per 10 ml. of reagent on rectangular-coordinate graph paper.

1N (approximate) Sodium Hydroxide. Dissolve 4 grams of sodium hydroxide pellets in 100 ml. of water.

0.001N (approximate) Hydrochloric Acid. Dilute 1 ml. of concentrated hydrochloric acid to 100 ml. with water and then dilute 1 ml. of this solution to 1 liter with water.

COLLECTION OF THE SAMPLE

Soak the serological stoppers and the 3-inch lengths of rubber tubing in 1N sodium hydroxide overnight. Rinse with distilled water, then with 0.001N hydrochloric acid, and again with distilled water. Allow to dry.

Place a serological stopper on the neck of the collection bottle. Attach a piece of rubber tubing to the sidearm of the bottle and evacuate to a pressure of about 25 mm. of mercury. Tighten the screw clamp on the rubber tubing and disconnect from the source of vacuum. Insert the solid-glass plug into the end of the rubber tubing. Add 10 ml. of absorbing solution to the bottle by poking the needle of a syringe (containing the absorbing solution) through the serological stopper. The vacuum of the bottle will draw the absorbing solution in. Remove the syringe. Number the bottle in any convenient manner. Load the bottle on the circular platform of the Chaney rotary sampler. The top of the bottle fits into a sleeve on a guide plate which has the time

of the sample marked on it, and which is on the same shaft as the platform. The circular platform rotates by means of a timing mechanism so that a new bottle is placed into position for sampling each hour. The sampler holds 8 bottles.

The sample is taken by means of a hypodermic needle connected to a piece of tubing leading to the atmosphere. When a bottle moves underneath the needle, the guide plate activates a microswitch mounted on the solenoid assembly. The solenoid is energized and the plunger of the solenoid moves the hypodermic needle down through the stopper on the bottle. After about 30 seconds, another microswitch on the solenoid assembly releases the solenoid. This procedure is repeated for each sample bottle. An electric interval timer turns the power to the sampler on and off at any preset time.

Upon arriving at the sampler location, turn the power switch and drive switch off. Remove the previous samples, and record the numbers of the bottles, times, and date. Place the next set of bottles in position on the platform and note the numbers of the bottles, times, and date. Check to see that the needle will hit the stopper, and not the guide plates, by turning the platform by hand slowly until the first microswitch clicks. Manually depress the lever arm holding the needle slowly to within about 1/4 inch of the stopper (do not puncture the stopper). The needle must be approximately in the center of the stopper. If it hits any of the metal parts, it must be adjusted or bent, so that it is in the correct position. This procedure is repeated for each bottle. Generally, if the needle is aligned for the first bottle, it will be correct for the others. Manually turn the platform to the correct time, check the timer for correctness, and turn the switches on.

If it is desired to take a sample manually, the sample bottle may be punctured with a needle, or the glass plug removed and the screw clamp opened for about 10 seconds. A 2-liter sample flask, similar to the ones used in the Phenoldisulfonic Acid Method for nitrogen oxides, may also be used. In this case, place 10 ml. of absorbing solution in the flask and evacuate to the vapor pressure of the solution. Close the screw clamp, and insert the solid-glass plug in the rubber tubing. Take the sample by opening the flask for about 10 seconds. Replace the screw clamp, solid-glass plug, and return to the laboratory for analysis.

SAMPLE PREPARATION

Shake the bottle (or flask) containing the sample for 15 minutes on a mechanical shaker to allow for complete color development.

ANALYTICAL PROCEDURE

Transfer the sample from the bottle (or flask) directly to the spectrophotometer cell and read the absorbance at 550 m μ against water. Obtain a blank value by reading the absorbance of the original absorbing solution. Subtract the blank value from the sample value to obtain the corrected absorbance. Read the weight of nitrogen dioxide corresponding to the corrected absorbance from the calibration curve.

ADDITIONAL NOTES

When operating the Coleman spectrophotometer, check the setting for zero absorbance before each reading since the instrument drifts gradually. To simplify this process, one of the two microcuvettes in the holder is always kept filled with water and the zero checked against this cell before each reading. Since it is important that the portion of the cuvette in the light path be completely full, the analyst should realize that the cuvette is tilted slightly and should fill it so that the side arms are about half full.

If only a few samples are to be analyzed, the spectrophotometer may be zeroed against the blank. However, if a large number of samples are to be analyzed, it is better to zero the instrument with water and subtract the blank. This will avoid the possibility of low sample values due to the gradual absorption of nitrogen dioxide from the laboratory atmosphere by the blank.

REPORTING AND CALCULATIONS

Calculate the parts per million of nitrogen dioxide as follows:

$$\frac{0.532\,W}{V_c} \qquad (1)$$

where

W = micrograms of nitrogen dioxide per 10 ml. of absorbing solution

V_c = volume of air sampled, liters, at 760 mm. of mercury and 25°C. Generally pressure and temperature corrections are neglected, and the measured volume of the bottle or flask is used

To convert to grains per standard cubic foot (60°F. and 1 atmosphere), multiply the parts per million by 8.48×10^{-4}.

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OXIDES OF NITROGEN
Phenoldisulfonic Acid Method APCD 12-56

Laboratory Methods

POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

OXIDES OF NITROGEN

PHENOLDISULFONIC ACID METHOD

APCD 12-56

SCOPE

This procedure is used for the determination of oxides of nitrogen (nitrous oxide excepted) in automobile exhaust and industrial effluents where the concentration range is 5 to several thousand p.p.m. There may be some question regarding its accuracy near the lower limit. The test is unsuitable for atmospheric sampling.

METHOD SUMMARY

The sample is collected in an evacuated flask containing a dilute solution of hydrogen peroxide and sulfuric acid. The hydrogen peroxide oxidizes the lower oxides of nitrogen (with the exception of nitrous oxide) to nitric acid. The resultant solution is then evaporated to dryness and treated with phenoldisulfonic acid reagent and ammonium hydroxide. The yellow trialkali salt of 6-nitro-1-phenol-2, 4-disulfonic acid is formed which is measured colorimetrically.

SPECIAL APPARATUS

COLLECTION:

Two-liter round-bottomed flask with a short length of 8-mm. glass tubing connected to the neck, 3-inch length of heavy-wall gum-rubber tubing, screw clamp, and solid-glass plug.

ANALYTICAL:

Klett-Summerson industrial colorimeter, 400- to 500-mμ blue filter (Klett-Summerson No. 42, or equivalent).

REAGENTS

COLLECTION:

3% Hydrogen Peroxide. Dilute 30% hydrogen peroxide 1:10 with water. This reagent should be prepared fresh daily.

0.1N (approximate) Sulfuric Acid. Dilute 2.8 ml. of concentrated sulfuric acid to 1 liter with water.

Absorbing Solution. Add 12 drops of hydrogen peroxide to each 100 ml. of 0.1N (approximate) sulfuric acid needed for the particular day's work.

ANALYTICAL:

1N (approximate) Sodium Hydroxide. Dissolve 40 grams of sodium hydroxide pellets in water and dilute to 1 liter.

Concentrated Ammonium Hydroxide.

Concentrated Sulfuric Acid.

Fuming Sulfuric Acid. 15-18% weight free sulfuric anhydride.

Phenoldisulfonic Acid Solution. Dissolve 25 grams of pure white phenol in 150 ml. of concentrated sulfuric acid on a steam bath. Cool and add 75 ml. of fuming sulfuric acid. Heat to 100°C. for 2 hours. Store in a brown glass stoppered bottle. This solution should be colorless if prepared from quality reagents.

Standard Potassium Nitrate Solution. Accurately weigh 0.5495 gram of potassium nitrate and dissolve in water. Make up to volume in a 1-liter volumetric flask with water. One milliliter of this standard solution contains the equivalent of 0.250 mg. of nitrogen dioxide. Add 25 ml. of absorbing solution to each of a series of 200-ml. casseroles. By means of a measuring pipet, transfer 0.1 ml. of the standard potassium nitrate solution to the first casserole, 0.2 ml. to the second, 0.3 ml. to the third, 0.4 ml. to the fourth, 0.5 ml. to the fifth, 0.6 ml. to the sixth, 0.7 ml. to the seventh, 0.8 ml. to the eighth, 1.0 ml. to the ninth, 1.2 ml. to the tenth, 1.4 ml. to the eleventh, 1.6 ml. to the twelfth, 1.8 ml. to the thirteenth, 2.0 ml. to the fourteenth, and use the fifteenth casserole for a blank. The casseroles then contain the equivalents of 0.025 mg., 0.050 mg., 0.075 mg., 0.100 mg., 0.125 mg., 0.150 mg., 0.175 mg., 0.200 mg., 0.250 mg., 0.300 mg., 0.350 mg., 0.400 mg., 0.450 mg., and 0.500 mg., of nitrogen dioxide, respectively.

Make the solutions in the casseroles alkaline to litmus with 1N sodium hydroxide and evaporate to dryness on a steam bath. Slowly add 1 ml. of phenoldisulfonic acid solution to each of the dry residues, and triturate thoroughly with a glass rod. Exercise caution in adding this reagent since violent spattering and consequent loss of sample may occur. Add 1 ml. of water and 4 drops of concentrated sulfuric acid to each casserole. Heat on a steam bath for 3 minutes with occasional mixing to insure complete reaction. Add about 25 ml. of water and then 5 ml. of concentrated ammonium hydroxide to each casserole. A slight turbidity may be encountered. If so, filter the solutions through separate fritted-glass filters into 50-ml. filter flasks with gentle suction. Wash the casseroles two or three times with small portions of water, passing the washings through the filters. Quantitatively transfer the filtrates to separate 50-ml. volumetric flasks. Make up to volume with water and mix well. Measure the light absorption of the solutions in a photoelectric colorimeter with a 400- to 500-mμ blue filter and a 20-mm. light path. Use the blank solution for zeroing the instrument. Prepare a calibration curve by plotting colorimeter readings vs. milligrams of nitrogen dioxide per 50 ml. of solution on rectangular-coordinate graph paper.

COLLECTION OF THE SAMPLE

Add 25 ml. of freshly prepared absorbing solution to the special 2-liter collection flask. Evacuate the flask to the vapor pressure of the solution, and tighten the clamp on the rubber-tubing sleeve. Stopper the open end of the rubber tubing with a small glass plug. Collect the sample by opening the flask at the source for about 10 seconds. Close the screw clamp, insert the glass plug, and return to the laboratory for analysis.

SAMPLE PREPARATION

Shake the flask for 15 minutes. Allow the flask to stand overnight to insure complete absorption of the oxides of nitrogen by the acid solution. When absorption is complete, all of the oxides of nitrogen with the exception of nitrous oxide will be converted to nitric acid.

Remove the glass plug, connect the rubber sleeve on the flask to an open-end mercury manometer, and open the screw clamp. Measure, in millimeters, the difference between the mercury levels. This reading is the difference between the pressure in the flask and atmospheric pressure. Record the room temperature and atmospheric pressure.

ANALYTICAL PROCEDURE

Transfer the contents of the 2-liter flask to a 200-ml. casserole. Wash the flask three times with 15-ml. portions of water and add the combined washings to the solution in the casserole. Make the solution alkaline to litmus with 1N sodium hydroxide.

Prepare a blank of 25 ml. of the original absorbing solution in a casserole making it alkaline to litmus. Evaporate the sample and blank solutions to dryness on a steam bath. Slowly add 1 ml. of phenoldisulfonic acid solution to each of the dry residues and triturate thoroughly with a glass rod. Exercise caution in adding this reagent since violent spattering and consequent loss of sample may occur. Add 1 ml. of water and 4 drops of concentrated sulfuric acid. Heat on a steam bath for 3 minutes with occasional mixing to insure complete reaction.

