

GUIDELINE SERIES

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A DESCRIPTION OF THE ANALYTICAL TECHNIQUES
AND ASSOCIATED SAROAD METHOD CODES USED IN
STORING DATA IN THE NATIONAL AEROMETRIC
DATA BANK



U.S. ENVIRONMENTAL PROTECTION AGENCY

Office of Air Quality Planning and Standards

Research Triangle Park, North Carolina

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

SUBJECT: Description of the Analytical Techniques and Associated SAROAD Codes Used in Storing Data in the National Aerometric Data Bank
DATE: 31 MAY 1974
FROM: OAQPS #1.2-017

TO: Robert E. Neligan, Director
Monitoring and Data Analysis Division

Surveillance and Analysis Division Directors, Regions I-X
Air and Water Analysis Division Directors, Regions I-X

Enclosed is a copy of guideline document OAQPS #1.2-017. The previous draft has been revised based on comments from the Regional Offices and NERC-RTP. The document relates SAROAD pollutant method codes with analytical techniques for which data have been submitted since 1969.

The principal purpose of this guidance is to establish uniformity in reporting data to the NADB as well as to prevent data from being reported under the wrong code. It is extremely important that air quality data be reported under the correct code number because all of our analyses and air quality trend statistics are derived from these code numbers. Incorrectly coded data may lead to incorrect statements that a site has exceeded standards.

The Regional Office must take the lead and supervise a survey of the various monitoring techniques and SAROAD method coding used at each site under their jurisdiction to verify if they differ from those described in this guideline. We would appreciate a reply from your office when you have surveyed the sites under your jurisdiction.

Should a technique or code be used that is not described in this document, please follow the instructions found on page 2 and report any differences to the Chief of the Data Processing Section, NADB, Durham, North Carolina (919/688-8247).

If there are any further questions or comments, please contact Mr. William Cox of the Monitoring and Reports Branch (919/688-8312).

Robert E. Neligan

Enclosure

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OAQPS 1.2-017

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Office of Air Quality Planning and Standards
and
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TABLE OF CONTENTS

	Page
Introduction	1
Suspended Particulates	3
Benzene Soluble Organic	3
Soiling Index	4
Light Scatter	4
Radioactivity	4
Metals, by Hi-Vol, AA, Emission Spectra	6
Arsenic	9
Mercury	9
Water Soluble Particulates	10
Benzo(A)Pyrene	15
Dustfall Procedures	16
Carbon Monoxide	23
Sulfur Dioxide	24
Hydrogen Sulfide	27
Sulfation Rate Procedures	28
Fluoride Ion	31
Nitrogen Oxides	32
Ammonium	36
Hydrocarbons	38
Aldehyde	39
Oxidants	40
Ozone	43

INTRODUCTION

The purpose of this document is to bring together for the first time a SAROAD code number with a description of the analytical technique used in gathering data stored in the National Aerometric Data Bank (NADB). It has long been needed. The SAROAD code numbers and methods in this compilation are only those for which data have been submitted since 1969. The titles of the methods (in capital letters following the code number) are those which were assigned in the past and which appear in the computer printout of Common Parameters and Methods (the "Parm File"), similar to Code Table 4 of the SAROAD Users Manual.

It is to be emphasized that we do not endorse all of the procedures described herein. Some are known to yield erroneous or misleading data. Nor do we endorse a particular manufacturer's instrument even though the name is referred to in a title. The rule governing the compilation was: every method used since 1969 together with its Parm File title is to be included for the purposes of completeness.

Beneath each SAROAD number and title there is a brief description of the sampling and analysis principles followed by references which the reader should consult for details. Whenever possible, we have given references to those publications which we think should be readily available to field workers. In no case have we included enough details for a worker to start an analysis program which will produce valid data. The references must be consulted.

Instrumental techniques have not been thoroughly referenced and the instrument user should consult the procedure prepared by the manufacturer.

Through this publication we hope to achieve some degree of uniformity in reporting data to the NADB. If, for example, data have been submitted to the Bank under a given code number, but the description of that method as found in this compilation is different from the method which was actually used to obtain the data, then the reporter must do one of three things:

- a. he must begin submitting data under the proper code number which agrees with the method actually used; (data previously reported must be re-reported under the correct code);
- b. the reporter must change his methodology to agree with the method described and data then submitted using that code number; or
- c. a new code number must be applied for.

We encourage the persons who submit data to the NADB to verify with the laboratory personnel that the SAROAD codes used agree with the analytical procedures described herein. If there are problems or questions, we urge you to call the chief of the data processing section, NADB, Durham, N.C. (FTS 919/688-8247); or your SAROAD contact or quality control coordinator in the Regional Office. Also, we will welcome your pointing out any errors and/or omissions in the text. There are a few blanks which we have not been able to fill in.

11101 91 SUSPENDED PARTICULATE - HI-VOL - GRAVIMETRIC
Air is drawn at 40 to 60 ft.³/min through a glass fiber filter, by means of a blower, and the suspended particles having a diameter between 100 and 0.1 μ m are collected. The suspended particulate is calculated by dividing the net weight of the particulate by the total air volume sampled and reported in density units as μ g/m³. Heavy loading of suspended particulate, oily particulates, or high humidity can cause reduced air flow through the filter. Therefore, flow rates should be measured before and after the sampling period.

1. "Rules and Regulations," Federal Register, Vol 36, No. 228, U.S. Government Printing Office, Washington, D.C., (Nov. 25, 1971), p 22388.
2. Intersociety Committee, "Methods of Air Sampling and Analysis," American Public Health Association, Washington, D.C., 1972, p 356.
3. "Air Quality Data for 1967," EPA-APTD-0741, Office of Technical Information and Publications, Research Triangle Park, North Carolina, 1971, p 17.

11103 91 BENZENE SOLUBLE ORGANICS - HI-VOL BENZENE EXTRACTION
An 8% aliquot of the filter is placed in a soxhlet extractor and extracted with 75 ml of benzene for 6 h. The benzene is evaporated and the residue is weighed and reported in aerometric units; μ g/m³. Errors may result from non-volatile material in the benzene used for extraction.

1. Stanley, T. W., J. E. Meeker and M. J. Morgan, (1967), Environ. Sci. and Tech. 1, (11), 927.
2. "Air Quality Data for 1967," EPA APTD-0741, Office of Technical Information and Publications, Research Triangle Park, North Carolina, 1971, pp 17-18.

11201 81 SOILING INDEX (COH) - TAPE SAMPLER TRANSMITTANCE

Air is drawn through a 1 in. diameter spot on a continuous strip of filter paper. The measurement is based on light transmission through the spot having the collected matter on it, and reported in COH's (coefficient of haze) per 1000 linear foot of sampled air. The standard is a clear spot on the paper. The inlet air funnel must be kept upside down, and sampling lines must be kept short.

1. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 23, p 420.
2. "Air Quality Data for 1967," EPA APTD-0741, Office of Technical Information and Publication, Research Triangle Park, North Carolina, 1971, p 20.

11202 91 SOILING INDEX (RUD) - TAPE SAMPLER - REFLECTANCE

The sampling procedure is similar to that of 11201 81. Measurement of the soiling is based on light reflectance from the spot and is reported in RUD's (reflectance unit density).

1. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 23, p 420.

11203 11 LIGHT SCATTER NEPHELOMETER

Air enters an optically black metal tube at 5 cfm. Light of 410 nm is scattered from particles in the air stream. The amount of light scattered at 90° from the main beam is measured by a photomultiplier tube.

11302 91 RADIOACTIVE-GROSS-BETA-HI-VOL PROPORTIONAL COUNTER

The radioactive matter on a filter paper is counted with a beta sensitive detector to establish the gross concentration of beta emitters in the sampled ambient air. The daughter products of natural radon and thoron in the atmosphere can be minimized by waiting three days until they

have decayed. A self-absorption correction must be made if inert matter on the filter interferes.

1. Intersociety Committee, "Methods of Air Sampling and Analysis," American Public Health Association, Wash., D.C., 1972, p 379.
2. Settler, L. R. and G. I. Coats, (1964), "The Determination of Airborne Radioactivity," Amer. Ind. Hygiene Assoc., J. 22, 64.
3. Schulte, H. F., Monitoring Airborne Radioactivity, "Air Pollution," Vol II, 2nd Ed., A. C. Stern, Ed., Academic Press, New York, N. Y., 1968, p 393.

