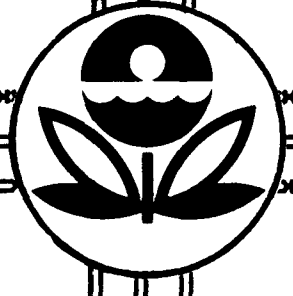
EPA-450/4-74-005
September 1974
(OAQPS No. 1.2-018)

GUIDELINE SERIES

DESIGNATION OF UNACCEPTABLE ANALYTICAL METHODS OF MEASUREMENT FOR CRITERIA POLLUTANTS



U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Waste Management
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

EPA-450/4-74-005
(OAQPS No. 1.2-018)

DESIGNATION OF UNACCEPTABLE ANALYTICAL METHODS OF MEASUREMENT FOR CRITERIA POLLUTANTS

Monitoring and Data Analysis Division
Office of Air Quality Planning and Standards
and
Quality Assurance and Environmental Monitoring Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina

September 1974

OAQPS GUIDELINE SERIES

The guideline series of reports is being issued by the Office of Air Quality Planning and Standards (OAQPS) to provide information to state and local air pollution control agencies; for example, to provide guidance on the acquisition and processing of air quality data and on the planning and analysis requisite for the maintenance of air quality. Reports published in this series will be available - as supplies permit - from the Air Pollution Technical Information Center, Research Triangle Park, North Carolina 27711; or, for a nominal fee, from the National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22151.

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Designation of Unacceptable Analytical Methods of Measurement For Criteria Pollutants

Introduction

It is well known to all who analyze the air to measure criteria pollutants that some techniques or methods are better than others. Because important decisions, such as air quality standards achievement and State Implementation Plan (SIP) revisions, are based on data derived from these methods, it is imperative that only good quality data be used. Toward this end, we are designating 14 analytical methods as unacceptable for continued use for these purposes. Accordingly, the objective of this guideline is to present the rational for those methods which are being designated unacceptable, and to provide guidance on the acceptability of methods for future measurements. This will enable the Regional Offices and the State agencies to make decisions concerning implementation of monitoring network requirements, consistent with the objectives and needs of their monitoring program.

Categories of Analytical Methods

Methods for measuring air pollutants fall into one of three categories: (1) approved, (2) unacceptable, and (3) those methods which are neither approved nor unacceptable (unapproved). At present, the only officially approved methods are the Federal reference methods described in appendices to 40 CFR Part 50, originally promulgated on April 30, 1971 (36FR8186) with the National Ambient Air Quality Standards (NAAQS). This Federal Register also introduced the concept of an "equivalent method", which is any method which can be demonstrated to be "equivalent" to the reference method. Thus, unapproved methods may become approved only by demonstrating equivalence to the reference method.

Those methods designated as unacceptable are not equivalent to the reference methods because they are known to yield measurements of poor accuracy and reliability. They are considered to be obsolete. In each case, suitable analytical methods which produce measurements of greater reliability are available to replace the unacceptable methods.

Reference and Equivalency Regulations

Regulations governing the procedures and criteria by which unapproved methods may be determined to be equivalent were proposed in the Federal Register on October 12, 1973 (38 FR 28438) as a new Part 53. Pending revision based on comments from interested persons, the new regulations, when finally promulgated, will require that a method must be tested according to prescribed procedures and meet certain prescribed specifications to be approved as an equivalent method. In essence, manual methods must demonstrate a consistent relationship to the reference method in side-by-side measurements of ambient air. Automated methods (automatic air analyzers) must demonstrate such a consistent relationship as well as meet certain performance specifications. The new regulations will also cover reference methods which are automated methods (i.e., CO and oxidants). An analyzer must meet prescribed performance specifications before it can be determined to be approved as a reference method.

Unapproved methods must be tested according to the prescribed procedures and submitted with an application for approval to the Quality Assurance and Environmental Monitoring Laboratory, NERC, RTP. Approved methods are to be published in the Federal Register. The regulations will apply to SO_2, CO, and oxidants corrected for SO_2 and NO_2.