Add about 25 ml. of water followed by 5 ml. of concentrated ammonium hydroxide. Filter the resulting solutions through separate fritted-glass filters into 50-ml. filter flasks with gentle suction. Wash the casseroles two or three times with small portions of water and pass the washings through the filters. Quantitatively transfer the filtrates to separate 50-ml. volumetric flasks. Make up to volume with water and mix well. Measure the light absorption of the solution in the Klett-Summerson colorimeter with a 400- to 500-m μ blue filter and a 20-mm. light path. Use the blank to zero the instrument. Where the concentration of oxides of nitrogen in the original gas sample is over 100 p.p.m. it may be necessary to dilute the solution further with water to obtain a reading. The blank must likewise be diluted and an appropriate correction made to Formula 1 below.

REPORTING AND CALCULATIONS

The concentration of oxides of nitrogen, as nitrogen dioxide, in parts per million (dry basis) is:

$$\frac{1356\,WAT}{v_m(P_r + \Delta P)} \qquad (1)$$

where

W = milligrams of nitrogen dioxide per 50 ml. of final solution, from the calibration curve

A = dilution factor for color measurement, where necessary

ΔP = sample flask differential pressure, millimeters of mercury (with respect to atmospheric pressure)

P_r = atmospheric pressure, millimeters of mercury (at the time of the ΔP measurement)

T = room temperature, degrees Kelvin (at the time of the ΔP measurement)

v_m = measured volume of sample flask, liters*

To obtain grains of nitrogen dioxide per standard cubic foot (60°F., 1 atmosphere), multiply the parts per million by 8.48×10^{-4}.

REFERENCES

Beatty, Robert L., Berger, L. B., and Schrenk, H. H., U. S. Bureau of Mines, Report of Investigation 3687 (1943).

Goldman, Frederick H., and Jacobs, Morris B., "Chemical Methods in Industrial Hygiene," Interscience, New York, 1953.

*The vapor pressure of water at ambient conditions and the volume occupied by the solution are neglected here. However, should the reader wish to place the results on a stack-conditions basis, a correction for moisture must be added to Formula 1. The moisture content is usually obtained in conjunction with some other test such as grain loading.

SULFUR OXIDES
Barium Sulfate Method APCD 13-49

Laboratory Methods

POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

SULFUR OXIDES

BARIUM SULFATE METHOD

APCD 13-49

SCOPE

This method is used for source testing only, since atmospheric concentrations of sulfur oxides are too low to yield accurate results. The lower limit of the method is about 5 p.p.m. each of sulfur dioxide and sulfur trioxide in a 60-cubic-foot sample.

METHOD SUMMARY

Sulfuric acid mist is collected in a Whatman thimble and sulfur dioxide in impingers containing caustic following the thimble. The sulfuric acid mist is extracted with water in a Soxhlet extractor. The sulfur dioxide in the impinger solution is oxidized with bromine water to sulfur trioxide. The extract and impinger solutions are analyzed by precipitating and weighing of barium sulfate.

SPECIAL APPARATUS

COLLECTION:

The apparatus consists of a Whatman thimble (single thickness, 43 x 123 mm.) in a Pyrex holder connected in series to three standard Greenburg-Smith impingers, mercury manometer, dry gas meter (Sprague No. 1A, Sprague Meter Co., Los Angeles, Calif., or equivalent), and air pump, assembled as shown in Figure 1.

ANALYTICAL:

Soxhlet extraction apparatus, 50-mm.

REAGENTS

COLLECTION:

5% Sodium Hydroxide. Dissolve 50 grams of sodium hydroxide pellets in water and dilute to 1 liter.

ANALYTICAL:

0.1% Methyl Red Indicator. Dissolve 0.1 gram of the solid in 100 ml. of 95% ethyl alcohol.

Saturated Bromine Water. Add 100 ml. of water to a reagent bottle and chill in a refrigerator or an ice bath. After the water is thoroughly chilled, add 3 to 4 ml. of chilled liquid bromine. Note: All bromine handling should be performed in the hood or out-of-doors.

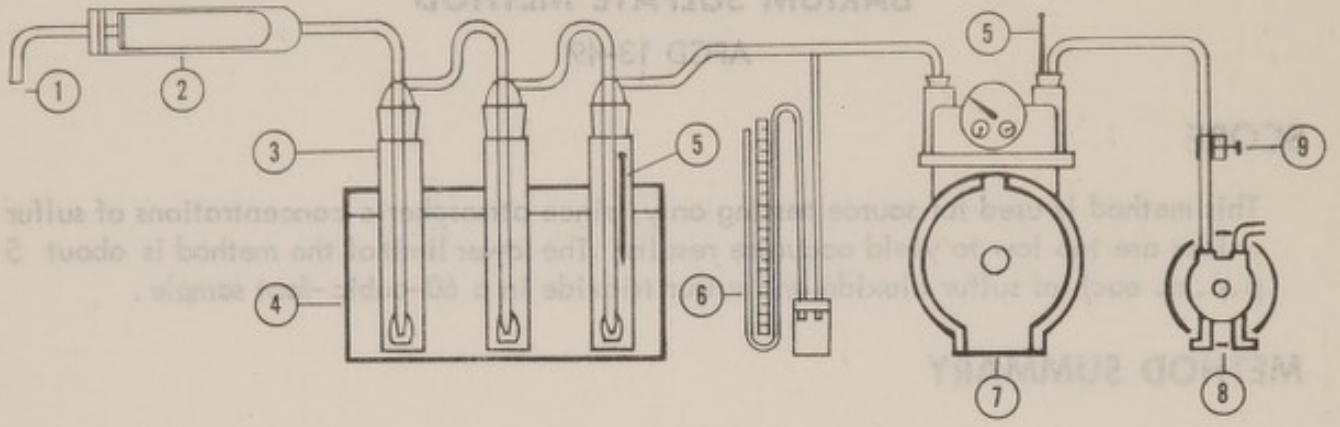

Figure 1. Sampling train used for sulfur oxides determination. ① Sample probe. ② Whatman thimble in Pyrex holder. ③ Standard Greenburg-Smith impingers. ④ Ice-bath container. ⑤ Thermometer. ⑥ Mercury manometer. ⑦ Dry gas meter. ⑧ Air pump. ⑨ Screw clamp to control gas flow rate.

10% Barium Chloride. Dissolve 10 grams of barium chloride ($BaCl_2 \cdot 2H_2O$) in 100 ml. of water.

Concentrated Hydrochloric Acid.

Silver Nitrate Solution. Dissolve 1 gram of silver nitrate in 100 ml. of water.

COLLECTION OF THE SAMPLE

Assemble the collection train as shown in Figure 1. Place a Whatman thimble in the Pyrex holder and exactly 100 ml. of 5% sodium hydroxide in each of the first two Greenburg-Smith impingers. The third impinger is operated dry to catch any carry over and to protect the meter. The impingers are immersed in an ice bath. The thimble temperature must be maintained above the condensation point of the water vapor. This is usually done by partly inserting the thimble holder into the stack, or regulating the length of the sampling tube so that no visible moisture is collected. A 1-hour sample is usually withdrawn through the train at 1 cubic foot per minute. It may be necessary to vary the sampling rate and time depending on the source. Record the meter temperature and pressure every 10 minutes and average the results. The thermometer shown in the last impinger in Figure 1 is used only when the total moisture content of the sample gas is to be determined.

SAMPLE PREPARATION

Remove the Whatman thimble from its holder and place it in a Soxhlet extractor. Position the thimble away from the siphon tube. Add 200 to 300 ml. of water to the Soxhlet flask. Extract the thimble for 4 hours adjusting the temperature to maintain reflux cycles of 8 to 10 minutes.

Pour the contents of the three impingers into a 250-ml. graduate and record the volume. Calculate the vapor equivalent of the water collected by means of Formula 1 (see REPORTING AND CALCULATIONS). Rinse the impingers two or three times with small portions of water. Combine the washings with the impinger solutions, and record the milliliters total. If the sulfur dioxide content of the sample is expected to be less than 10 p.p.m., transfer the total solution to a 400-ml. beaker. If not, transfer a 100-ml. aliquot of the sample solution to a 400-ml. beaker and dilute with 100 ml. of water.

ANALYTICAL PROCEDURE

Transfer the solution from the extractor to a 400-ml. beaker. Neutralize with concentrated hydrochloric acid to the methyl red end point and add 2 ml. of the acid in excess. Boil gently for 1 hour to drive off any sulfur dioxide that may be present. If necessary, filter the solution through Whatman No. 1 filter paper to remove silica and foreign matter. This solution is used for the sulfur trioxide determination.

Add saturated bromine water to the sample from the impingers until a red color persists, indicating a definite excess, and boil. Add more bromine water if the color disappears. At the end of 5 minutes, continue to boil until the solution is colorless and no odor of bromine can be detected in the vapors. Neutralize with concentrated hydrochloric acid to the methyl red end point and add 2 ml. of the acid in excess. If necessary, filter the solution through Whatman No. 1 filter paper to remove silica and foreign matter. This solution is used for the sulfur dioxide determination.

Heat the extraction and impinger samples to boiling and add hot 10% barium chloride solution rapidly to each while stirring until no more precipitate forms. Allow the precipitates to settle and add a few more drops of 10% barium chloride solution to each to test for completeness of precipitation. Digest the precipitates for several hours at 60°C. Filter each through a separate Gooch crucible which has been previously ignited to constant weight. Wash the precipitates with hot water until no silver chloride precipitate is formed upon addition of silver nitrate to the filtrate. Ignite to constant weight at 800°C.

REPORTING AND CALCULATIONS

The vapor equivalent of the condensate, v_w, in cubic feet, at meter conditions is:

$$\frac{0.00267\ VT}{P} \qquad (1)$$

where

V = milliliters of water condensed in the impingers (difference between the initial and final volumes)

T = average meter temperature, degrees Rankine

P = average meter pressure, inches of mercury, absolute

The concentration of sulfur trioxide in parts per million is:

$$\frac{206\ W_1 T}{P(v_m + v_w)} \qquad (2)$$

and of sulfur dioxide is:

$$\frac{206\ W_2 TA}{P(v_m + v_w)} \qquad (3)$$

where

W_1 = grams of barium sulfate precipitated from the extraction sample

W_2 = grams of barium sulfate precipitated from the impinger sample

T = average meter temperature, degrees Rankine

$$A = \frac{\text{(milliliters total impinger solutions and washings)}}{\text{(milliliters actually used for the analysis)}}$$

v_m = measured volume of gas sample, cubic feet at meter conditions

v_w = vapor equivalent of condensate, cubic feet at meter conditions

P = average meter pressure, inches of mercury, absolute

To calculate grains of sulfur trioxide per standard cubic foot (60°F., 1 atmosphere) multiply the parts per million by 1.47×10^{-3}.

To calculate grains of sulfur dioxide per standard cubic foot (60°F., 1 atmosphere) multiply the parts per million by 1.18×10^{-3}.

OZONE, Rubber Cracking Method APCD 14-56

Laboratory Methods

POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

OZONE

RUBBER CRACKING METHOD

APCD 14-56

SCOPE

This method is used for the determination of ozone in the atmosphere. The lower limit of the test is about 0.05 p.p.m. (N. B.)

METHOD SUMMARY

Air is passed at a constant rate across a folded strip of calibrated rubber stock, and the length of time required for cracks to appear at the fold is measured. The concentration of the ozone present in the air stream is directly proportional to the time for initial cracking.

SPECIAL APPARATUS

AIR SAMPLING:

The apparatus consists of an air pump, a flowmeter calibrated for 1 liter per minute, a 13-mm. inside-diameter sampling tube, and a stopcock for adjusting the flow rate. It is assembled as shown in Figure 1. A 4X magnifying glass, a brass clip or copper wire, a stopwatch, a pair of forceps, and a jar of calibrated rubber strips are also needed.