12101-12185

ATOMIC ABSORPTION (AA)

Aliquots of samples from the low temperature ashing procedure are sprayed into a reducing flame by an atomizer, where metal ions are reduced to the atomic state. The atoms absorb monochromatic light produced by a lamp having a cathode made of the element to be measured. The light absorbed by the atoms in the flame is a measure of their concentration. The influence of one element on the excitation potential of another does not interfere. The analysis of Al, Sb, As, Be, Bi, Ba, Cd, Ca, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Hg, Sn, Ti, V, and Zn is done by AA. The AA is more sensitive than emission spectra for most metals.

1. W. Slavin, "Atomic Absorption Spectroscopy," Interscience Publishers, New York, 1968, pp 69-74.
2. Perkin Elmer Corp., Methods Manual-Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin Elmer Corp., 1968.
3. F. J. Welcher, Standard Methods of Chemical Analysis, D. Van Nostrand Company, Inc., Princeton, New Jersey, 1966, p 105.
4. Thompson, R. J., G. B. Morgan, and L. J. Purdue, (1970), "Analysis of Selected Elements in Atmospheric Particulate Matter by Atomic Absorption," Atomic Absorption Newsletter 9, (No. 3), 55.

12102-12185

EMISSION SPECTRA

A solution containing metallic ions is placed between two electrodes and subjected to 13-15 kilovolts AC discharge. The spark so created generates enough heat to atomize the ions and the high voltage excites many electrons per atom. Spectra characteristic of each element are formed when the electrons return to

their normal energy levels. Internal standards are used to reference a known spectral line so that other lines can be located. NASN uses indium and yttrium as internal standards. Metals as Sb, Be, Bi, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Sn, Ti, Sm, V, and Zn are analyzed by emission spectra.

1. H. H. Willard, L. L. Merritt, J. A. Dean, "Instrumental Methods of Analysis," D. Van Nostrand Company, Inc. 4th Edition, 1965, p 280.
2. F. J. Welcher, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, Inc., Princeton, New Jersey, 1966, p 141.
3. "Air Quality Data for 1967," EPA-APTD 0741, (1971), Office of Technical Information and Publication, Research Triangle Park, N.C., 1971, p 19.

12102-12185

LOW TEMPERATURE ASHING PROCEDURE

Particulates are ashed to remove organic matter. A 1 or 2 in. by 7 in. strip of the exposed glass filter (or a composite of 5-8 strips) is heated at 150°C for 1 h. at 1 torr with an O₂ flow of 3000 ml/h. The ashed filter is fluxed for 3 h. with 8 ml of 20% HCl and 32 ml of 40% HNO₃. The acid extract is concentrated to 1 or 2 ml by evaporation, centrifuged, and the residue is washed three times with dilute HCl. Samples from non-urban air are then diluted with distilled H₂O to 3 ml/2 in. strip and samples from urban air are diluted to 4.4 ml/9 in.² of filter taken. Samples so prepared are ready for emission spectra analysis, but must be diluted 10 fold for AA analysis.

1. Thompson, R. J., G. B. Morgan and L. J. Purdue, (1970) "Analysis of Selected Elements in Atmospheric Particulate Matter by Atomic Absorption," Atomic Absorption Newsletter 9, 54.

12102-12185

MUFFLE FURNACE PROCEDURE

Prior to the invention of the low temperature asher, organic material was removed by heating samples to 500°C for 1 h. in a muffle furnace. Samples are then extracted twice for 1 h. with 40 ml of 1:1 redistilled HNO_3 at a temperature just below boiling. The solution is filtered, evaporated to 4 ml and diluted to 10.4 ml with H_2O . The samples are then analyzed by the emission spectrograph. Metals as Sb, As, Be, Bi, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Sn, Ti, V, and Zn are measured by this procedure. This procedure may volatilize some portion of some of the metals and thus result in an unknown fraction recovered.

12103 93 ARSENIC - HI-VOL NASN-ARSINE-COLORIMETRIC

The arsenates and oxides of arsenic are extracted from a 2 in. square exposed filter by digestion for 1 hr with 30 ml of 6 N HCl at 90°C, and then reduced to the trivalent state with KI and SnCl₂. Arsine is then generated by Zn and HCl Gutzeit procedure. The evolved arsine passes through a H₂S scrubber and into an absorber containing silve diethyldithiocarbamate. The resulting red complex is measured spectrophotometrically at 535 nm. Antimony likewise forms stibine which also complexes with the carbamate but at low concentrations does not interfere with arsenic determination. High concentrations of Ni, Cu, Cr, and Co interfere with arsine formation. Many interferences can be minimized by using an internal standard of added arsenic.

1. Intersociety Committee, "Methods of Air Sampling and Analysis," American Public Health Association, Wash., D.C., 1972, p. 289.

12142 92 MERCURY - ACID ICL ATOMIC ABSORPTION

This is a flameless AA technique. The total mercury is collected through a glass impinger in 30 ml of 0.1N acidic iodine monochloride at a flow-rate of 200 ml/min. HgI₂ is reduced to elemental mercury by hydroxylamine hydrochloride in basic solution which is aerated to vaporize the mercury. The vapor is passed into a quartz absorption cell where it absorbs light at 253.7 nm. This method is not applicable to atmosphere containing less than 50 ng Hg/m³ of air due to high and erratic blanks.

1. Hatch, R. W. and W. L. Ott, (1968), "Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectrophotometry," Anal. Chem. 40, p 2085.
2. Lynch, A. L., R. F. Stalzer, and D. T. Lefferts, (1968), "Methyl and Ethyl Mercury Compounds -- Recovery from Air and Analysis," Am. Ind. Hygiene Assoc. J., 79.

12202 91 FLUORIDE-HI-VOL WILLARD-WINTER/SPECIFIC ION ELECTRODE

The Willard-Winter distillation is carried out to remove interfering ions. Two 1 3/4 in. diameter circles of the filter are placed in a platinum dish, covered with 10 ml of $\text{Ca}(\text{OH})_2$ suspension (2.5% Ca by weight), and evaporated to dryness over a steam bath. The residue is heated for 30 min. in an oven at 150°C, and ignited in a muffle furnace at 550°C for 5-6 h. The ash is mixed with 1g AgClO_4 and steam distilled using 10 ml of 60% HClO_4 at 135°C. A total of 190 ml of distillate is collected. The fluoride ion concentration is then measured with a specific ion electrode. See 42513 91.

1. M. B. Jacobs, (1960), "The Chemical Analysis of Air Pollutants," Chemical Analysis, Vol 10, Interscience Publishers, Inc., New York, N.Y., p 200.

12203 91 CHLORIDE-HI-VOL-THIOCYANATE

Chloride in the aqueous extract of the hi-vol particulate sample forms mercuric chloride and liberates SCN^- ion from mercuric thiocyanate. The SCN^- ion forms a colored complex with Fe^{+++} ion from ferric ammonium sulfate. The complex is measured colorimetrically at 416 nm.

1. R. B. Fisher, "Quantitative Chemical Analysis," W. B. Saunders Co., Philadelphia, Pa. 1957, p 238.
2. Morgan, G. B., E. C. Tabor, C. Golden, and H. Clements, Automated Laboratory Procedure for the Analysis of Air Pollutants 66-p 108B, Technicon Industrial Systems, Tarrytown, N.Y., p 536.

12301 91 AMMONIUM - HI-VOL NESSLER

Ammonium ion is removed from an 8% aliquot of the filter by fluxing the filter in 50 ml of H_2O for 30 min, then placed in a Nessler tube with 4 ml of Nessler reagent. Should

the solution become cloudy, Rochelle salt solution (10g of $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ in 200 ml of .01N NaOH) is added dropwise with shaking. The absorption is read using a No. 54 filter with a 50 ml glass cell, using a reagent blank as reference. (Rochelle salt prevents Ca and Mg precipitation at the high pH of the Nessler reagent).

1. M. B. Jacobs, (1960), "The Chemical Analysis of Air Pollutants," Chemical Analysis, Vol 10, Interscience Publishers, Inc., New York, p 216.
2. G. B. Morgan, E. C. Tabor, C. Golden, and H. Clements Automated Laboratory Procedures for the Analysis of Air Pollutants 66-p 108B, Technicon Industrial Systems, Tarrytown, N. Y., p 536.

12301 92 AMMONIUM-HI-VOL SODIUM PHENOLATE

Ammonium ions are extracted from a 3/4 in. by 8 in. strip of the exposed filter by fluxing with 25 ml of H_2O . The filtrate is diluted to 50 ml and sodium phenolate and sodium hypochlorite are added producing a blue complex when pH is above 7.0. The absorbance is read spectrophotometrically at 626 nm.