Acceptability of Analytical Methods

Table I lists those analytical methods for which data were submitted by the States in 1972. We have listed the individual methods as "approved", "unapproved" and "unacceptable". Use of methods designated "unacceptable" should be discontinued as soon as possible. Data derived from those methods will not be accepted or used by the NADB after September 1974.

For SO_2, CO, and oxidants corrected for SO_2 and NO_2, unapproved methods may be used until the equivalency regulations are promulgated. After promulgation of those regulations and additional approved methods become available, unapproved methods may be used only until they can be replaced with approved methods, and not later than 5 years after promulgation after which time only approved methods are to be used. For NO_2 and hydrocarbons corrected for methane, guidance for selecting adequate automated methods may be found in the forthcoming EPA Environmental Monitoring Series document (EPA-650/4-74-018), Guidelines for Determining Performance Characteristics of Automated Methods for Measuring Nitrogen Dioxide and Hydrocarbons Corrected for Methane in Ambient Air.

Until these regulations and guidelines become available, the following guidance should be considered:

Discussion of Criteria Pollutants

1. TSP - The high-volume method is the Federal reference method for total suspended particulates. Since the air quality standard is defined by the method, the high-volume sampler is the only acceptable method. No procedures for determining equivalency of alternate methods have been developed; so all other methods are to be considered unacceptable.

2. Carbon Monoxide - The non-dispersive infrared (NDIR) is the Federal reference method for CO. Automated analyzers based on other principles have not yet been tested with respect to equivalency, and are therefore unapproved.

Table I. 1972-1973 POLLUTANT-METHOD-STATIONS SUMMARY

REVISED

Pollutant	Code	Method	1972 No. of Stations	1972 Percent of Total	1973 No. of Stations	1973 Percent of Total	Approved	Unapproved	Unacceptable[b]
TSP 11101	91	Hi-Vol (FRM)[a]	2828	100	3602	100	X		
CO 42101	11	NDIR (FRM)	223	99	278	96	X		
	12	Coulometric	1	0	2	0			X
	21	Flame Ionization	2	1	10	4		X	
			226	100	290	100			
SO_2 42401	11	Colorimetric	68	5	89	5		X	
	13	Conductimetric	80	7	108	6		X	
	14	Coulometric	76	6	172	9		X	
	15	Autometer[c]	1	0	1	0		X[c]	
	16	Flame Photometric	12	0	29	1		X	
	31	Hydrogen Peroxide[c]	38	3	38	2		X[c]	
	33	Sequential Conductimetric	3	0	6	0		X	
	91	West-Gaeke-Sulfamic Acid (FRM)	1040	76	1510	77	X		
	92	West-Gaeke Bubbler	45	3	11	0			X
	93	Conductimetric Bubbler	2	0	0	0			X
			1365	100	1964	100			
NO_2 42602	11	Colorimetric	110	12	136	8		X	
	12	Colorimetric	15	1	14	1		X	
	13	Coulometric	5	0	10	1		X	
	14	Chemiluminescence	36	3	8	0		X	
	71	J-H Bubbler (orifice)	11	1	14	1			X
	72	Saltzman	11	1	5	0			X
	84	Sodium Arsenite (orifice)	5	0	26	1		X	
	91	J-H Bubbler (frit)	816	79	995	60			X
	94	Sodium Arsenite (frit)	28	3	456	28		X	
	95	TEA						X	
	96	TGS						X	
			1037	100	1664	100			
Photochemical O_x (Oxone) 44101	11	Alkaline KI Instrumental	49	13	10	2			X
	13	Coulometric[d]	10	3	10	2		X[d]	
	14	Neut KI Colorimetric	75	21	89	21		X	
	15	Coulometric	13	4	22	5		X	
	51	Phenolphthalin	5	1	3	1			X
	81	Alkaline KI Bubbler	64	18	79	18			X
	82	Ferrous Oxidation	85	23	91	21			X
44201	11	Chemiluminescence (FRM)	62	17	131	30	X		
	13	Coulometric[d]	1	0	1	0		X[d]	
			364	100	436	100			

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a FRM = Federal Reference Method.

b See Appendix B for an explanation of why these methods are unacceptable.

c These methods should be reported under method code 42401 13.

d These methods should be under method code 44101 15.