CALIBRATION:

The apparatus for calibrating the rubber stock is shown in Figure 2. It consists of three midget impingers, a 13-mm. inside-diameter sampling tube, a flowmeter calibrated for 1 liter per minute, a 2-liter flask with standard-taper joint, an ultraviolet source, and the following electrical equipment:

Powerstat - Superior Electric Co., type 116, primary 115 volts, 60 cycles, 7.5-amperes output, or equivalent.

Constant-Voltage Transformer - Solar Electric Co., No. 3001, primary 95 to 125 volts, 60 cycles, secondary 115 volts, 0.52 ampere, or equivalent.

Step-Up Transformer - primary 115 volts, secondary 2500 volts, 30 ma. A 5000-volt neon transformer (General Electric Co., No. 9T61Y3026, or Acme Co., No. 305-T) which is center-tapped giving 2500-volts secondary off either side is satisfactory.

N. B.: This laboratory method has been augmented since Sept. 1957 for air monitoring purposes by an automatic recording instrument, Ozone Photometer, manufactured by Harold Kruger Instruments, San Gabriel, California, to District specifications and later modified by the Los Angeles County Air Pollution Control District.

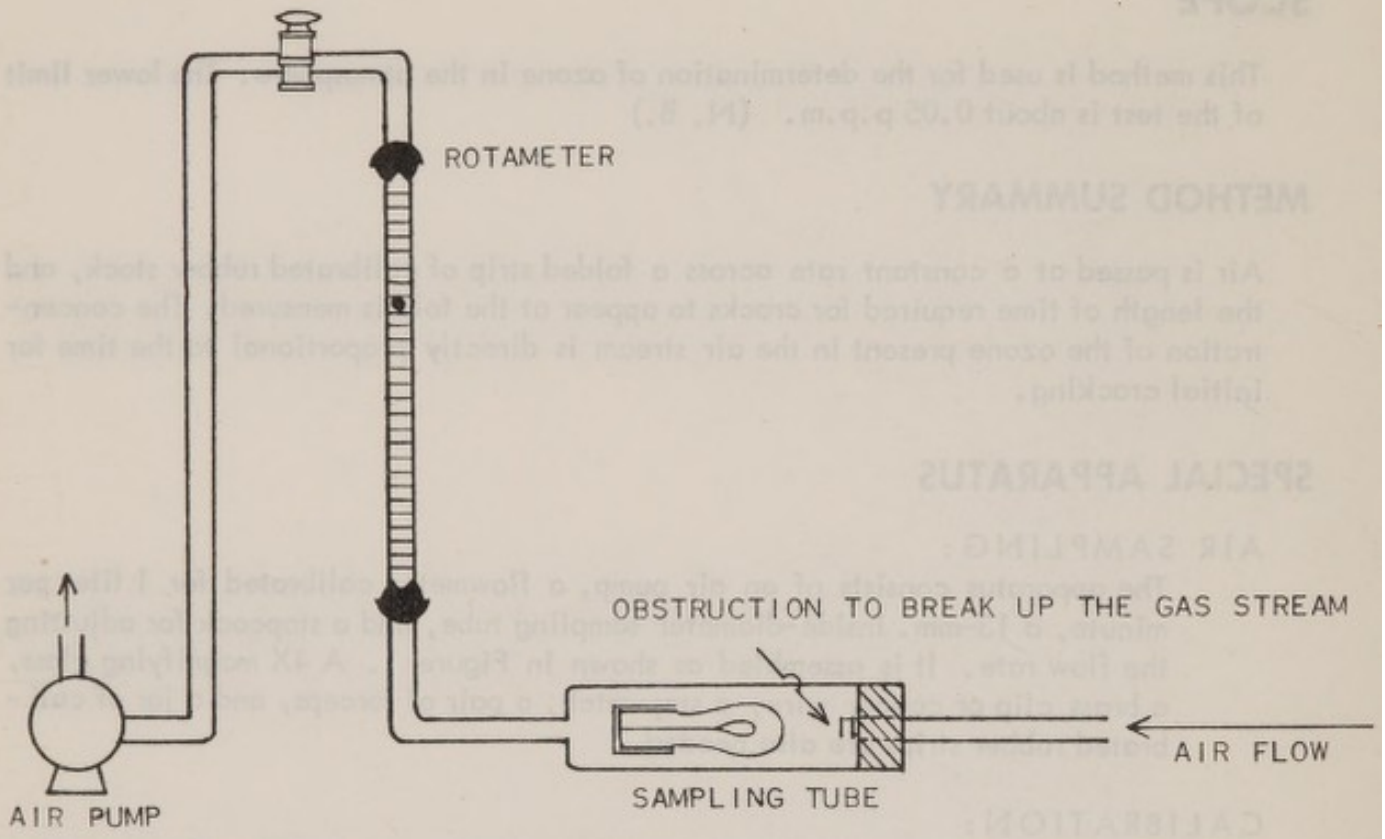

Figure 1. Air sampling equipment for ozone measurement. The sizes of components are exaggerated in order to better illustrate the position of the rubber strip.

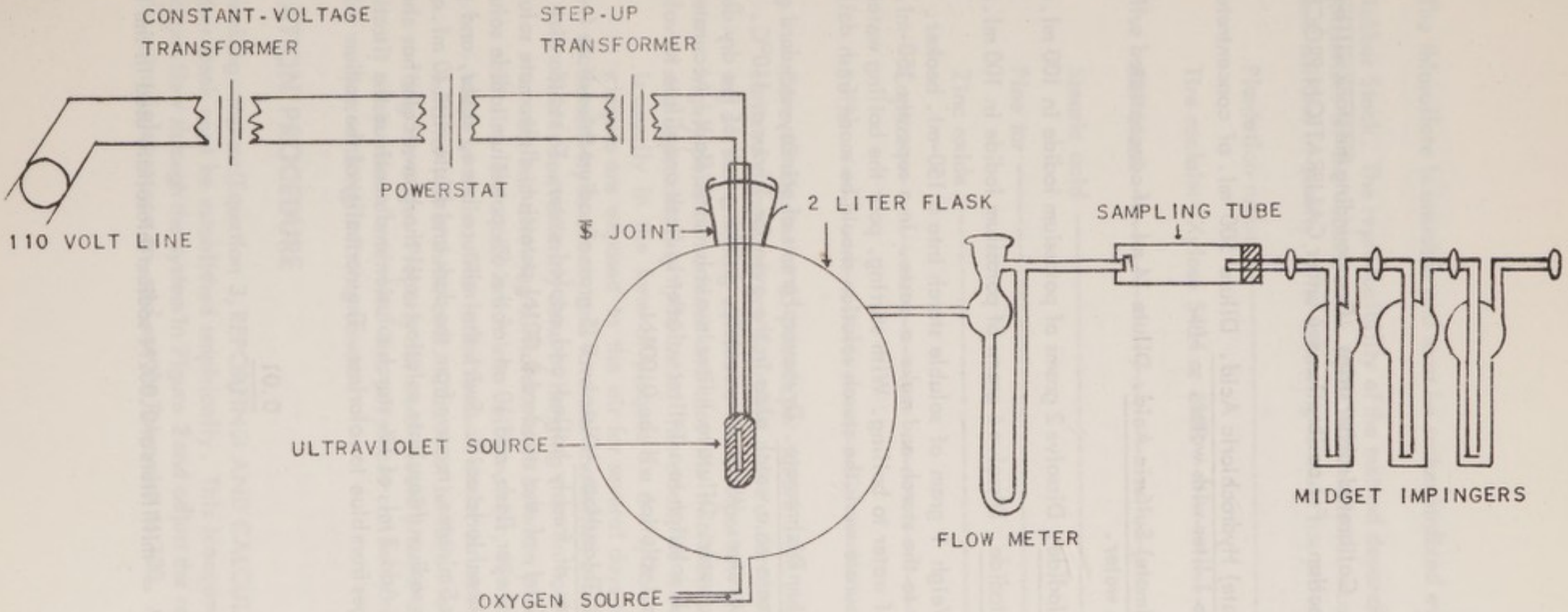

Figure 2. Variable-output ozonator with sampling tube and midget impingers.

REAGENTS

AIR SAMPLING:

Rubber Stock. Calibrated rubber strips. Compounding the stock will be discussed later in this section. For calibration see under CALIBRATION PROCEDURE.

CALIBRATION:

6N (approximate) Hydrochloric Acid. Dilute 500 ml. of concentrated hydrochloric acid to 1 liter with water.

0.5N (approximate) Sulfuric Acid. Dilute 14 ml. of concentrated sulfuric acid to 1 liter with water.

2% Potassium Iodide. Dissolve 2 grams of potassium iodide in 100 ml. of water.

6% Potassium Iodide. Dissolve 6 grams of potassium iodide in 100 ml. of water.

1% Starch. Weigh 1 gram of soluble starch into a 150-ml. beaker. Add 1 or 2 ml. of water to the starch and make a paste. In a separate 150-ml. beaker, heat 100 ml. of water to boiling. With stirring, pour the boiling water into the paste. For accurate work the starch solution should be made fresh daily.

0.001N Potassium Dichromate. Dry several grams of primary-standard grade potassium dichromate on a watch glass in the oven for 1 hour at 110°C. Allow to cool in a desiccator. Weigh, accurately, 4.903 grams of the dry dichromate and dissolve in water. Dilute to 1 liter in a volumetric flask. Accurately transfer 10 ml. of this solution to a 1-liter volumetric flask and dilute to volume with water. The final solution will be 0.001N.

0.002N Sodium Thiosulfate. Dissolve 0.5 gram of sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 1 liter of freshly boiled and cooled water. To standardize this reagent, pipet 10 ml. of the standard 0.001N potassium dichromate solution into a 250-ml. Erlenmeyer flask, add 10 ml. of the 6% potassium iodide solution and 1 ml. of 6N hydrochloric acid. Swirl the mixture once, cover, and place in the dark. After 5 minutes, remove from the dark and dilute with 40 ml. of water. Titrate with the sodium thiosulfate solution until the brown color has changed to a light yellow. Add 2 ml. of 1% starch solution and continue the titration until the color changes from blue to colorless. The normality of the sodium thiosulfate equals:

$$\frac{0.01}{V} \qquad (1)$$

where

V = milliliters of 0.002N sodium thiosulfate used in the titration

The thiosulfate is unstable and must be restandardized every 3 or 4 days.

Rubber Stock. The reproducibility of the method depends in large part upon the properties of the rubber stock used. The material must be sensitive to ozone and uniform in quality. The following formula has proven satisfactory:

Plantation rubber	100 parts
Tire reclaim- Xylose 5484 or 6008	125
SRF black	33
Stearic acid	1.5
Pine tar	8.0
Zinc oxide	4.0
Captax	0.7
Sulfur	5.0

Cure 40 minutes at 45 pounds per square inch steam pressure. Well vulcanized compounds are desirable, since undercures with bloom make reading of the cracking difficult. It is important that the mold used have highly polished surfaces and that the thickness of the stock be uniform and approximately 1/16 inch. The stock, as received in the laboratory, is usually in the form of plaques 6 x 6 x 1/16 inches. Prior to use, the plaques are exposed to the air for several days to reduce tack, increase sensitivity to ozone, and to render the initial cracking more easily visible. This is conveniently done by hanging them on hooks suspended from a cord or wire and allowing sufficient room between plaques for free circulation of air. The stock is cut into uniform strips, 40 x 8 mm., using a sharp razor blade or a die. The latter is much easier to use since a razor blade is dulled after two or three cuts. Care must be taken to avoid tearing or bevelling the edge. Properly cut stock should present a smooth rectangular cut when viewed endwise. The cut pieces can be stored indefinitely in clean jars with tight fitting covers.