1. Russell, J. A., (1944), "The Colorimetric Estimation of Small Amounts of Ammonia by the Phenol-Hypochlorite Reaction," J. Biol. Chem. 156, 457.
2. Morgan, G. B., E. C. Tabor, C. Golden, and H. Clements, Automated Laboratory Procedure for the Analysis of Air Pollutants 66-p 108B, Technicon Industrial Systems, Tarrytown, N. Y., p 536.
3. "Air Quality Data for 1967," EPA-APTD 0741, Office of Technical Information and Publication, Research Triangle Park, N.C., 1971, p 18.

12306 91 NITRATE-HI-VOL 2,4 XYLENOL

Nitrate nitrates 2,4-xyleneol. The nitrated 2,4-xyleneol is separated from other water soluble colored substances by NaOH and toluene. A 3/4 in. strip of the filter is fluxed in 25 ml of H₂O, filtered (Whatman No. 1), and washed until 50 ml of filtrate is obtained. A 5 ml sample and 15 ml of 85% H₂SO are mixed, cooled, and 1 ml of 1% xyleneol is added. The solution is heated at 60°C for 0.5 h and diluted to 80 ml. Then, 10 ml of toluene is added and the mixture is shaken for 2 min. in a separatory funnel. The lower layer is discarded, 10 ml of 0.4N NaOH added, and the funnel again shaken for 5 min. The lower aqueous layer is drawn through cotton into a cuvette. The absorbance is measured at 435 nm.

1. "Selected Methods for the Measurement of Air Pollutants, U.S. Department of Health, Education, and Welfare 999-AP-11, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio, May 1965, p I-1.
2. Pate, J. B., E. C. Tabor, (1962), "Analytical Aspects of Glass Fiber Filters," Am. Ind. Hyg. Assoc. J. 23.
3. Barnes, H., (1950), "A Modified 2,4-Xyleneol Method for Nitrate Estimation," Analyst 75, 388.

12306 92 NITRATE-HI-VOL REDUCTION-DIAZO COUPLING

The nitrate is reduced to nitrite by alkaline hydrazine, converted to HNO₂ which diazotizes sulfanilamide, and coupled with N (1-naphthyl)-ethylenediamine dihydrochloride which absorbs light at 535 nm.

1. Morgan, G. B., E. C. Tabor, C. Golden and H. Clements, Automated Laboratory Procedure for the Analysis of Air Pollutants 66, p 108B, Technicon Industrial System, Tarrytown, N. Y., p 536.

2. "Air Quality Data for 1967," EPA-APTD 0741, Office of Technical Information and Publication, Research Triangle Park, N.C., 1971, p 18.

12306 93 NITRATE-HI-VOL SPECIFIC ION ELECTRODE

The aqueous extract of a hi-vol glass fiber filter is analyzed for nitrate ion by means of a specific ion electrode.

12345 91 PHOSPHATE - HI-VOL-MOLYBDATE - STANNOUS CHLORIDE

Phosphate ions in the water extract of the filter are precipitated as ammonium molybdophosphate in an acid medium, which is then reduced to a molybdenum blue complex with stannous chloride. The absorbance is read at 650 nm.

1. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 23, pp 41-49.

2. Lundell, G. E. and J. I. Hoffman, (1923), "Notes on the Determination of Phosphate," Ind. and Eng. Chem. Anal. Ed. 15, 71.

12403 91 SULFATE - HI-VOL COLORIMETRIC

Water soluble sulfate is reacted with excess reagent containing equivalent amounts of methylthymol blue and BaCl_2 . Ba^{++} and $\text{SO}_4^{=}$ ions form BaSO_4 leaving a $[\text{SO}_4^{=}]$ equivalent of free methylthymol blue. If the pH is changed from 2.9 to 12.4 by KOH, Ba^{++} ion forms a chelate with the free dye. The unchelated dye is yellow and absorbs light at 460 nm.

1. Morgan, G. B., E. C. Tabor, C. Golden and H. Clements Automated Laboratory Procedure for the Analysis of Air Pollutants 66, p 106B, Technicon Industrial Systems Tarrytown, N. Y., p 538.

2. A. L. Lazrus, K. C. Hill and J. P. Lodge, "A New Colorimetric Microdetermination of Sulfate Ion in Rainwater," personal communication, Division of Atmospheric Surveillance, Research Triangle Park, N.C., 1965.
3. "Air Quality Data for 1967," EPA-APTD 0741, Office of Technical Information and Publication, Research Triangle Park, N.C., 1971, p 19.

12403 92 SULFATE-HI-VOL TURBIDIMETRIC

The water soluble sulfate extract of the filter forms BaSO_4 in a BaCl_2 solution. Suspended BaSO_4 particles scatter light, and the diminished intensity of a light beam is measured by a turbidimeter.

An aliquot of the filter extract is chosen so that the sample contains the equivalent of 1 to 20 $\mu\text{g}/\text{m}^3$ of $\text{SO}_4^{=}$. To the sample diluted to 20 ml, 1 ml of 10N HCl is added, followed by 4 ml of a glycerol/absolute ethanol solution (1:2v/v). After mixing, the absorbance is measured at 500 nm and compared with H_2O . Then 0.25g of BaCl_2 crystals are added and shaken to dissolve the crystals. After standing for 40 min. at 20°C, the absorbance is measured again.

1. "Selected Methods for the Measurement of Air Pollutants," U.S. Department of Health, Education, and Welfare 999 AP-11, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio, May 1965, p I-1.
2. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 23, pp 50-53.

12602 91 HYDROGEN ION CONCENTRATION - HI-VOL pH METER

The water soluble extract of the filter is tested by a pH meter and the hydrogen ion is calculated from the pH value.

17242 91 BENZO(A)PYRENE - HI-VOL THIN LAYER CHROMATOGRAPHY

This is a technique whereby the benzene soluble organics are separated by means of thin layer chromatography. The isolated benzo(A)pyrene as indicated by comparison with a standard is removed from the thin layer plate and excited with radiant energy of 470 nm. The fluorescence is measured at 540 nm.

1. Intersociety Committee, "Methods of Air Sampling and Analysis," American Public Health Association, Wash., D.C., 1972, p 159.

21101 51 TOTAL DUSTFALL - BUCKET GRAVIMETRIC

A 1 gallon container having a mouth diameter of 4.4 in. is placed in a copper can (5 in. high and 5 in. diameter) on stand, (4 ft. above a roof and four stories from the ground). Five hundred to 1500 ml of antifreeze-treated water is placed in the container. The collected sample is filtered using Whatman No. 41H paper which is then dried and weighed. The filtrate is evaporated at 105°C, the residue weighed, and both weights added for total dustfall.

1. M. B. Jacobs, "The Chemical Analysis of Air Pollutants," Chemical Analysis, Vol 10, Interscience Publishers, Inc., New York, N.Y., (1960), p 37.

21101 71 TOTAL DUSTFALL - BUCKET - GRAVIMETRIC (APCA)

The dust falls into a glass or stainless steel container, 5 in. in diameter and 10-15 in. high. The top of the container is maintained at from 8 to 50 ft. above the ground and 4 ft. above any surface. Neighboring roof surfaces must subtend an angle of 30° or less from the horizontal. Distilled water should be maintained in the container and a quaternary ammonium salt is added (1 to 2 mg/l) to suppress algal growth. Isopropyl alcohol may be added as antifreeze. The 30 day sample is filtered through a 20 mesh screen to remove extraneous material and treated as method 21101 51 except that samples having antifreeze are evaporated to dryness at 105°C, 300 ml distilled water is added, and the sample again evaporated to dryness.

1. "Recommended Standard Method for Containing Dustfall Survey (APMI-a)," (Nov. 1955), APCA Journal 5, (No. 3), p 176.

21101 81 DUSTFALL - BUCKET GRAVIMETRIC (ASTM)

A 6 in. diameter, 12-18 in. high, glass, plastic, or stainless steel cylinder, mounted with a bird ring, is

use to collect the dustfall. The analysis is the same as method 21101 71.

1. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 23, p 425.
2. Nader, J. S., (1958), "Dust Retention Efficiencies of Dustfall Collector," APCA Journal 8, p 35.