3. Sulfur Dioxide - The manual West-Gaeke - sulfamic acid (24-hour bubbler) method is the Federal reference method for SO_2. The other manual methods listed are unacceptable. The similarly named "West-Gaeke" method (SAROAD method code 42401 92) is not equivalent to the reference method (SAROAD method code 42401 91). Since no continuous method has yet been tested for equivalency, they are classified as unapproved.

4. Nitrogen Dioxide - The manual NASN bubbler method is the Federal reference method for NO_2. However, in the June 8, 1973, issue of the Federal Register (38 FR 15174), it was proposed that the NASN method be withdrawn as the reference method and a new one designated after testing of proposed candidate methods. Although the method was not officially withdrawn, the problems with variable collection efficiency and NO interferences are such that it must be considered unacceptable. All other methods, both manual and continuous, have been classified as unapproved.

5. Photochemical Oxidants (Ozone) - The reference method for photochemical oxidants is a continuous chemiluminescence method based on the gas-phase reaction of ozone with ethylene. This method is specific for ozone. All other methods listed in Table I are total oxidant methods. Six of these methods for total oxidants are being designated unacceptable. While the remaining automated methods are not being designated unacceptable, strong consideration should be given to replacing them with the reference method.

6. Total Hydrocarbons Corrected for Methane - This category is unique in that, while hydrocarbons corrected for methane is a criteria pollutant, the ambient air quality standard is only a guide for achieving the oxidant standard. A gas chromatographic flame ionization technique is the federal reference method for hydrocarbons corrected for methane, but this method is difficult and expensive to use. Other methods are now becoming available and, as mentioned before, guidance for selection of adequate automated methods may be obtained in the EPA Environmental Monitoring Series document (EPA-650/4-74-018), Guidelines for Determining Performance Characteristics of Automated Methods for Measuring NO_2 and Hydrocarbons Corrected for Methane in the Ambient Air.

Pollutant Method Code

Correct identification of the pollutant method is of utmost importance in the reporting of air quality data. It will be of little help to upgrade the West-Gaeke bubbler procedure (SAROAD method code 42401 92) for example, to the West-Gaeke-Sulfamic Acid method (SAROAD method code 42401 91) unless the method codes under which the data are reported to the NADB are also changed. See OAQPS Guideline #1.2-017, A Description of the Analytical Techniques and Associated SAROAD Method Codes Used in Storing Data in the National Aerometric Data Bank, for a description of the analytical technique associated with the SAROAD method code.

After the equivalency regulations are promulgated, the pollutant method code will become even more important since there may be a unique identification code for each method which passes the equivalency testing and becomes approved as a reference or equivalent method. This new code may identify not only the method principle but also the instrument model and manufacturer.

Summary of Regional Office Responsibilities

The Regional Offices should see that those methods designated in Table 1 as unacceptable are replaced with approved methods as soon as practical. This will insure adequate data for air quality trend analyses and compliance with NAAQS after 9/1/74 when data from unacceptable methods will no longer be used. After promulgation of the equivalency regulations, EPA Regional Offices should assist in the conversion to the exclusive use of approved methods for SO_2, CO and oxidants corrected for SO_2 and NO_2 and similarly assistance should be provided for selecting adequate methods for NO_2 and total hydrocarbons corrected for methane according to the available guidelines.

To help the Regional Offices identify which states reported data by which method in 1972, we have included Table II, a printout of the data from which Table I was prepared. Note that the printout is by pollutant code and method. Appendix A, which is an extract from OAQPS Guideline #1.2-017, presents a description of the analytical technique associated with the SAROAD method code. Lastly, Appendix B, contains a short paragraph for each method which has been designated unacceptable, giving the rationale for that designation.