CALIBRATION PROCEDURE

The cracking constant (Equation 3, REPORTING AND CALCULATIONS) for each batch of rubber stock must be established empirically. This is accomplished as follows: Start the oxygen flow through the system in Figure 2 and adjust the rate to 1 liter per minute. Turn the ultraviolet source on, and set the Powerstat to 100. After 5 minutes, turn the

Powerstat down to the setting that will generate the desired concentration of ozone (usually 0.50 p.p.m.). After 15 minutes, bubble the stream containing ozone, for a measured period of time, through a series of three midget impingers each containing 10 ml. of 2% potassium iodide. Quantitatively transfer the contents of the impingers to a 250-ml. Erlenmeyer flask containing 5 drops of 0.5N sulfuric acid. Add about 1 ml. of 1% starch and titrate with the standard 0.002N sodium thiosulfate to a colorless end point. Run a blank determination using the same quantities of reagents. The concentration of ozone being generated in parts per million is:

$$\frac{VN \times 1.22 \times 10^4}{v_c} \qquad (2)$$

where

V = milliliters of 0.002N sodium thiosulfate used for titrating the sample (blank must be subtracted)

N = exact normality of the sodium thiosulfate solution

v_c = volume of gas sampled in liters (flowmeter is calibrated to give results at 760 mm. of mercury and 25°C.)

The size of the sampling tube is critical, since, with a given flow rate, the cross section of the tube will influence the velocity of flow over the rubber strip. The District is presently employing sampling tubes which have an inside diameter of 13 mm. for all calibrating and air-monitoring procedures. All connections ahead of the sampling tube should be made of Tygon or consist of ground-glass joints.

Remove the impingers from the train. Select representative rubber strips from the batch to be calibrated and expose them, individually, to the standardized ozone-oxygen gas stream in the following manner: Fold the rubber strip in the middle and secure it with a brass clip or by wrapping with copper wire, 10 mm. from the open end, as illustrated in Figure 3. Examine the strip to see that the rubber surface is smooth and the cut edges are unbroken. This is best seen by viewing the loop through a 4X magnifying glass against a white background using oblique illumination. Insert the strip into the sampling tube with the loop toward the oncoming gas stream. As the exposure time is increased, a point is reached where the cut edges begin to exhibit a serrated appearance when viewed through the magnifying glass. The surface of the strip will appear dulled at the crown of the loop. Small cracks begin to appear on this surface and, in combination with the serrated edges, are taken to be the point of initial cracking. Stretching the strip will accentuate the dull appearance, but will not cause cracking if the process has not already started. Familiarity with this phenomenon will enable the operator to establish, for himself, the condition of the rubber strip which he will thereafter recognize as the point of initial cracking (sometimes termed "unit cracking").

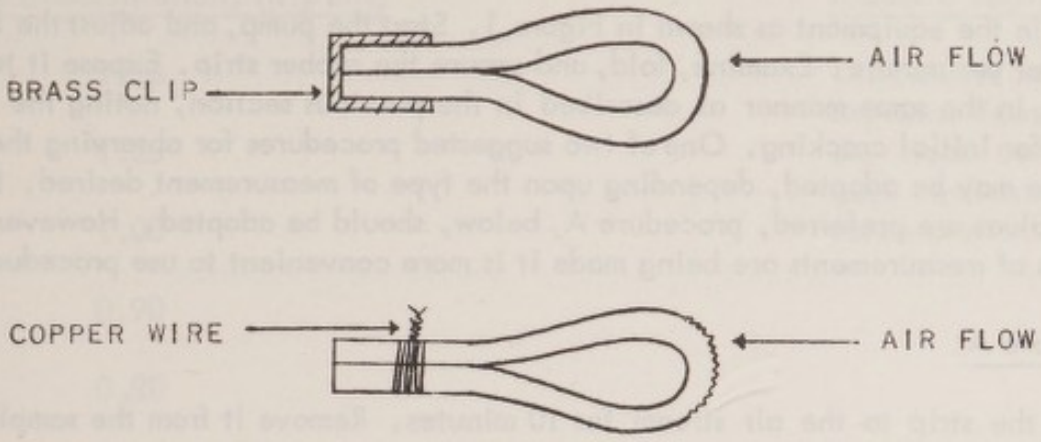

Figure 3. The above drawings show the rubber strips prior to and following exposure to ozone respectively. Note that the feather edge is exaggerated in the lower view. The drawings also illustrate how the strips may be secured using either a clip or a wire.

The time for initial cracking must be carefully measured using several strips representative of the batch of stock received. Use Equation 3 to calculate the batch constant.

AIR SAMPLING PROCEDURE

Assemble the equipment as shown in Figure 1. Start the pump, and adjust the flow rate to 1 liter per minute. Examine, fold, and secure the rubber strip. Expose it to the air stream, in the same manner as described in the previous section, noting the time required for initial cracking. One of two suggested procedures for observing the cracking time may be adopted, depending upon the type of measurement desired. If definitive values are preferred, procedure A, below, should be adopted. However, where a series of measurements are being made it is more convenient to use procedure B.

Procedure A

Expose the strip to the air stream for 10 minutes. Remove it from the sampling tube and examine it for cracking. If not cracked, continue to expose and examine it at intervals of 2 or 3 minutes. If still not cracked in 20 minutes, expose the strip for another 10 minutes, remove and examine it. If cracking cannot be observed in 30 minutes, continued exposure is pointless because the ozone concentration is extremely low.

If the piece is cracked after the initial 10-minute exposure, select a new piece, examine and wrap it. Expose it for 5 minutes, and in 1-minute intervals thereafter, until cracking seems imminent. Then proceed in 1/2-minute intervals until initial cracking is observed. Should it crack in 5 minutes, select another new strip and this time expose it for 2 minutes, followed by 1/2-minute intervals. If cracked in 2 minutes, select a new strip and expose for smaller increments of time until initial cracking is observed. Report the length of time for cracking to become definite on the surface as well as the edges. When the cracking time is short, it is a good idea to repeat the measurement immediately for a check.

Calculate the concentration of the ozone according to Equation 3.

Procedure B

This procedure is based upon exposure of the rubber strips for definite time intervals which indicate directly various increments of ozone concentrations. A table is constructed prior to sampling as follows:

TABLE I

SAMPLE OZONE CALIBRATION CHART

Ozone Concentration, (p.p.m.)	Exposure Time, Minutes
1.50	This column contains the exposure times based on the stock constant for each indicated ozone concentration.
1.25	
1.00	
0.90	
0.80	
0.70	
0.60	
0.50	
0.45	
0.40	
0.35	
0.30	
0.25	
0.20	
0.15	
0.10	
0.05	

Estimate the concentration of ozone that might be present, and refer to the above table for the exposure time corresponding to this value. Expose the rubber strip to the air stream for this predetermined period at 1 liter per minute. If initial cracking is observed at the end of this time, expose a new strip for the interval corresponding to two or four concentration levels above the estimated concentration. If initial cracking is still observed, repeat the process until initial cracking is no longer evident.

If the first strip is not cracked, or if a subsequent strip is not cracked, continue to expose it for the time interval corresponding to the next lower concentration. Continue this process until initial cracking is observed. If five exposures of one strip have been made, discard it, and start over again with a new strip exposing it for the greatest accumulated time interval. The concentration of ozone present is, therefore, that which corresponds to the total exposure time in Table I. No interpolation is made between values.

REPORTING AND CALCULATIONS

Calculate the batch constant according to the following Equation:

$$k = Ct \qquad (3)$$

where

k = batch constant

C = concentration of ozone, parts per million

t = exposure time for initial cracking, minutes

This equation can be rearranged to solve either for C or the ozone concentration in parts per million.

The ozone concentration in grains per standard cubic foot (60°F., 1 atmosphere) can be obtained by multiplying the parts per million by 8.83×10^{-4}.

ADDITIONAL NOTES

For higher concentrations of ozone, the accuracy of the method can be increased by increasing the cracking time. This is accomplished by either altering the composition of the rubber stock to give a larger cracking constant or, in most cases, by simply decreasing the flow rate.

REFERENCE

Bradley, C.E., and Haagen-Smit, A.J., Rubber Chem. and Tech., 24, 750-5(1951).

APCD

FLUORIDES APCD 15-57

Laboratory Methods

POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

FLUORIDES

APCD 15-57

SCOPE

The following procedure is used primarily for the determination of fluorides in vegetation samples. It can also be applied to atmospheric samples and source tests. The lower limits of the method are 0.02 p.p.m. in a 60-cubic-foot air sample, 3 p.p.m. in a 2-liter grab sample, and 1 p.p.m. in a vegetation sample where the total ash weight is 2 grams.

METHOD SUMMARY

Vegetation samples are macerated in a Waring Blendor to which calcium oxide has been added. The calcium fixes any volatile fluorides that may be present. The sample is dried and ashed, and a portion is fused with sodium hydroxide in a nickel crucible. The fused mixture is dissolved in water and silver perchlorate is added to precipitate any halogens present. Fluorides are then separated as hydrofluosilicic acid by means of steam distillation in the presence of perchloric acid. The fluoride ion concentration in the distillate is determined by titration with standard thorium nitrate using Alizarin Red S indicator. Atmospheric and source samples are collected in dilute caustic, then reduced in volume, distilled, and titrated in the same manner as vegetation samples.

SPECIAL APPARATUS

COLLECTION:

For Air Sampling. Two standard Greenburg-Smith impingers connected in series to a stopcock, rotameter, and air pump assembled as shown in Figure 1, or a square polyethylene vessel used as a dust fall jar.

For Source Testing. Two-liter round-bottomed flask, 1-inch length of 8-mm. glass tubing connected to the neck, 3-inch length of heavy-wall gum-rubber tubing, screw clamp, and solid-glass plug.

For Vegetation Sampling. No special apparatus is necessary.

ANALYTICAL:

Waring Blendor and the steam distillation apparatus shown in Figure 2.

REAGENTS

Fluoride-Free Water: Redistill water in an all-Pyrex still. Add 3 pellets of sodium hydroxide and a pinch of potassium permanganate to the distilling flask. Tapered

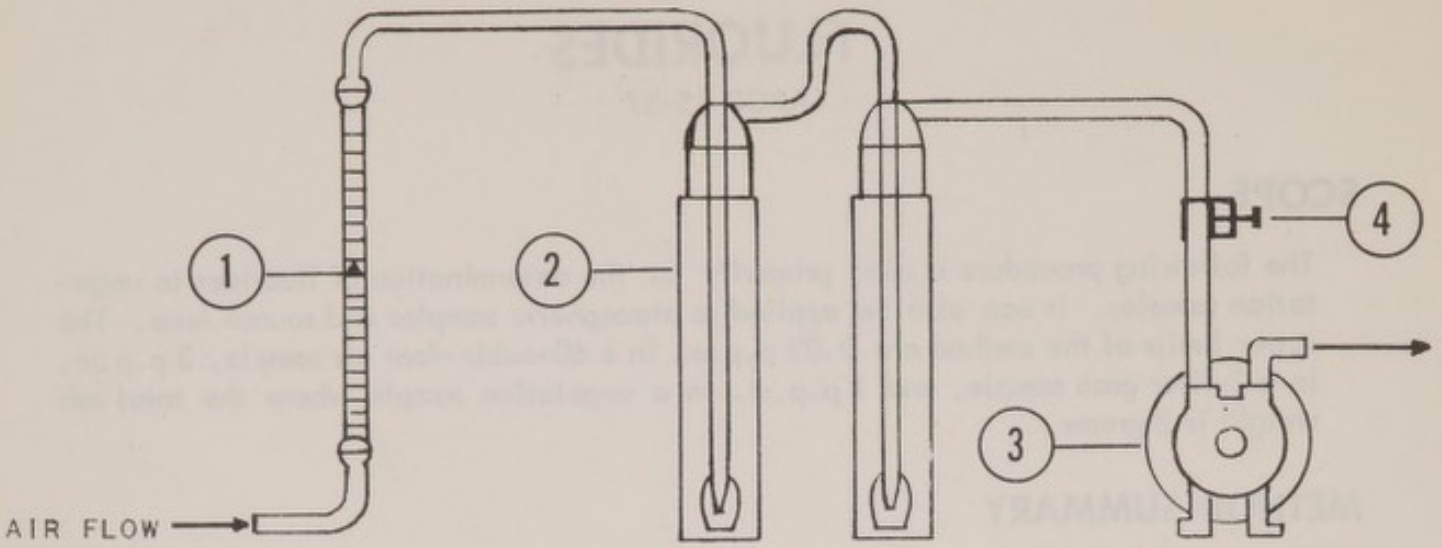

Figure 1. Air sampling apparatus. ①Rotameter. ②Standard Greenburg-Smith impingers. ③Air pump. ④Screw clamp to control gas flow rate.