21102 81 ORGANIC FRACTION - BUCKET GRAVIMETRIC (ASTM)

The water insoluble residue and the filter from method 21101 81 are dried, weighed, placed in a soxhlet apparatus, and extracted for 2 h using 50 ml of benzene. Benzene should remain in the flask at all times. The remaining residue and paper are dried at 105°C and weighed to report the weight loss as organic fraction, BSO (benzene soluble organics).

1. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 23, p 427.

21113 71 INORGANIC FRACTION - BUCKET GRAVIMETRIC (APCA)

21113 81 INORGANIC FRACTION - BUCKET GRAVIMETRIC (ASTM)

The combined weight of water insolubles and soluble matter corrected for any solid present in a distilled water blank.

1. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Material, Philadelphia, Pa., Part 23, p 428.

21114 71 WATER SOLUBLE WEIGHT - BUCKET GRAVIMETRIC (APCA)

The sample is filtered through a 20 mesh screen to remove extraneous material and if antifreeze was used, the filtrate is evaporated to dryness over a steam bath or in an oven at 105°C. Thirty ml of distilled H₂O is added, heated to boil, and the sample filtered through an alundum crucible. If no antifreeze was used, the sample is adjusted to 300 ml and filtered through the crucible. The filtrate is evaporated to a small volume. The filtrate is placed in a weighed platinum crucible (if fluoride is present) or else a borosilicate dish and evaporated to 25 ml. It is evaporated slowly to dryness on a steam bath or in an oven at 105°C. Dryings are repeated for 3 h periods until constant weight is obtained.

1. "Recommended Standard Method for Continuing Dustfall Survey, (APMI-a)," (Nov. 1955), APCA Journal 5 (No. 3), 177.

21114 81 WATER SOLUBLE WEIGHT - BUCKET GRAVIMETRIC (ASTM)

The soluble material, described as the water soluble weight in method 21101 81, is evaporated in a tared platinum dish if fluoride or caustic materials are present or else a borosilicate dish. The dish is heated slowly until 25 ml remain. Then a steam bath or a thermoregulated hot plate is used to evaporate to dryness at a temperature of 99°C. Drying is continued in an oven at 105°C until a constant

weight is obtained. The water soluble weight is the difference between this constant weight and tare.

1. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 23, p.427.

21115 51 WATER INSOLUBLE WEIGHT - BUCKET JACOBS METHOD

The collected sample is filtered through a 20 mesh sieve, and the coarse material discarded. The insoluble material in the sample is collected on a 9 cm Whatman No. 41 H filter. Alternatively, a tared gooch crucible equipped with a light asbestos mat or an alundum crucible could be used. The weight of the dry solid is reported as water insoluble weight.

1. M. B. Jacobs, (1960), "The Chemical Analysis of Air Pollutants," Chemical Analysis, Vol 10, Interscience Publishers Inc., New York, N.Y., p 38.

21115 71 WATER INSOLUBLE WEIGHT - BUCKET GRAVIMETRIC (APCA)

The water soluble weight was obtained to report the total dustfall, method 21101 71. The sample is filtered through a 20 mesh screen, the volume made to 300 ml, boiled, and filtered through a weighed 35 ml alundum filter crucible. The crucible is dried in an oven at 105°C for 3 h, cooled, and the drying is repeated to constant weight. The increased weight of the crucible is reported as water insoluble weight.

1. "Recommended Standard Method for Continuing Dustfall Survey (APMI-a), (Nov. 1955), APCA Journal 5 (No. 3), 176.

21115 81 WATER INSOLUBLE WEIGHT - BUCKET GRAVIMETRIC (ASTM)

The material collected on a dried and weighed filter from method 21101 81, is dried in a weighing bottle overnight at 105°C. The net weight less the weight of the filter paper and weighing bottle is the water insoluble weight.

1. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials Philadelphia, Pa., Part 213, p 427.

21116 71 TOTAL WEIGHT ASH - BUCKET GRAVIMETRIC (APCA)

The water insolubles and the water solubles are ignited in a dish at red heat for 20 to 30 min, cooled in a desiccator, reheated and cooled until a constant weight is obtained. The dish must have been pretreated in the same manner. The excess weight is the total weight ash.

1. M. B. Jacobs, (1960), "The Chemical Analysis of Air Pollutants," Chemical Analysis, Vol 10, Interscience Publishers Inc., New York, N.Y., p 47.

21116 81 TOTAL WEIGHT ASH - BUCKET GRAVIMETRIC (ASTM)

The total weight ash is the weight of the insoluble and soluble materials after the removal of BSO and the combustible materials.

22114 92, 22126 92, 22132 92, and 22136 92

COPPER, IRON, MANGANESE, NICKEL - BUCKET ATOMIC ABSORPTION
Thirty ml of $\text{HNO}_3/\text{H}_2\text{O}$ (1/1) is added to the dustfall
in a beaker, heated below boiling for 1 h, and concentrated
to remove excess HNO_3 . The solids are removed by
centrifuging. The solution is analyzed by AA.

1. Water, Atmospheric Analysis, (1971), "Annual Book of
ASTM Standards," American Society for Testing and Materials,
Philadelphia, Pa., Part 23, p 678.

22403 81 SULFATES - BUCKET TURBIDIMETRIC (ASTM)

Turbid samples are filtered and the temperature adjusted
to between 15 and 30°C. Ten ml glycerin solution (glycerin/
 H_2O , 1/1), and 5 ml of NaCl solution (240g of NaCl and 20 ml
conc. HCl/liter) are added to 50 ml of the sample. A 40 mm
cell filled with the treated sample is used as the blank
sample by setting the colorimeter to zero absorbance at 380-
400 nm. The cell sample is combined with the remaining
treated sample, 0.3g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ crystals added, and the
mixture stirred for 1 min. After standing for 4 min the
mixture is stirred again for 15 sec. The cell is then
filled with the turbid solution and absorbance measured
again at the same wavelength as the blank sample.

1. Water, Atmospheric Analysis, (1971), "Annual Book of
ASTM Standards," American Society for Testing and Materials,
Philadelphia, Pa., Part 23, p 51.

22602 81 pH (DUSTFALL) - BUCKET pH METER

Total acidity of the water soluble portion of the total dust-
fall is obtained by using a pH meter, or less accurately
by use of pH test paper.

1. M. B. Jacobs, (1960), "The Chemical Analysis of Air
Pollutants," Chemical Analysis, Vol 10, Interscience Publishe:
Inc., New York, N.Y., p 40.

25101 81 DUSTFALL COMBUSTIBLE-BUCKET GRAVIMETRIC - 500-DEG.
C. LOSS (ASTM)

After the DSO has been remove from the water insoluble material, the material and the filter paper are ashed at 500°C in a tared crucible and the weight loss is reported as, "Combustibles and volatile particulates other than benzene soluble."

1. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 23, p 428.

42101 11 CARBON MONOXIDE - INSTRUMENTAL - NON-DISPERSIVE
INFRA-RED

The non-dispersive infrared instrument has a sample cell, a reference cell, and a detector. The detector is divided by a flexing diaphragm into two equal cells filled with equal concentrations of CO. The reference cell is filled with a CO free air.

When infrared radiation is passed into the sample cell some of the radiation is absorbed by CO in this cell in proportion to the concentration of CO and the rest is transmitted to the detector.

In the detector, the radiation causes the CO to expand flexing the diaphragm in proportion to the transmitted infrared radiation. Since the reference cell is filled with zero CO air, the reference cell side of the detector exerts a constant pressure on the diaphragm. When the CO is introduced into the sample cell, unequal amounts of residual radiation reaches the two compartment of the detector causing an unequal expansion of the detector gas. This unequal expansion causes the diaphragm to deflect, creating a change of electrical capacitance in an external circuit, and ultimately an amplified signal which is suitable for input to a servo-type recorder. The detector is calibrated by placing CO standards in the sample cell and recording the electrical signals.

1. "Rules and Regulations," Federal Register, Vol 36, No. 228, (Nov. 25, 1971), p 22391.

42101 12 CARBON MONOXIDE - INSTRUMENTAL - COULOMETRIC

Atmospheric air is drawn through a heated I_2O_5 column where I_2 is liberated. The I_2 is directed into an electrochemical cell where I_2 is measured coulometrically.

1. Beckman Instrumentation, Bulletin 3000 4411-4, Beckman Instruments, Inc., Fullerton, California.

42101 21 CARBON MONOXIDE - INSTRUMENTAL - FLAME IONIZATION

Ambient air is passed through two gas chromatographic columns in series, the first retains most pollutants but passes CO and CH_4 , and the second passes only CO. The CO then flows through a Ni catalyst where

it is converted to CH_4 which is measured by a flame ionization detector. The resulting measured current is related to the CO concentration of the input ambient air by dynamic calibration with known CO concentration standards.