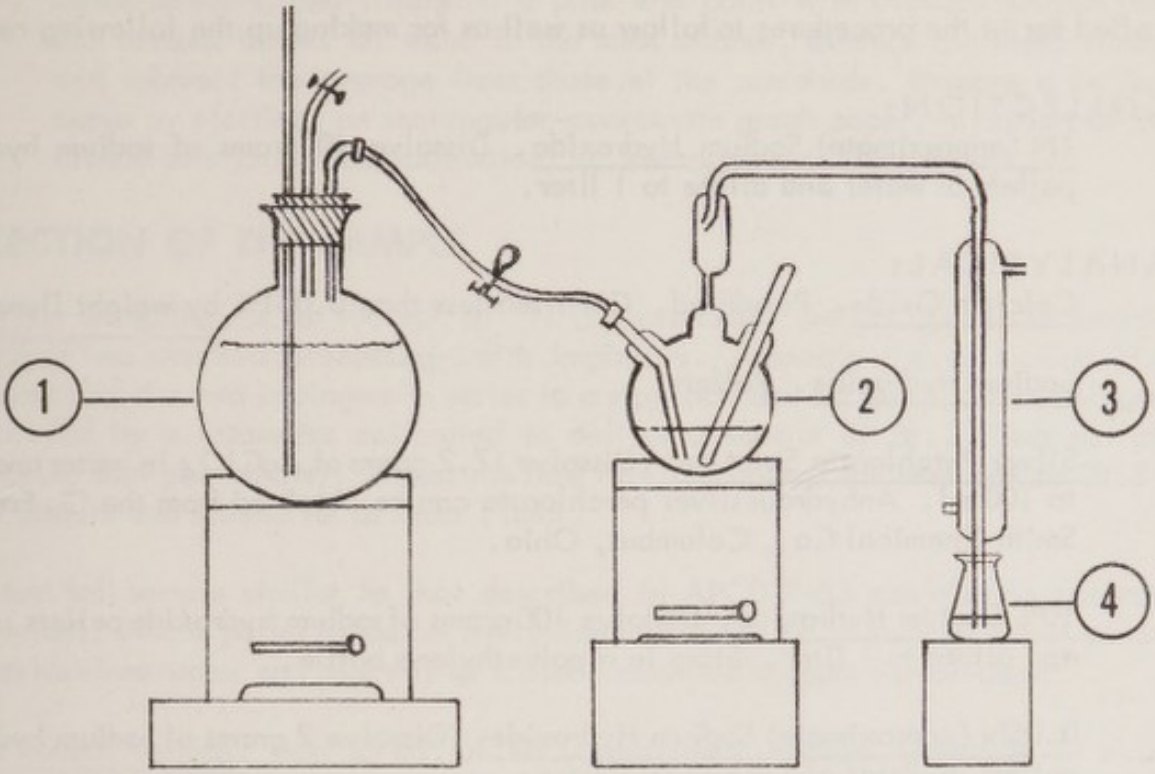

Figure 2. Distillation apparatus for fluorides. ① Steam generator. ② Distilling flask. ③ Condenser. ④ Receiving flask.

glass joints can be lightly lubricated with silicone grease. Discard the first and last quarter of the distillate, and store the remainder in polyethylene bottles since fluorides may be leached from glass containers. This water should be used wherever water is called for in the procedures to follow as well as for making up the following reagents.

COLLECTION:

1N (approximate) Sodium Hydroxide. Dissolve 40 grams of sodium hydroxide pellets in water and dilute to 1 liter.

ANALYTICAL:

Calcium Oxide. Powdered. Certified less than 0.001% by weight fluoride.

Sodium Hydroxide. Pellets.

Silver Perchlorate Solution. Dissolve 17.2 grams of $AgClO_4$ in water and dilute to 100 ml. Anhydrous silver perchlorate can be obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio.

10% Sodium Hydroxide. Dissolve 100 grams of sodium hydroxide pellets in water and dilute to 1 liter. Store in a polyethylene bottle.

0.05N (approximate) Sodium Hydroxide. Dissolve 2 grams of sodium hydroxide pellets in water and dilute to 1 liter.

Concentrated Perchloric Acid.

0.05N (approximate) Perchloric Acid. Dilute 4.3 ml. of concentrated perchloric acid to 1 liter with water.

Alizarin Red S Indicator. Dissolve 0.1 gram of sodium alizarinsulfonate in 1 liter of water.

Standard Sodium Fluoride Solution. Dissolve 0.2210 gram of sodium fluoride in water and make up to 1 liter. From this stock solution prepare the standard by diluting 5 ml. to 100 ml. One milliliter of the latter solution is equivalent to 5 µg. of fluoride ion.

Chloroacetate Buffer Solution. Dissolve 9.45 grams of monochloroacetic acid and 2.0 grams of sodium hydroxide pellets in 100 ml. of water.

0.005N Thorium Nitrate. Dissolve 0.6902 gram of $Th(NO_3)_4 \cdot 4H_2O$ in water and make up to 1 liter. Prepare a calibration curve for each new batch of 0.005N thorium nitrate solution. Dilute 2, 4, 6, 8, and 10 ml. of the standard to 100 ml. each in separate Erlenmeyer flasks. To each flask add 2 ml. of Alizarin Red S and then dropwise add 0.05N sodium hydroxide to a pink end point. Using a pH meter adjust the pH to $3 \pm .02$ with 0.05N perchloric acid.

Transfer the solutions to separate Nessler tubes, add 1 ml. of the chloroacetate buffer to each, and titrate to a pink end point with 0.005N thorium nitrate. Run several blanks on water in the same manner, average the blank titrations, and subtract the average from those of the standards. Prepare a calibration curve by plotting, on rectangular-coordinate graph paper, milliliters of thorium nitrate solution (blank subtracted) vs. micrograms of fluoride ion.

COLLECTION OF THE SAMPLE

For Air Sampling. Add 100 ml. of 1N (approximate) sodium hydroxide solution to each of two standard Greenburg-Smith impingers. Assemble the collection train by connecting the two impingers in series to a stopcock and air pump. The impingers are preceded by a rotameter calibrated to deliver a sample at 28.3 liters per minute (1 cubic foot per minute). Adjust the flow rate by means of the stopcock to 28.3 liters per minute and sample for at least 1 hour.

A dust fall sample similar to that described in APCD 7-53 can also be analyzed for fluorides. Add a pellet of sodium hydroxide to a square polyethylene vessel containing fluoride-free water and place it on a clean elevated support out-of-doors.

For Source Testing. Add 25 ml. of 1N (approximate) sodium hydroxide to a 2-liter round-bottomed flask. Connect the flask to a vacuum source and evacuate to boiling (vapor pressure of the solution). Pinch off the rubber tubing with the screw clamp and disconnect from the source of vacuum. Insert the solid-glass plug into the open end of the rubber tubing. To collect the sample, remove the glass plug and open the screw clamp for about 10 seconds at the source. Retighten the screw clamp and replace the glass plug.

For Vegetation Samples. Select a representative sample of the suspected vegetation using leaves of all ages unless otherwise desired.

SAMPLE PREPARATION

For Air Sampling. Pour the solution from the two impingers into a stainless steel beaker. Rinse the impingers twice with a small amount of water and combine the washings with the solution in the beaker. Evaporate to 25 ml. and then neutralize with concentrated perchloric acid.

For Source Testing. Shake the 2-liter round-bottomed flask for 15 minutes with frequent rotation to provide a thorough scrubbing action. Determine the pressure in the flask by connecting it to an open-end mercury manometer and measuring the difference, in millimeters, between the mercury levels. Note the temperature and atmospheric pressure. Pour the contents into a stainless steel beaker. Rinse the flask with a small amount of water and combine the washings with the solution in the beaker. Neutralize with concentrated perchloric acid.

For Vegetation Samples. Leaves from the suspected vegetation should be processed soon after collection to prevent change in the moisture content. Rinse dust and insecticides off the leaves using detergent and water, and dry with a blotter. Since the fluorine is organically bound, the sample must be decomposed prior to distillation. Accurately weigh 1 gram of calcium oxide into a Waring Blendor and add sufficient water to cover the knives. Note that all water used throughout this procedure is fluoride-free. Cut the leaves into small pieces and weigh 25 grams into the mixer. Thoroughly macerate the leaves and transfer the mixture to a 250-ml. nickel crucible. Dry to constant weight at 70°C. In order to obtain the loss on drying, 1.32 grams must be subtracted from the total weight of the dried leaves since the calcium oxide is converted to calcium hydroxide. Ash the dried material in a muffle furnace at 550 to 600°C. and weigh. The loss on ignition may be reported if desired. The calcium hydroxide remains undecomposed and 1.32 grams will have to be subtracted from the ash weight for this calculation. Accurately weigh a 2-gram portion of the ash and fuse with 5 grams of sodium hydroxide in a nickel crucible. Dissolve the fused mixture in water.

ANALYTICAL PROCEDURE

Set up the distillation apparatus as shown in Figure 2. The spray trap and glass tubing to the condenser should be wrapped with asbestos. Ground-glass joints should be used instead of rubber where perchloric acid is involved. These can be lubricated lightly with a silicone grease. The distillate receiver should have a capacity of 600 ml., and the distilling flask 200 ml.

Transfer the solution to be analyzed to the 200-ml. distilling flask. Add several glass chips and 10 drops of silver perchlorate. Slowly add 15 ml. of concentrated perchloric acid. Avoid frothing and overheating. The analyst should use a shield and goggles since perchloric acid is dangerous (explosive). Place 50 ml. of water and sufficient 10% sodium hydroxide to maintain alkalinity in the receiver. It is usually necessary to distill a separate sample to determine how much sodium hydroxide will be needed. Dip the end of the condenser below the surface of the liquid in the receiver. Heat the steam generator to boiling, slowly raise the temperature in the distilling flask to 120 to 125°C., and admit the steam. Keep the liquid in the flask at 135 ± 4°C. during distillation. Regulate the steam flow to provide about 500 ml. of distillate in 1 1/2 hours.

Remove a suitable aliquot of the distillate so that the amount of thorium nitrate required for titration does not exceed 1.5 ml. Dilute the aliquot to 100 ml. and adjust the pH to 3 ± .02 with 0.05N perchloric acid and 0.05N sodium hydroxide. Transfer to a Nessler tube for titration. View the color over a mirror using close fluorescent lighting. Add 2 ml. of the Alizarin Red S indicator and 1 ml. of the chloroacetate buffer. Titrate the solution with 0.005N thorium nitrate. Cap the Nessler tube and shake to mix. View the solution by reflected light after each addition. The color should change from yellow-green through salmon to buff-pink, which is the end point. A slight excess of thorium ion produces a light pink; a large excess, a rose color.

Prepare several fresh blanks for end point color comparison when the samples are being titrated. The colored lake is not stable, so blanks must be made up fresh each hour. The 1.5-ml. sample titration was specified so that final end points of blank and sample would be viewed through comparable lengths of solutions in the Nessler tubes.

To prepare a blank place 100 ml. of water and 2 ml. of Alizarin Red S indicator into a 150-ml. beaker. Add 1 drop of 0.05N sodium hydroxide and stir. A pink or red color should develop. If no color develops, add an additional drop of sodium hydroxide. Adjust the pH to 3 ± .02 with 0.05N perchloric acid and add 1 ml. of chloroacetate buffer. Transfer the mixture to a 100-ml. Nessler tube and titrate with 0.005N thorium nitrate to the buff-pink end point. The blank titrations should amount to about 0.1 ml. Subtract this from the sample titration and read the concentration of fluoride ion from the previously prepared calibration curve. Run several blanks to assure accurate results.

REPORTING AND CALCULATIONS

For Air Sampling. Calculate the parts per million (by volume) of fluorides as follows:

$$\frac{1.29\, W_t A}{v_m} \qquad (1)$$

where

W_t = micrograms of fluoride ion determined by titration (from calibration graph)

v_m = sample volume, liters at ambient conditions

A = aliquot factor = $\frac{\text{(milliliters of total distillate)}}{\text{(milliliters of distillate taken for titration)}}$

For Source Testing. Calculate the parts per million (by volume) of fluorides as follows:

$$\frac{3.28\, W_t T A}{v_m (P_r + \Delta P)} \qquad (2)$$

where

W_t = micrograms of fluoride ion determined by titration (from calibration graph)

V_m = measured volume of sample flask, liters*

A = aliquot factor = $\frac{\text{(milliliters of total distillate)}}{\text{(milliliters of distillate taken for titration)}}$

ΔP = sample flask differential pressure, millimeters of mercury (with respect to atmospheric pressure)

P_r = atmospheric pressure, millimeters of mercury (at the time of the ΔP measurement)

T = room temperature, degrees Kelvin (at the time of the ΔP measurement)

For Vegetation Sampling. Calculate the percent weight moisture in the leaves as follows:

$$\frac{(W_d - 1.32)100}{W_s} \qquad (3)$$

Calculate the parts per million of fluoride by weight (dried basis) as follows:

$$\frac{W_t A}{(W_d - 1.32)} \qquad (4)$$

where

W_s = original weight of leaves, grams (usually 25 grams)

W_d = grams of residue after drying at 70°C.

W_t = micrograms of fluoride ion determined by titration (from calibration graph)

A = aliquot factor = $\left[\frac{\text{milliliters of total distillate}}{\text{milliliters aliquot of distillate taken for titration}}\right]$ $\left[\frac{\text{grams of ashed residue from muffle furnace}}{\text{grams of ashed sample used for the distillation (usually 2 grams)}}\right]$

*Where moisture was present in the original sample and it is desired to put the sample volume on a stack-conditions basis, a correction must be applied to Formula 2. The moisture is usually determined in conjunction with some other test such as grain loading.

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ORGANIC ACIDS, TOTAL APCD 16-57

Laboratory Methods

POLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

ORGANIC ACIDS, TOTAL

APCD 16-57

SCOPE

The method to be described here is applicable to source sampling where relatively large amounts of acids are present. In its present form, it is impractical for atmospheric monitoring since 8 to 14 hours of sampling would be required. The lower limit of the method is about 0.2 p.p.m. in a 60-cubic-foot sample.

METHOD SUMMARY

The procedure involves the collection of the sample by bubbling through dilute caustic followed by acidification and ether extraction of the free organic acids. A liquid-liquid extractor is used to provide multiple contact of ether and aqueous media. The organic acids in ether are subsequently titrated with a standard base. Although the test is non-specific, it is believed to be correct in magnitude.

SPECIAL APPARATUS

COLLECTION:

Three standard Greenburg-Smith impingers held in a combination ice bath and rack, connected in series to a mercury manometer, dry gas meter (Zephyr No. 1A, Sprague Meter Co., Los Angeles, Calif., or equivalent), and air pump, with a screw clamp to control the gas flow rate. The apparatus is assembled as shown in Figure 1.

ANALYTICAL:

Liquid-liquid extractor (Corning Glass Works, No. 92232, Corning, N. Y.) as shown in Figure 2.

REAGENTS

COLLECTION:

5% (approximate) Sodium Hydroxide. Dissolve 50 grams of sodium hydroxide flakes or pellets in water and make up to 1 liter.

ANALYTICAL:

5% Sodium Hydroxide. Same solution as used for collection.

Ether. Ordinary reagent-grade ethyl ether is used with no special pretreatment.

Concentrated Sulfuric Acid.

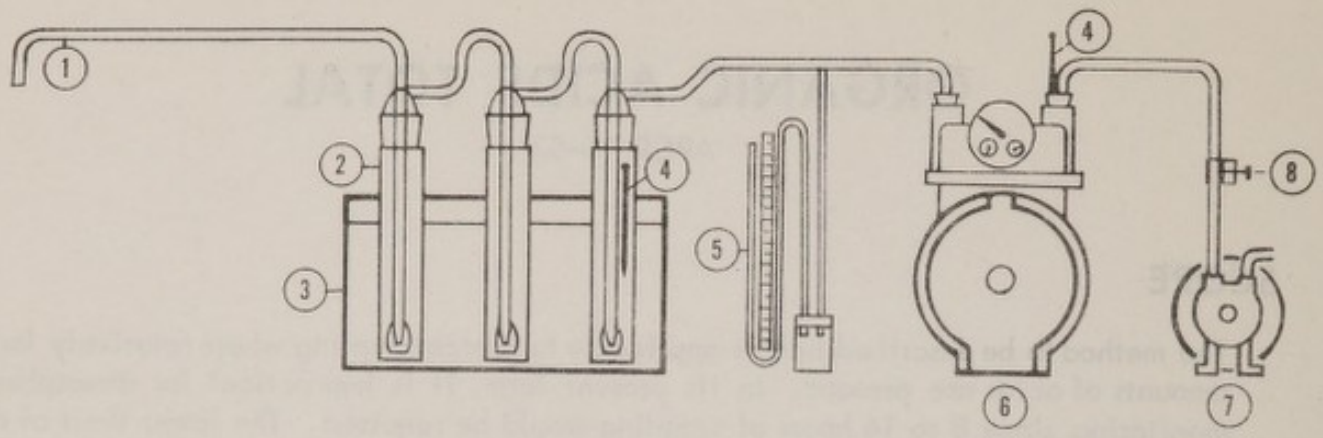

Figure 1. Sampling apparatus. ① Sample probe. ② Standard Greenburg-Smith impingers. ③ Ice-bath container. ④ Thermometer. ⑤ Mercury manometer. ⑥ Dry gas meter. ⑦ Air pump. ⑧ Screw clamp to control gas flow rate.

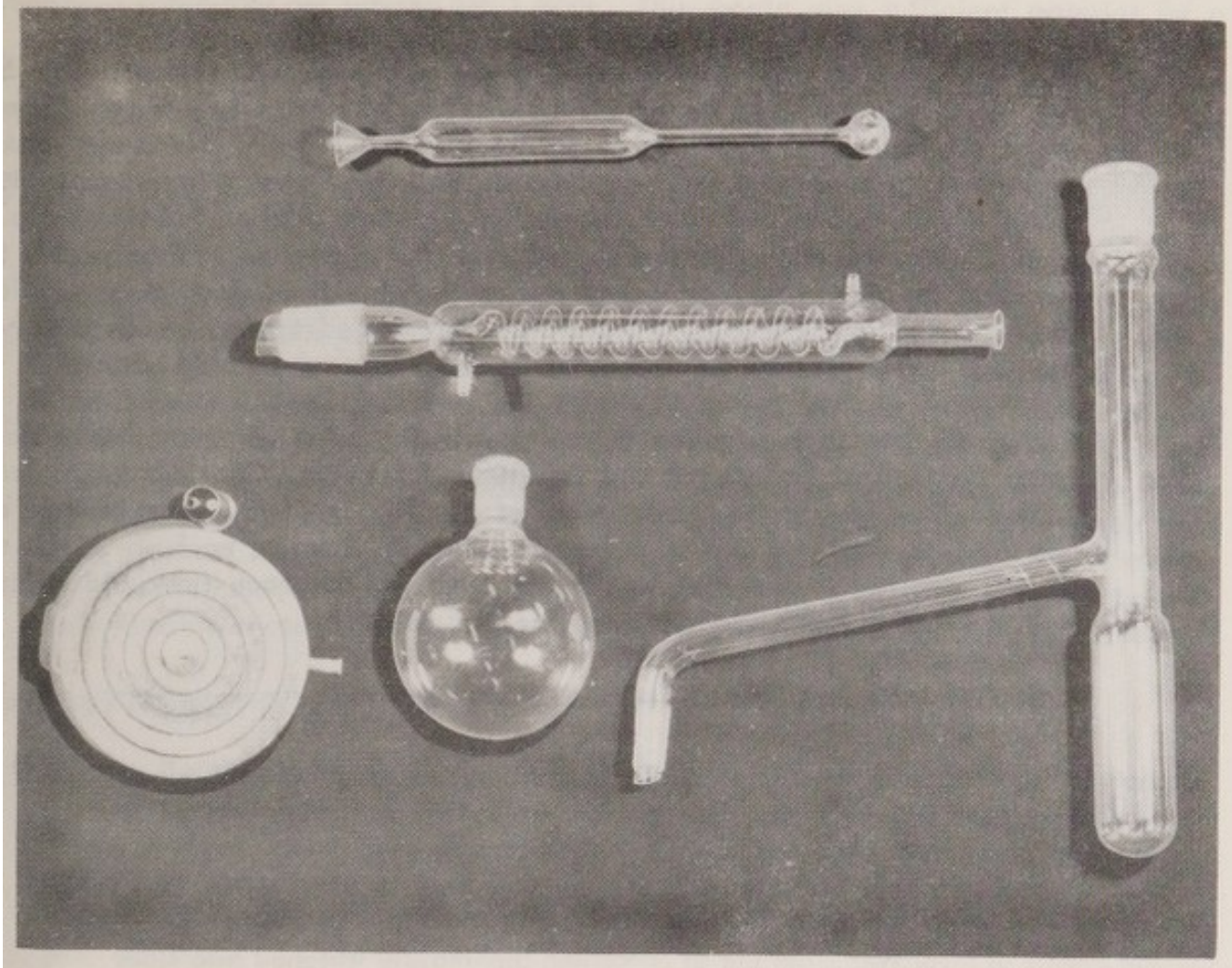

Figure 2. Equipment used for extraction of organic acids shown disassembled to afford a better view of all of the parts.

0.1N Sodium Hydroxide. Dissolve 50 grams of sodium hydroxide pellets in 50 ml. of water in a polyethylene bottle. Allow to settle overnight or centrifuge. Weigh 8 grams of the clear supernatant liquid into a 100-ml. Erlenmeyer flask. Transfer the solution to a 1-liter volumetric flask and make up to the mark with freshly boiled and cooled water. Thoroughly mix the solution and transfer to a clean, dry polyethylene bottle for storage. Perform these operations quickly to avoid contamination by carbon dioxide from the air. If considerable quantities of standard sodium hydroxide solutions are to be handled regularly, a large polyethylene bottle with siphon arrangement and Ascarite tube should be used.