1. Rotterdam, Warsaw, and Bucharest, "The Status of Instrumentation in Air Pollution Control," Environmental Control Seminar Proceeding, U.S. Department of Commerce, (May 5-June 4, 1971), p 217.

42102 11 CARBON DIOXIDE-INSTRUMENTAL INFRARED ABSORPTION

This procedure is similar to the NDIR procedure for carbon monoxide, 42101 11, except that water does not have to be removed from the air stream.

42401 11 SULFUR DIOXIDE-INSTRUMENTAL-WEST GAEKE-COLORIMETRIC

A continuous analyzing system is setup such that the ambient air flows through a glass beaded absorption column concurrently with 0.02M sodium tetrachloromercurate. Dichlorosulfitomercurate ion is formed reacted with acid-bleached pararosaniline and formaldehyde to produce a red-purple pararosaniline methylsulfonic acid which is quantitatively measured colorimetrically. The zero (100%T) baseline is established with pure reagents for 1 h and the instrument is then dynamically calibrated with known SO_2 concentration standards. Air flow rate and reagent flow rate must be calibrated and maintained accurately.

42401 13 SULFUR DIOXIDE-INSTRUMENTAL-CONDUCTIMETRIC

Sulfur dioxide is absorbed in acidic H_2O_2 which oxidizes the SO_2 to H_2SO_4 . The resulting change in conductivity can be measured, compensated for temperature, and related to the input SO_2 concentration by dynamic calibration with known SO_2 concentration standards. However, specificity is poor because any materials that alter the conductivity of the reagent are potential interfering agents.

1. Beckman Air Quality Analyzer Operating and Service Manual, Scientific and Process Inst. Div.,

Fullerton, California, 16TW352, (Aug. 1966).

2. Thomas, M.D., (1932), "Automatic Apparatus for the Determination of Small Concentrations of Sulfur Dioxide in Air," Anal. Chem. 5, 253.

3. M. B. Jacobs, "The Chemical Analysis of Air Pollutants," Chemical Analysis, Vol 10, Interscience Publishers, Inc., New York, N.Y., (1960), p 394.

4. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 23, p 272.

42401 14 SULFUR DIOXIDE-INSTRUMENTAL-COULOMETRIC

The air to be measured is passed through a cell containing a neutral buffered iodide or bromide electrolyte where an electrical current or potential maintains a constant concentration of free I_2 or Br_2 . When SO_2 in the input air reacts with the I_2 or Br_2 , the change in electrical current or potential necessary to restore or maintain the original concentration of I_2 or Br_2 (coulometric titration) is a quantitative measure of the SO_2 input. If the input flow rate is constant, the SO_2 concentration can be related to the electrical signal by dynamic calibration with known SO_2 concentration standards.

42401 15 SULFUR DIOXIDE-INSTRUMENTAL-THOMAS AUTOMETER

The Thomas Autometer is a conductimetric analyzer developed in 1929. There are later models. The method is similar to method 42401 13.

42401 16 SULFUR DIOXIDE-INSTRUMENTAL-GC FLAME PHOTOMETRIC

Chromatographic columns are used to separate SO_2 , H_2S , CS_2 , and CH_3SH . Effluent from the columns is burned in a hydrogen-rich flame. A photomultiplier tube is used to detect the 395 nm emission band characteristic of sulfur. The electrical signal is related to the input concentration by dynamic calibration with known SO_2 , H_2S , CS_2 , or CH_3SH concentration standards.

1. H. H. Willard, L. L. Merritt, and J. A. Dean, "Instrumental Methods of Analysis," D. Van Nostrand Company, Inc., 4th Edition, 1965, p 309.

42401 31 SULFUR DIOXIDE-DAVIS INSTRUMENT-HYDROGEN PEROXIDE
The Davis instrument is a conductimetric instrument,
and as such, it is much like method 42401 13.

42401 33 SULFUR DIOXIDE-DAVIS INSTRUMENT-SEQUENTIAL-CONDUCTIMETRIC
Water is deionized by passage through an amberlite
resin column, then its conductivity is measured. C

Ambient air, having first passed through a scrubber
of amberlite resin and soda-lime to remove CO_2 , is
next passed through the deionized water where the SO_2
is absorbed. The increased conductivity of the water
is a measure of the SO_2 concentration of the air.

1. Thomas, M.D. and J. N. Abersold, (1929), "Automatic
Apparatus for the Determination of Small Concentrations
of Sulfur Dioxide in Air," Anal. Chem. 1, 14.

42401 91. SULFUR DIOXIDE-GAS BUBBLER-WEST-GAEKE-SULFAMIC ACID
Sulfur dioxide is collected in a tetrachloromercurate
solution, forming a stable dichlorosulfitomercurate
complex. When acid bleached pararosaniline is added
to the collected SO_2 together with formaldehyde,
the amino groups ($-\text{NH}_3^+$) form a red violet compound
called pararosaniline methylsulfonic acid which is
measured spectrophotometrically. The method is des-
cribed in the Federal Register. (The NASN procedure,
however, uses 1.725 g/l sulfamic acid rather than
6 g/l and does not use EDTA). The sulfamic acid
eliminates interference from oxides of nitrogen.

1. "Rules and Regulations," Federal Register, Vol 36,
No. 228, U.S. Government Printing Office, Washington, D.C.
(Nov. 25, 1971), p 22385.

2. West, P. W. and G. C. Gaeke, (1956), "Fixation
of Sulfur Dioxide as Disulfito-Mercurate (II) and
Subsequent Colorimetric Estimation," Anal. Chem. 23,
1819.

3. Intersociety Committee, "Methods of Air Sampling
and Analysis," American Public Health Association,
Washington, D.C., 1972, p 447.

4. "Air Quality Data for 1967," EPA-APTD 0741, Office of

Technical Information and Publication, Research Triangle Park, N.C., 1971, p 20.

42401 92 SULFUR DIOXIDE-GAS BUBBLER-WEST-GAEKE

This method is similar to method 42401 91 except that the sample absorbing reagent is 0.1M TCM, the starch which is used for standardization is made without mercuric iodide, and sulfamic acid is not used except when high concentrations of NO_2 are expected. The sulfamic acid is added to the sample after collection.

1. "Selected Methods for the Measurement of Air Pollutants" U.S. Department of Health, Education, and Welfare 999 AP-11, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio, May 1965, p A-1.
2. Nauman, R. V., et al., (1960), Anal. Chem. 32, 1307.
3. West, P.W. and F. Ordoveza, (1962), Anal. Chem. 34, 1324.

42401 93 SULFUR DIOXIDE-GAS BUBBLER-CONDUCTIMETRIC

This manual conductimetric method uses the same principle as the instrumental conductimetric method. The absorber is a multiple jet bubbler system and the sampling is not continuous. The details are described in the reference.

1. Intersociety Committee, "Methods of Air Sampling and Analysis," American Public Health Association, Washington, D.C., 1972, p 456.

42402 71 HYDROGEN SULFIDE-TAPE SAMPLER AISI LEAD ACETATE PAPER

Filter paper (Whatman, No. 1) is cut into 2 by 4 in. strips, impregnated with $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)$ (10g/100 ml H_2O plus 5 ml CH_3COOH) and dried in H_2S free air. Air is pumped over the strips. A concentration of 0.025 mg/l of H_2S gives a positive test for H_2S . The stain on the paper is compared with a color chart for H_2S concentration.

1. M. B. Jacobs, (1960), "The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents," Chemical Analysis, Vol 1, Interscience Publishers, Inc., New York, N.Y., p 103.

147

42402 91 HYDROGEN SULFIDE-GAS BUBBLER METHYLENE BLUE
(100 ml tube + orifice)

Air is bubbled through a $\text{Cd}(\text{OH})_2$ solution in a large impinger at 1 cfm for 30 min. Ferric chloride solution and p-aminodimethylaniline test solution are added to the impinger and agitated. The sample is diluted and allowed to stand for 30 min. The sulfide ion forms a methylene blue complex. The absorbance of the sample is compared with a standard which consists of 45 ml of the $\text{Cd}(\text{OH})_2$ solution, amine test solution, and the ferric chloride.

1. Intersociety Committee, "Methods of Air Sampling and Analysis," American Public Health Association, Washington, D.C., 1972, p 426.
2. M. B. Jacobs, (1960), "The Chemical Analysis of Air Pollutants," Chemical Analysis, Vol 10, Interscience Publishers, Inc, New York, N.Y., p 185.
3. Lodge, J. P., et al., (1966), "The Use of Hypodermic Needles as Critical Orifice," J. Air Poll. Control Assoc. 16, 197.
4. Scaringelli, F. P., S. A. Frey, B. E. Saltzman, (1967), "Evaluation of Teflon Permeation Tubes for use with Sulfur Dioxide," Am. Ind. Hyg. Assoc. J. 28, 260.

42410 71 SULFATION RATE-LEAD PLATE GRAVIMETRIC (HUEY)

The PbO_2 is converted to PbSO_4 by the SO_2 in the ambient air and the $\text{SO}_4^{=}$ is removed by Na_2CO_3 and boiling H_2O . Barium chloride is used to precipitate the $\text{SO}_4^{=}$ as BaSO_4 . The dried BaSO_4 is weighed and the SO_2 equivalence is reported.

42410 72 SULFATION RATE-LEAD PLATE COLORIMETRIC (HUEY)

42410 73 SULFATION RATE-LEAD PLATE TURBIDIMETRIC (HUEY)

Sulfur dioxide reacts with lead peroxide to form lead sulfate. The amount of $\text{SO}_4^{=}$ formation per unit time is the sulfation rate. The $\text{SO}_4^{=}$ is removed from the plate by boiling Na_2CO_3 solution and the pH is adjusted between 2.5 and 4.0 so that sulfaspent or sulfaver precipitates the $\text{SO}_4^{=}$. The absorbance of the stirred precipitate is read at 450 nm, turbidimetrically.

1. Intersociety Committee, "Methods of Air Sampling and Analysis," American Public Health Association, Wash., D.C., 1972, p 442.
2. Huey, N. A., M. A. Wallar, and C. D. Robson, (June 1969) "Field Evaluation of an Improved Sulfation Measurement System." Paper No. 69-133, Air Pollution Control Association Annual Meeting.
3. Hickey, H. R., and E. R. Hendrickson, (1965), "A Design Basis for Lead Dioxide Cylinder," J. Air Poll. Control Assoc. 15, 409.

42410 72 SULFATION RATE-LEAD PLATE COLORIMETRIC (HUEY)

42410 73 SULFATION RATE-LEAD PLATE TURBIDIMETRIC (HUEY)

Sulfur dioxide reacts with lead peroxide to form lead sulfate. The amount of $\text{SO}_4^{=}$ formation per unit time is the sulfation rate. The $\text{SO}_4^{=}$ is removed from the plate by boiling Na_2CO_3 solution and the pH is adjusted between 2.5 and 4.0 so that sulfaspend or sulfaver precipitates the $\text{SO}_4^{=}$. The absorbance of the stirred precipitate is read at 450 nm, turbidimetrically.

1. Intersociety Committee, "Methods of Air Sampling and Analysis," American Public Health Association, Wash., D.C., 1972, p 442.
2. Huey, N. A., M. A. Wallar, and C. D. Robson, (June 1969) "Field Evaluation of an Improved Sulfation Measurement System." Paper No. 69-133, Air Pollution Control Association Annual Meeting.
3. Hickey, H. R., and E. R. Hendrickson, (1965), "A Design Basis for Lead Dioxide Cylinder," J. Air Poll. Control Assoc. 15, 409.

1. Wilsdon, B. H. and F. J. McConnel, (1934), "The Measurement of Atmospheric Sulfur Pollution by Means of Lead Peroxide, J. Soc. Chem. Ind. 53, 385.
2. Kainzer, A., (1957), Zement-Kalk-Gyis 10, 281.
3. "Standard Methods for the Examination of Water and Waste-water," 12th Ed., American Public Health Assoc., Inc., New York, N. Y., 1965, p 147-151.

42410 94 SULFATION RATE-LEAD CANDLE POTASSIUM CARBONATE (NASN)
This method substitutes K_2CO_3 for Na_2CO_3 in method 42410 91.

42410 95 SULFATION RATE-LEAD CANDLE TURBIDIMETRIC
Gaseous and particulate fluoride in ambient air are collected by filtration and chemisorption on filter paper impregnated with sodium formate. Water soluble fluorides are extracted from the filter, made basic with Na_2CO_3 , and complexed with citrate ion to reduce the iron and aluminum interference. The fluoride ion concentration is measured with a specific ion electrode.

1. Thompson, R. J., T. B. McMullen and G. B. Morgan, (1971), "Fluoride Concentrations in the Ambient Air," J. Air Poll. Control Assoc. 21, 484.

42513 91 FLUORIDE HI-VOL SPECIFIC ION ELECTRODE
The concentration of fluoride in an aqueous sample is measured by means of the fluoride-specific ion electrode.

1. Elfers, L. A. and Decker, C. E., (1968), Anal. Chem., Vol. 40, p 1658.
2. Frant, M. S. and J. W. Ross, Jr., (1966), "Electrode for Sensing Fluoride Ion Activity in Solution," Science 154, 1553.

42601 11 NITRIC OXIDE-INSTRUMENTAL COLORIMETRIC

NO is converted to NO₂ by passing the ambient air through an aqueous KMnO₄ solution. The resulting NO₂ is measured colorimetrically. An independent measurement of the ambient NO₂ concentration is required. This value, subtracted from the first, gives a value for the NO concentration. See Methods 42602 11 and 42602 12 for NO₂ measurement procedure.

1. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 23, p 523.
2. Rogers, L. M., (1958), "Nitric Oxide and Nitrogen Dioxide in the Los Angeles Atmosphere," J. of Air Poll. Control Assoc. 8, 124.
3. Saltzman, B. E., (1954), "Colorimetric Micro-Determination of Nitrogen Oxide in the Atmosphere, Anal. Chem., 26, 1949.
4. Thomas, M. D., et.al., (1956), Automatic Apparatus for Determination of Nitric Oxide and Nitrogen Dioxide in the Atmosphere, Anal. Chem. 28, 1810.

42601 14 NITRIC OXIDE-INSTRUMENTAL CHEMILUMINESCENCE

When O₃ reacts with NO to form NO₂, some of the liberated energy appears in the form of light of 600-875 nm. The reaction is extremely rapid. The instrument generates an excess of O₃ such that the quantity of light emitted from the reaction and measured by the instrument, is a direct measure of the NO concentration in the sampled air. See also 42602 14.

1. Fontijn, A., A. J. Sabadell and J. R. Ronco, (1970), Anal. Chem. 42, 575.
2. Stevens, R. K., et.al., "Field Performance Characteristics of Advanced Monitors for Oxides of Nitrogen, Ozone, Sulfur Dioxide, Carbon Monoxide, Methane, and Nonmethane Hydrocarbons," Environmental Protection Agency, Research Triangle Park, N.C., presented at the APCA Meeting, June 1972.

42601 91 NITRIC OXIDE-GAS BUBBLER SALTZMAN (100 ML TUBEN + ORIFICE)
Nitrogen oxide is oxidized to NO_2 by KMnO_4 and the Method 42602 72 is followed.

1. Intersociety Committee, "Methods of Air Sampling and Analysis," American Public Health Association, Wash., D.C., 1972, p 329.

42602 11 NITROGEN DIOXIDE-INSTRUMENTAL COLORIMETRIC

The Lyshkow modification of the Griess-Saltzman reagent is used in various continuous NO_2 analyzers. Users should consult the manufacturer's literature for details of reagent preparation.

1. "Rules and Regulations" Federal Register, Vol 38, No. 110, USGPO Wash., D.C., (June 8, 1973), p 15176.
2. Lyshkow, N. A., (1965), "A Rapid Sensitive Colorimetric Reagent for Nitrogen Dioxide in Air" J. Air Poll. Control Assoc. 15 (No. 10). 481.

42602 12 NITROGEN DIOXIDE-INSTRUMENTAL-COLORIMETRIC

The original Griess-Saltzman reagent is used in various continuous NO_2 analyzers. Users should consult the manufacturer's literature for details of reagent preparation.

1. "Rules and Regulation," Federal Register, Vol 38, No. 110, USGPO, Wash., D.C., (June 8, 1973) p 15176.
2. Saltzman, B. E., (1954) "Colorimetric Micro Determination of Nitrogen Dioxide in the Atmosphere" Anal. Chem. 26, 1949.