Standardize the sodium hydroxide as follows: Dry some potassium biphthalate (primary-standard grade) in an oven at 110°C. for 1 hour. Cool in a desiccator. Accurately weigh, to the nearest tenth of a milligram, two 1-gram portions of the salt into separate 250-ml. Erlenmeyer flasks. Dissolve each in 25 ml. of water. Add two drops of phenolphthalein indicator to each flask and titrate with the sodium hydroxide to a faint pink end point.

Calculate the normality as follows:

$$\frac{4.90\ W}{V} \qquad (1)$$

where

W = grams of potassium biphthalate weighed into flask

V = milliliters of sodium hydroxide used

Phenolphthalein Indicator. Dissolve 0.05 gram of the solid in 50 ml. of 95% ethyl alcohol and add 50 ml. of water.

pH Indicating Paper. Hydrion, pH 1-6, test paper is satisfactory.

COLLECTION OF THE SAMPLE

Set up the apparatus so that the sample gas passes through the three impingers (connected in series), then through the dry gas meter, and out the air pump. Place the mercury manometer between the last impinger and the gas meter, and the screw clamp between the gas meter and the air pump. Place a thermometer in the last impinger and another in the gas meter (Figure 1). The former is used only in conjunction with other tests when the total moisture in the stack gases is to be determined. It is not pertinent to this procedure, and is left in place merely for convenience.

Add exactly 100 ml. of 5% sodium hydroxide solution to the first two impingers and operate the third impinger dry to protect the meter and to catch any carryover. Place

the impingers in an ice bath. Draw the sample through the train at 28.3 liters per minute (1 cubic foot per minute) for 1 hour. This should give sufficient material for a 5-ml. titration with 0.1N sodium hydroxide where the acids amount to at least 10 p.p.m. Record meter temperatures and pressures at 10-minute intervals during sampling and obtain an average.

SAMPLE PREPARATION

Pour the solution from the three impingers into a clean, dry 250-ml. graduate (or larger, depending on the moisture content of the gas) and note the volume. This is necessary to calculate the correct volume of the sample. Rinse the impingers twice with a small amount of water and add the washings to the solution in the graduate. When the acids amount to more than 50 p.p.m., an appropriate aliquot of the caustic solution is taken. Transfer the solution to be analyzed, or an aliquot, to a 500-ml. Erlenmeyer flask. Place an appropriate quantity of the original sodium hydroxide absorbing solution (depending on the amount of dilution during sampling) in another Erlenmeyer flask for a blank. Chill the sample and blank in an ice bath and cover each with a layer of ether. Ether from the same batch should be used for both. Add concentrated sulfuric acid slowly to each with stirring to a pH of 2 to 3 (test externally with pH paper).

ANALYTICAL PROCEDURE

Transfer the sample and blank mixtures to separate 500-ml. liquid-liquid extractors. A long-stemmed funnel is useful for making the transfers. The final aqueous levels should be 3 or 4 inches below the side arms. Carefully insert the inner collector tubes, and attach the condensers and 500-ml. round-bottomed flasks. Slowly add ether through the condensers allowing it to rise in the extractors. Continue adding ether until about 200 ml. has overflowed into the flasks. Heat the flasks to steady boiling on water baths or with Glass-Col heating mantles, and allow the extractions to proceed for 8 hours.

After the flasks have cooled, tilt the extractors to allow as much as possible of the ether to decant over into the flasks without removing any aqueous material. Transfer the ether extracts to separatory funnels and remove any traces of aqueous material that may be present. Add about 40 ml. of water and 3 drops of phenolphthalein indicator to each of the ether solutions in the separatory funnels. Titrate the mixtures in the funnels with 0.1N sodium hydroxide to the phenolphthalein end point. As the end point is approached stopper the separatory funnels and shake with each small titration increment until a pink color persists.

REPORTING AND CALCULATIONS

The vapor equivalent of the condensate, v_w, in cubic feet at meter conditions is:

$$\frac{0.00267\ VT}{P} \qquad (2)$$

where

V = milliliters of water condensed in impingers (difference between initial and final volumes)

P = average meter pressure, inches of mercury absolute

T = average meter temperature, degrees Rankine

The parts per million of total organic acids in the gas sample (wet basis) is calculated as follows:

$$\frac{48.2\ NAT\ (V_a - V_b)}{P\ (v_m + v_w)} \qquad (3)$$

where

V_a = milliliters of 0.1N sodium hydroxide used for the sample titration

V_b = milliliters of 0.1N sodium hydroxide used for the blank titration

N = exact normality of the 0.1N sodium hydroxide

A = aliquot factor = $\dfrac{\left[\text{milliliters of combined impinger solutions and washings}\right]}{\left[\text{milliliters taken for analysis}\right]}$

v_m = measured volume of gas sample, cubic feet at meter conditions

v_w = vapor equivalent of condensate, cubic feet at meter conditions

T = average temperature of gas meter, degrees Rankine

P = average meter pressure, inches of mercury (absolute)

Note that the acids are presumed to be monocarboxylic. To obtain grains per standard cubic foot (as acetic acid), multiply the parts per million calculated in Formula 3 by 1.1×10^{-3}.

APCD

APPENDIX

Laboratory Methods

OLLUTION CONTROL DISTRICT/COUNTY OF LOS ANGELES
434 South San Pedro Street, Los Angeles 13, California

ISSUED 1958

APPENDIX

USEFUL EQUIVALENTS

1 cubic meter	= 35.32 cubic feet
1 $cm.^3$	= 0.0610 cubic inch
1 cubic foot	= 28.32 liters
1 cubic foot	= 7.48 gallons (U. S.)
1 liter	= 0.0353 cubic foot
1 liter	= 1000 ml.
1 liter	= 1.057 quarts (U. S.)
1 meter	= 3.28 feet
1 meter	= 39.37 inches
1 inch	= 25.40 mm.
1 inch	= 25,400 microns
1 kg.	= 2.20 pounds
1 pound	= 453.6 grams
1 ounce	= 28.35 grams
1 cubic foot of water @ 62°F.	= 63.32 pounds
1 gallon of water @ 62°F.	= 8.34 pounds
1 cubic foot of air at STP	= 0.075 pound
1 pound per square inch	= 2.31 feet of water @ 39.1°F.

1 inch of mercury @32°F.	=	13.59 inches of water @4°C.
1 inch of mercury @32°F.	=	0.49 pound per square inch
1 mm. of mercury @ 0°C.	=	1.36 grams/cm^2
1 atmosphere	=	14.70 pounds per square inch
1 atmosphere	=	29.92 inches of mercury @ 32°F.
1 atmosphere	=	760 mm. of mercury @ 0°C.
1 B.T.U.	=	0.25 kg. cal.
1 B.T.U.	=	3.92×10^{-4} horsepower - hour
1 horsepower	=	550 foot pounds per second
1 horsepower	=	0.75 kilowatt (g = 980)
°F.	=	(1.8)(°C.) + 32
°C.	=	$\frac{°F. - 32}{1.8}$
π	=	3.1416
Circumference of circle	=	πd
Area of circle	=	$\frac{\pi d^2}{4}$
Surface area of sphere	=	πd^2
Volume of sphere	=	$\frac{\pi d^3}{6}$

INTERNATIONAL ATOMIC WEIGHTS
1955

	Symbol	Atomic Number	Atomic Weight[a]
Actinium	Ac	89	227
Aluminum	Al	13	26.98
Americium	Am	95	[243]
Antimony	Sb	51	121.76
Argon	A	18	39.944
Arsenic	As	33	74.91
Astatine	At	85	[210]
Barium	Ba	56	137.36
Berkelium	Bk	97	[249]
Beryllium	Be	4	9.013
Bismuth	Bi	83	209.00
Boron	B	5	10.82
Bromine	Br	35	79.916
Cadmium	Cd	48	112.41
Calcium	Ca	20	40.08
Californium	Cf	98	[249]
Carbon	C	6	12.011
Cerium	Ce	58	140.13
Cesium	Cs	55	132.91
Chlorine	Cl	17	35.457
Chromium	Cr	24	52.01
Cobalt	Co	27	58.94
Columbium (see Niobium)			
Copper	Cu	29	63.54
Curium	Cm	96	[245]
Dysprosium	Dy	66	162.51
Erbium	Er	68	167.2
Europium	Eu	63	152.0
Fluorine	F	9	19.00
Francium	Fr	87	[223]
Gadolinium	Gd	64	157.26
Gallium	Ga	31	69.72
Germanium	Ge	32	72.60
Gold	Au	79	197.0
Hafnium	Hf	72	178.50
Helium	He	2	4.003
Holmium	Ho	67	164.94
Hydrogen	H	1	1.0080
Indium	In	49	114.82
Iodine	I	53	126.91
Iridium	Ir	77	192.2
Iron	Fe	26	55.85
Krypton	Kr	36	83.80
Lanthanum	La	57	138.92
Lead	Pb	82	207.21
Lithium	Li	3	6.940
Lutetium	Lu	71	174.99
Magnesium	Mg	12	24.32
Manganese	Mn	25	54.94
Mandelevium	Mv	101	256
Mercury	Hg	80	200.61
Molybdenum	Mo	42	95.95
Neodymium	Nd	60	144.27
Neptunium	Np	93	[237]
Neon	Ne	10	20.183
Nickel	Ni	28	58.71
Niobium (Columbium)	Nb	41	92.91
Nitrogen	N	7	14.008
Osmium	Os	76	190.2
Oxygen	O	8	16
Palladium	Pd	46	106.4
Phosphorus	P	15	30.975
Platinum	Pt	78	195.09
Plutonium	Pu	94	[242]
Polonium	Po	84	210
Potassium	K	19	39.100
Praseodymium	Pr	59	140.92
Promethium	Pm	61	[145]
Protactinium	Pa	91	231
Radium	Ra	88	226.05
Radon	Rn	86	222
Rhenium	Re	75	186.22
Rhodium	Rh	45	102.91
Rubidium	Rb	37	85.48
Ruthenium	Ru	44	101.1
Samarium	Sm	62	150.43
Scandium	Sc	21	44.96
Selenium	Se	34	78.96
Silicon	Si	14	28.09
Silver	Ag	47	107.880
Sodium	Na	11	22.991
Strontium	Sr	38	87.63
Sulfur	S	16	32.066[b]
Tantalum	Ta	73	180.95
Technetium	Tc	43	[99]
Tellurium	Te	52	127.61
Terbium	Tb	65	158.93
Thallium	Tl	81	204.39
Thorium	Th	90	232.05
Thulium	Tm	69	168.94
Tin	Sn	50	118.70
Titanium	Ti	22	47.90
Tungsten	W	74	183.86
Uranium	U	92	238.07
Vanadium	V	23	50.95
Xenon	Xe	54	131.3
Ytterbium	Yb	70	173.04
Yttrium	Y	39	88.92
Zinc	Zn	30	65.38
Zirconium	Zr	40	91.22

a A value given in brackets denotes the mass number of the isotope of longest known half-life.
b Because of natural variations in relative abundance of the sulfur isotopes, its atomic weight has a range of ±0.003.