42602 13 NITROGEN DIOXIDE-INSTRUMENTAL-COULOMETRIC

Air to be measured is passed through a cell containing neutral buffered iodide-iodine solution causing an established equilibrium between iodine and iodide

to be unbalanced. The current required to re-establish the equilibrium (coulometric titration) is a measure of the input NO_2 concentration. If the input flow rate is constant, the NO_2 concentration can be related to the electrical signal by dynamic calibration with known NO_2 concentration standards.

42602 14 NITROGEN DIOXIDE-INSTRUMENTAL-CHEMILUMINESCENCE

The ambient air to be measured is drawn over a heated catalytic converter which reduces NO_2 to NO . The NO is then analyzed by method 42601 14, and the original NO_2 concentration is obtained by subtracting the concurrent NO concentration.

1. "Rules and Regulation," Federal Register, Vol 38, No. 110, USGPO, Wash., D.C., (June 8, 1973) p 15176.
2. $\text{NO}/\text{NO}_x/\text{NO}_2$ Analyzer Bulletin, Bulletin 4133, Beckman Instruments, Inc., Fullerton, Calif.

42602 71 NITROGEN DIOXIDE-GAS BUBBLER-JACOBS-HOCHHEISER-50 ML TUBE + ORIFICE

Ambient air to be measured is bubbled through a sodium hydroxide solution where NO_2 forms a stable solution of sodium nitrite. The nitrite ion produced is reacted with phosphoric acid, sulfanilamide, and N-1 naphthylethylenediamine dihydrochloride, and measured colorimetrically at 540 nm

42602 72 NITROGEN DIOXIDE-GAS BUBBLER-SALTZMAN (50 ML TUBE + ORIFICE)

The sample is absorbed in the Griess-Saltzman reagent and after 15 min the stable pink color is measured colorimetrically at 550 nm,

1. Intersociety Committee, "Methods of Air Sampling and Analysis," American Public Health Association, Washington, D.C., 1972, p 329.
2. Saltzman, B. E., (1954), "Colorimetric Micro-Determination of Nitrogen in the Atmosphere," Anal. Chem. 26, 1949.

42602 84 NITROGEN DIOXIDE-GAS BUBBLER-NASN SODIUM ARSENITE-ORIFICE

The method is much like method 42602 71 except for the absorber (1.0g/1 of NaAsO_2). Ambient air is introduced into the absorber by means of an orifice in the bubbler. The orifice is usually not calibrated.

1. "Rules and Regulation," Federal Register, Vol 38, No. 110, USGPO, Wash., D.C., (June 8, 1973), p 15175.
2. Christie, A. A., R. G. Lidzey, and D. W. F. Radford (1970), "Field Methods for the Determination of Nitrogen Dioxide in Air." Analyst 95, 519.
3. Merryman, E. L., et.al., "Effects of NO , CO_2 , CH_4 , H_2O and Sodium Arsenite on NO_2 Analysis," presented at the Second Conference on Natural Gas Research and Technology. Atlanta, Georgia, June 5, 1972.

42602 91 NITROGEN DIOXIDE-GAS BUBBLER-JACOBS-HOCHHEISER (100 ML TUBE + FRIT)

This method is identical to method 42602 71, except that a fritted bubbler is used instead of an orifice bubbler and the volume of the absorbing solution is doubled.

1. "Selected Methods for the Measurement of Air Pollutants," U.S. Department of Health, Education, and Welfare 999-AP-11, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio, May 1965, p C-4.
2. Purdue, L. J., et.al., (1972), "Reinvestigation of the Jacobs-Hochheiser Procedure for Determining Nitrogen Dioxide in Ambient Air," Environ. Sci. and Tech. 6, 152.

42602 94 NITROGEN DIOXIDE-GAS BUBBLER-NASN-SODIUM ARSENITE-FRIT

This method is identical to method 42602 71 except that 1.0g/1 of NaAsO_2 is added to the absorbing solution, and a fritted bubbler is used instead of an orifice bubbler.

1. Christie, A. A., R. G. Lidzey, and D. W. F. Radford, (1970), "Field Methods for the Determination of Nitrogen Dioxide in Air." Analyst 95, 519.
2. Merryman, E. L., et.al., "Effects of NO, CO₂, CH₄, H₂O and Sodium Arsenite on NO₂ Analysis," presented at the Second Conference on Natural Gas Research and Technology. Atlanta, Georgia, June 5, 1972.
3. "Selected Method for the Measurement of Air Pollutants," U.S. Department of Health, Education, and Welfare 999-AP-11, Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio, May 1965, p C-4.

42603 11 OXIDES OF NITROGEN-INSTRUMENTAL COLORIMETRIC

The total oxides of nitrogen (NO + NO₂) are measured by the methods 42601 11 and 42602 12. The instrument reports the total as NO_x (total oxides of nitrogen).

1. Intersociety Committee, "Methods of Air Sampling and Analysis," American Public Health Association, Wash., D.C., 1972, p 325.

42604 91 AMMONIA-GAS BUBBLER NESSLER REAGENT-50 ML TUBE + ORIFICE

Ammonia reacts with the alkaline HgI₂.2KI solution (Nessler reagent) to produce an orange colored complex that is measured colorimetrically at 400 to 425 nm. The absorbing solution (3.27N H₂SO₄) is returned to the laboratory after the sampling period and Nessler reagent added. Rochelle salt is added to prevent Ca and Mg precipitation.

1. M. B. Jacobs, (1960), "The Chemical Analysis of Air Pollutants," Chemical Analysis, Vol 10, Interscience Publishers, Inc., New York, N. Y., p 216.
2. Morgan, G. B., E. C. Tabor, C. Golden, and H. Clements Automated Laboratory Procedure for the Analysis of Air Pollutants 66-p 108B, Technicon Industrial System, Tarrytown, N. Y., p 538.

3. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 23, p 236-331.

42604 92 AMMONIA-GAS BUBBLER-SODIUM PHENOLATE

The chemical principle used is the same as method 12301. 92. Ammonia is collected in 0.0504 N H_2SO_4 as $(\text{NH}_4)_2\text{SO}_4$ producing a blue complex with sodium phenolate and sodium hypochlorite.

1. Russell, J. A., (1944), "The Colorimetric Estimation of Small Amounts of Ammonia by the Phenol-Hypochlorite Reaction," J. Biol. Chem., 156, 457.

43101 11 TOTAL HYDROCARBONS-INSTRUMENTAL FLAME IONIZATION
Ambient air is passed into the instrument where the organic compounds present are burned in a hydrogen-rich flame. A sensitive electrometer coupled with a recorder measures the current resulting from the ions produced in the flame. The response is approximately proportional to the number of carbon atoms in the sample. The analyzer is calibrated using methane and the results are reported as methane equivalents.

1. Intersociety Committee, "Methods of Air Sampling and Analysis," American Public Health Association, Wash., D.C., 1972, p 184.

2. "Rules and Regulations," Federal Register, Vol 36, No. 228, U.S. Government Printing Office, Wash., D.C., (Nov. 25, 1971), p 22394.

43102 11 NONMETHANE HYDROCARBONS-INSTRUMENTAL FLAME IONIZATION
Measured volumes of air are delivered semicontinuously (4-12 times per hour) to a hydrogen flame ionization detector to measure its total hydrocarbon (THC) content. An aliquot of the same air sample is introduced into a stripper column which removes H_2O , CO_2 and hydrocarbons other than CH_4 . CH_4 and CO are passed to a gas chromatographic column where they are separated. The CH_4 is eluted first, and is measured by the flame ionization detector. This value subtracted from that for THC results in a measure of the non-methane hydrocarbon (NMHC) concentration of the sampled air. See also 42101 21.

1. "Rules and Regulations," Federal Register, Vol 36, No. 228, (Nov. 25, 1971), p 22394.

169

43201 11 METHANE-INSTRUMENTAL FLAME IONIZATION

A stripper chromatographic column (charcoal) is used to remove H_2O , CO_2 , and hydrocarbons other than CH_4 . Methane and CO are then separated by a gas chromatographic column and the CH_4 measured by a hydrogen flame ionization detector.

1. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 23, p 783.
2. "Rules and Regulations," Federal Register, Vol 36, No. 228, U.S. Government Printing Office, Wash., D.C., (Nov. 25, 1971), p 22394.
3. Ortman, G. C., (1966), Anal. Chem. 36, 644.

43501 11 ALDEHYDE-INSTRUMENTAL COLORIMETRIC

This method is an automated MBTH technique. See 43501 91.