REPRINTED FROM J.A.C.S. 27, 3235-40 (1956)

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18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2 5 7	9 12 14	16 19 21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2 4 7	9 11 13	16 18 20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2 4 6	8 11 13	15 17 19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2 4 6	8 10 12	14 16 18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2 4 6	8 10 12	14 16 17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2 4 6	7 9 11	13 15 17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2 4 5	7 9 11	12 14 16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2 4 5	7 9 10	12 14 16
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2 3 5	7 8 10	11 13 15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2 3 5	6 8 9	11 12 14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2 3 5	6 8 9	11 12 14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1 3 4	6 7 9	10 12 13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1 3 4	6 7 9	10 11 13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1 3 4	5 7 8	10 11 12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1 3 4	5 7 8	9 11 12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1 3 4	5 7 8	9 11 12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1 2 4	5 6 8	9 10 11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1 2 4	5 6 7	9 10 11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1 2 4	5 6 7	8 10 11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1 2 4	5 6 7	8 9 11
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1 2 3	5 6 7	8 9 10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1 2 3	4 5 7	8 9 10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1 2 3	4 5 6	8 9 10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1 2 3	4 5 6	7 8 9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1 2 3	4 5 6	7 8 9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1 2 3	4 5 6	7 8 9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1 2 3	4 5 6	7 8 9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1 2 3	4 5 6	7 8 9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1 2 3	4 5 6	7 7 8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1 2 3	4 5 6	7 7 8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1 2 3	4 5 6	7 7 8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1 2 3	4 4 5	6 7 8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1 2 3	3 4 5	6 7 8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1 2 3	3 4 5	6 7 8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1 2 3	3 4 5	6 7 7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1 2 2	3 4 5	6 6 7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1 2 2	3 4 5	6 6 7
N	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9

The proportional parts are stated in full for every tenth at the right-hand side. The logarithm of any number of four significant figures can be read directly by add-

N	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1 2 2	3 4 5	5 6 7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1 2 2	3 4 5	5 6 7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1 1 2	3 4 5	5 6 7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1 1 2	3 4 4	5 6 7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1 1 2	3 4 4	5 6 7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1 1 2	3 4 4	5 6 6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1 1 2	3 3 4	5 6 6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1 1 2	3 3 4	5 5 6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1 1 2	3 3 4	5 5 6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1 1 2	3 3 4	5 5 6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1 1 2	3 3 4	5 5 6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1 1 2	3 3 4	5 5 6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1 1 2	3 3 4	5 5 6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1 1 2	3 3 4	4 5 6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1 1 2	3 3 4	4 5 6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1 1 2	3 3 4	4 5 6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1 1 2	3 3 4	4 5 6
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1 1 2	3 3 4	4 5 6
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1 1 2	2 3 4	4 5 5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1 1 2	2 3 4	4 5 5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1 1 2	2 3 3	4 5 5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1 1 2	2 3 3	4 4 5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1 1 2	2 3 3	4 4 5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1 1 2	2 3 3	4 4 5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1 1 2	2 3 3	4 4 5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1 1 2	2 3 3	4 4 5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1 1 2	2 3 3	4 4 5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1 1 2	2 3 3	4 4 5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1 1 2	2 3 3	4 4 5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1 1 2	2 3 3	4 4 5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1 1 2	2 3 3	4 4 5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1 1 2	2 3 3	4 4 5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	1 1 2	2 3 3	4 4 5
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0 1 1	2 2 3	3 4 4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0 1 1	2 2 3	3 4 4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0 1 1	2 2 3	3 4 4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0 1 1	2 2 3	3 4 4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0 1 1	2 2 3	3 4 4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0 1 1	2 2 3	3 4 4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0 1 1	2 2 3	3 4 4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0 1 1	2 2 3	3 4 4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0 1 1	2 2 3	3 4 4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0 1 1	2 2 3	3 4 4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0 1 1	2 2 3	3 3 4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0 1 1	2 2 3	3 3 4
N	0	1	2	3	4	5	6	7	8	9	1 2 3	4 5 6	7 8 9

ing the proportional part corresponding to the fourth figure to the tabular number corresponding to the first three figures. There may be an error of 1 in the last place.

TEMPERATURE CONVERSION CHART

Centigrade		*Fahrenheit*	*Centigrade*		*Fahrenheit*
-10.0	14	57.2	16.1	61	141.8
-9.4	15	59.0	16.7	62	143.6
-8.9	16	60.8	17.2	63	145.4
-8.3	17	62.6	17.8	64	147.2
-7.8	18	64.4	18.3	65	149.0
-7.2	19	66.2	18.9	66	150.8
-6.7	20	68.0	19.4	67	152.6
-6.1	21	69.8	20.0	68	154.4
-5.6	22	71.6	20.6	69	156.2
-5.0	23	73.4	21.1	70	158.0
-4.4	24	75.2	21.7	71	159.8
-3.9	25	77.0	22.2	72	161.6
-3.3	26	78.8	22.8	73	163.4
-2.8	27	80.6	23.3	74	165.2
-2.2	28	82.4	23.9	75	167.0
-1.7	29	84.2	24.4	76	168.8
-1.1	30	86.0	25.0	77	170.6
-0.6	31	87.8	25.6	78	172.4
0.0	32	89.6	26.1	79	174.2
0.6	33	91.4	26.7	80	176.0
1.1	34	93.2	27.2	81	177.8
1.7	35	95.0	27.8	82	179.6
2.2	36	96.8	28.3	83	181.4
			28.9	84	183.2
2.8	37	98.6			
3.3	38	100.4	29.4	85	185.0
3.9	39	102.2	30.0	86	186.8
4.4	40	104.0	30.6	87	188.6
5.0	41	105.8	31.1	88	190.4
5.6	42	107.6	31.7	89	192.2
6.1	43	109.4	32.2	90	194.0
6.7	44	111.2	32.8	91	195.8
7.2	45	113.0			
7.8	46	114.8	33.3	92	197.6
8.3	47	116.6	33.9	93	199.4
8.9	48	118.4	34.4	94	201.2
9.4	49	120.2	35.0	95	203.0
10.0	50	122.0	35.6	96	204.8
10.6	51	123.8	36.1	97	206.6
11.1	52	125.6	36.7	98	208.4
			37.2	99	210.2
11.7	53	127.4			
12.2	54	129.2	37.8	100	212.0
12.8	55	131.0	43	110	230
13.3	56	132.8	49	120	248
13.9	57	134.6	54	130	266
14.4	58	136.4	60	140	284
15.0	59	138.2	66	150	302
15.6	60	140.0	71	160	320
			77	170	338

$^{o}F. = (1.8)\ (^{o}C.) + 32$

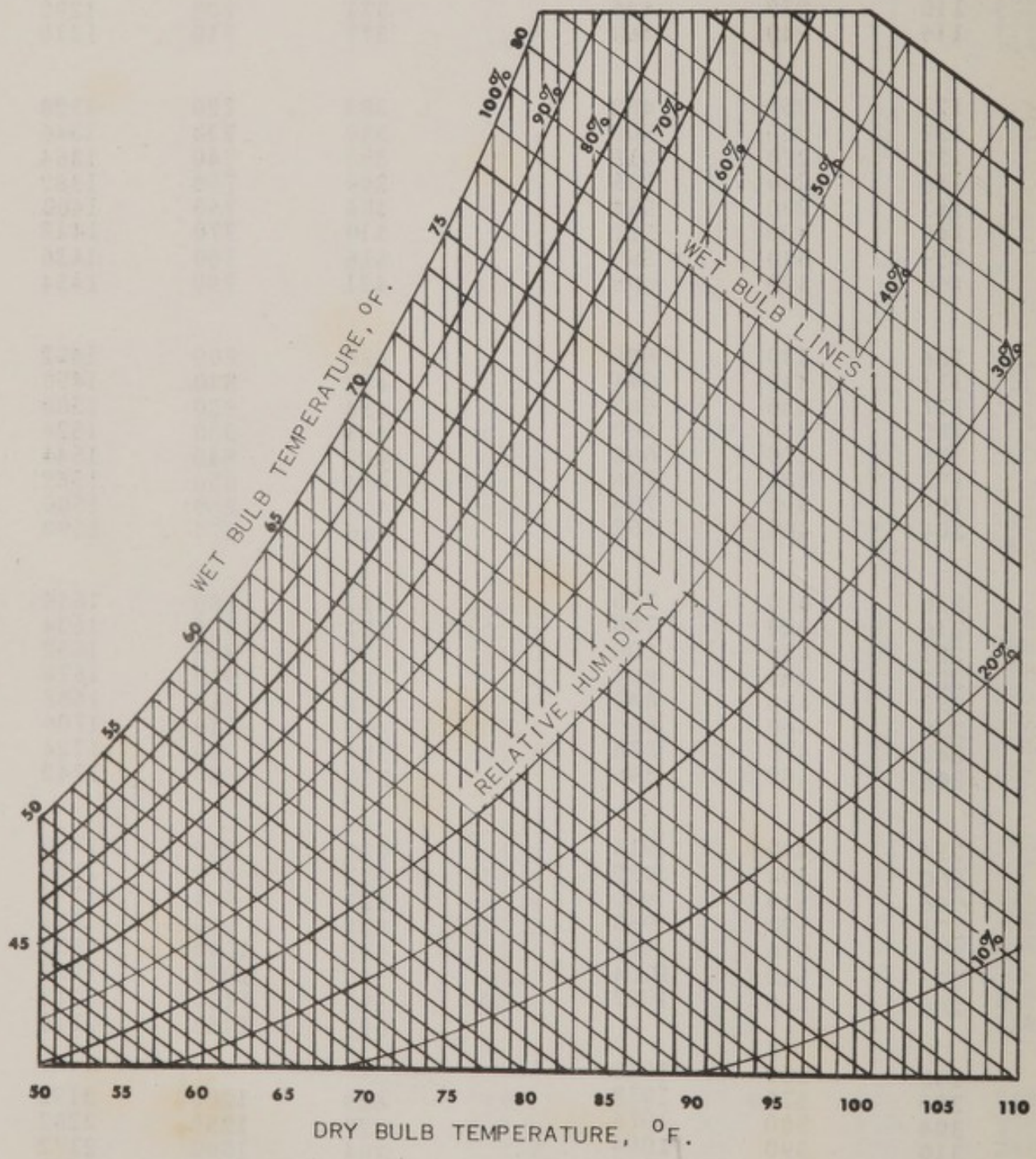
$^{o}C. = \frac{^{o}F. - 32}{1.8}$

1957

TEMPERATURE CONVERSION CHART (Continued)

entigrade		*Fahrenheit*	*Centigrade*		*Fahrenheit*
82	180	356	338	640	1184
88	190	374	343	650	1202
93	200	392	349	660	1220
99	210	410	354	670	1238
100	212	414	360	680	1256
104	220	428	366	690	1274
110	230	446	371	700	1292
116	240	464	377	710	1310
121	250	482	382	720	1328
127	260	500	388	730	1346
132	270	518	393	740	1364
138	280	536	399	750	1382
143	290	554	404	760	1400
149	300	572	410	770	1418
154	310	590	416	780	1436
160	320	608	421	790	1454
166	330	626	427	800	1472
171	340	644	432	810	1490
177	350	662	438	820	1508
182	360	680	443	830	1526
188	370	698	449	840	1544
193	380	716	454	850	1562
199	390	734	460	860	1580
204	400	752	466	870	1598
210	410	770	471	880	1616
216	420	788	477	890	1634
221	430	806	482	900	1652
227	440	824	488	910	1670
232	450	842	493	920	1688
238	460	860	499	930	1706
243	470	878	504	940	1724
249	480	896	510	950	1742
254	490	914	516	960	1760
260	500	932	521	970	1778
266	510	950	527	980	1796
271	520	968	532	990	1814
277	530	986	538	1000	1832
282	540	1004	566	1050	1922
288	550	1022	593	1100	2012
			621	1150	2102
293	560	1040			
299	570	1058	649	1200	2192
304	580	1076	677	1250	2282
310	590	1094	704	1300	2372
316	600	1112	732	1350	2462
321	610	1130	760	1400	2552
327	620	1148	788	1450	2642
332	630	1166	816	1500	2732

PSYCHROMETRIC CHART



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