43501 91 ALDEHYDE-GAS BUBBLER MBTH

Water soluble aliphatic aldehydes (measured as formaldehyde HCHO) in the ambient air are measured using an aqueous 3- methyl - 2- benzothiazolone hydrazone hydrochloride (MBTH) which forms an azine. The excess MBTH is oxidized with ferric chloride and reacts with the azine to form a blue cationic dye in acidic media, measurable at 628 nm, colorimetrically.

1. "Selected Methods for the Measurement of Air Pollutants" U.S. Department of Health, Education, and Welfare, 999-AP-11 Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio May 1965, p F-1.
2. Sawicki, E., et.al., (1961), Anal. Chem. 33, p 93.
3. Hauser, T. R. and R. L. Cummins, (1964) ibid., 36, 679.
4. "Air Quality Data for 1967," EPA-APTD-0741, Office of Technical Information and Publication, Research Triangle Park, N.C., 1971, p 20.

- 44101 11 TOTAL OXIDANT-INSTRUMENTAL-ALKALINE KI
Identical to method 44101 14 except 1 N sodium hydroxide is used instead of the phosphate buffer in the absorbing solution.
- 44101 13 TOTAL OXIDANTS-INSTRUMENTAL-MAST MODEL 742-2
Identical to method 44101-15.
1. Mast, G. M. and H. E. Saunders, (Oct. 1962), "Research and Development of the Instrumentation of Oxone Sensing," Instrument Soc. of Amer. Trans., 1, 375.
 2. Bufalini, J. J., (1968), "Gas Phase Titration of Atmospheric Oxone," Environ Sci Technol 2, 703.
 3. Wartburg, A. F., and B. E. Saltzman, (1965), "Absorption Tube for Removal of Interfering SO₂ in Analysis of Atmospheric Oxidant" Anal. Chem. 37, 779.
- 44101 14 TOTAL OXIDANT-INSTRUMENTAL-COLORIMETRIC-NEUTRAL KI
Air to be measured is contacted with neutral phosphate buffered potassium iodide. Oxidants convert the KI to I₂ or KI₃ which is measured spectrophotometrically at 352 nm. If the input air flowrate is constant, the color density can be related to the oxidant concentration. Analyzers are calibrated dynamically with known standard concentrations of ozone. Sulfur dioxide interference may be minimized by use of a CrO₃ pre-scrubber, which also causes an NO interference.
1. Intersociety Committee, "Methods of Air Sampling and Analysis," American Public Health Association, Wash., D.C., 1972, p 356.
 2. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 23, p 518.
 3. Wartburg, A. F., and B. E. Saltzman, (1965), "Absorption Tube for Removal of Interfering SO₂ in Analysis of Atmospheric Oxidant" Anal. Chem. 37, 779.
- 112

- 44101 11 TOTAL OXIDANT-INSTRUMENTAL-ALKALINE KI
Identical to method 44101 14 except 1 N sodium hydroxide is used instead of the phosphate buffer in the absorbing solution.
- 44101 13 TOTAL OXIDANTS-INSTRUMENTAL-MAST MODEL 742-2
Identical to method 44101-15.
1. Mast, G. M. and H. E. Saunders, (Oct. 1962), "Research and Development of the Instrumentation of Oxone Sensing," Instrument Soc. of Amer. Trans., 1, 375.
2. Bufalini, J. J., (1968), "Gas Phase Titration of Atmospheric Oxone," Environ Sci Technol 2, 703.
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1. Intersociety Committee, "Methods of Air Sampling and Analysis," American Public Health Association, Wash., D.C., 1972, p 356.
2. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 23, p 518.
3. Wartburg, A. F., and B. E. Saltzman, (1965), "Absorption Tube for Removal of Interfering SO₂ in Analysis of Atmospheric Oxidant" Anal. Chem. 37, 779.
- 175

44101 15 TOTAL OXIDANT-INSTRUMENTAL-COULOMETRIC-NEUTRAL KI
Air to be measured is passed through a cell containing potassium iodide and two electrodes. Oxidants convert iodide ions to I_2 which is reduced at the cathode of the cell causing a current to flow thru an external circuit. If the flow rate is constant, this electrical signal can be related to the input concentration of oxidants. Analyzers are calibrated dynamically with known standard concentrations of ozone.

44101 51 TOTAL OXIDANT-GAS BUBBLER-PHENOLPHTHALIN
Phenolphthalin, in the presence of $CuSO_4$ is oxidized to phenolphthalein by ambient air oxidants. Air is passed through 10 ml of reagent at 800 ml/min for 10 min. The color is read using a colorimeter and a green filter.

1. M. B. Jacobs, (1960), "The Chemical Analysis of Air Pollutants," Chemical Analysis, Vol 10, Interscience Publishers, Inc., New York, N. Y., p 226.

44101 81 TOTAL OXIDANT-GAS BUBBLER-ALKALINE KI
Oxidants in sampled ambient air are absorbed in an alkaline KI solution in a bubbler. A stable product is formed which can be stored with little loss for several days. Analysis is completed by addition of phosphoric acid-sulfuric acid reagent, liberating iodine, which is then determined spectrophotometrically at 352 nm.

1. Selected Methods for the Measurement of Air Pollutants U.S. DHEW 999-AP-11, RATSEC Cincinnati, Ohio, 1965, p E-1.
 2. Water, Atmospheric Analysis, (1971), "Annual Book of ASTM Standards," American Society for Testing and Materials, Philadelphia, Pa., Part 23, p 391.
 3. M. B. Jacobs, (1960), "The Chemical Analysis of Air Pollutants," Chemical Analysis, Vol 10, Interscience Publishers, Inc., New York, N. Y., p 219.
- 177

44101 82 TOTAL OXIDANT-GAS BUBBLER-FERROUS OXIDATION

Air to be measured is filtered through a Whatman No. 4 paper at 1 cfm then bubbled through two impingers in series containing acidified ferrous ammonium sulfate absorbing solution. After sampling ammonium thiocyanate is added, and the resultant color is measured with a colorimeter and green filter.

1. M. B. Jacobs, (1960), "The Chemical Analysis of Air Pollutants," Chemical Analysis, Vol 10, Interscience Publishers, Inc., New York, N. Y., p 228.

44101 83 TOTAL OXIDANT-GAS BUBBLER NEUTRAL BUFFERED KI

This is the reference method for standardization and calibration of total oxidant and ozone measuring techniques. Maximum sampling time is 30 minutes. Sulfur dioxide interferes.

1. Intersociety Committee, "Methods of Air Sampling and Analysis," American Public Health Association, Wash., D.C., 1972, p 351.
2. "Rules and Regulations" Federal Register, Vol 36, No. 228, U.S. Government Printing Office, Wash., D.C., (Nov. 25, 1971), p 22392.
3. "Selected Methods for the Measurement of Air Pollutants" U.S. DHEW, 999-AP-11, R. A. Taft Sanitary Engineering Center, Cincinnati, Ohio, May 1965, p D-1.

44103 11 INSTRUMENTAL - TOTAL OXIDANT - $0.2(\text{NO} + \text{NO}_2)$

44201 11 OZONE - INSTRUMENTAL-CHEMILUMINESCENCE

Ambient air to be measured and ethylene are delivered simultaneously to a mixing cell where ozone reacts with the ethylene to emit light which is measured by a photomultiplier tube. If the air and ethylene flowrates are constant, the resulting photomultiplier signal can be related to the input ozone concentration. Analyzers are calibrated with known ozone concentration standards.

1. "Rules and Regulations," Federal Register Vol 36, No. 228, U.S. Government Printing Office, Washington, D.C., (Nov. 25, 1971), p 22392.
2. "A Chemiluminescence Detector for Ozone Measurement," Bureau of Mines Report of Investigation RI-7650, United States Department of the Interior, U.S. Government Printing Office, Washington, D.C., 1972.

44201 13 OZONE - INSTRUMENTAL - COULOMETRIC

This method is identical to method 44101 15.

1. Mast, G. M. and H. E. Saunders, (Oct. 1962), "Research and Development of the Instrumentation of Ozone Sensing," Instrument Soc. of Amer. Trans., 1, 375.
2. Bufalini, J. J., (1968), "Gas Phase Titration of Atmospheric Ozone," Environ. Sci. Tech. 2, 703.
3. Wartburg, A. F., and B. E. Saltzman, (1965), "Absorption Tube for Removal of Interfering SO₂ in Analysis of Atmospheric Oxidant" Anal. Chem. 37, 779.

181