Table II. INVENTORY OF AIR POLLUTANT MONITORING SITES, BY STATE, 1972

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	11101	91	ALABAMA	63
STATE	COUNT	11101	91	ALASKA	19
STATE	COUNT	11101	91	ARIZONA	33
STATE	COUNT	11101	91	ARKANSAS	32
STATE	COUNT	11101	91	CALIFORNIA	19
STATE	COUNT	11101	91	COLORADO	69
STATE	COUNT	11101	91	CONNECTICUT	26
STATE	COUNT	11101	91	DELAWARE	16
STATE	COUNT	11101	91	DIST COLUMBIA	2
STATE	COUNT	11101	91	FLORIDA	45
STATE	COUNT	11101	91	GEORGIA	31
STATE	COUNT	11101	91	HAWAII	14
STATE	COUNT	11101	91	IDAHO	30
STATE	COUNT	11101	91	ILLINOIS	54
STATE	COUNT	11101	91	INDIANA	128
STATE	COUNT	11101	91	IOWA	30
STATE	COUNT	11101	91	KANSAS	59
STATE	COUNT	11101	91	KENTUCKY	90
STATE	COUNT	11101	91	LOUISIANA	12
STATE	COUNT	11101	91	MAINE	7
STATE	COUNT	11101	91	MARYLAND	85
STATE	COUNT	11101	91	MASSACHUSETTS	52
STATE	COUNT	11101	91	MICHIGAN	109
STATE	COUNT	11101	91	MINNESOTA	59
STATE	COUNT	11101	91	MISSISSIPPI	2

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	11101	91	MISSOURI	49
STATE	COUNT	11101	91	MONTANA	2
STATE	COUNT	11101	91	NEBRASKA	36
STATE	COUNT	11101	91	NEVADA	41
STATE	COUNT	11101	91	NEW HAMPSHIRE	26
STATE	COUNT	11101	91	NEW JERSEY	79
STATE	COUNT	11101	91	NEW MEXICO	28
STATE	COUNT	11101	91	NEW YORK	233
STATE	COUNT	11101	91	NORTH CAROLINA	199
STATE	COUNT	11101	91	NORTH DAKOTA	16
STATE	COUNT	11101	91	OHIO	137
STATE	COUNT	11101	91	OKLAHOMA	95
STATE	COUNT	11101	91	OREGON	48
STATE	COUNT	11101	91	PENNSYLVANIA	105
STATE	COUNT	11101	91	PUERTO RICO	5
STATE	COUNT	11101	91	RHODE ISLAND	23
STATE	COUNT	11101	91	SOUTH CAROLINA	75
STATE	COUNT	11101	91	SOUTH DAKOTA	2
STATE	COUNT	11101	91	TENNESSEE	98
STATE	COUNT	11101	91	TEXAS	192
STATE	COUNT	11101	91	UTAH	8
STATE	COUNT	11101	91	VERMONT	2
STATE	COUNT	11101	91	VIRGINIA	122
STATE	COUNT	11101	91	WASHINGTON	57

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	11101	91	WEST VIRGINIA	38
STATE	COUNT	11101	91	WISCONSIN	7
STATE	COUNT	11101	91	WYOMING	4
STATE	COUNT	11101	91	GUAM	11
STATE	COUNT	11101	91	VIRGIN ISLANDS	4
POLUTCOD	COUNT	11101	91		2828
STATE	COUNT	42101	11	ALABAMA	2
STATE	COUNT	42101	11	ALASKA	1
STATE	COUNT	42101	11	ARIZONA	3
STATE	COUNT	42101	11	CALIFORNIA	51
STATE	COUNT	42101	11	COLORADO	1
STATE	COUNT	42101	11	DIST COLUMBIA	2
STATE	COUNT	42101	11	FLORIDA	6
STATE	COUNT	42101	11	GEORGIA	2
STATE	COUNT	42101	11	HAWAII	1
STATE	COUNT	42101	11	ILLINOIS	1
STATE	COUNT	42101	11	INDIANA	3
STATE	COUNT	42101	11	IOWA	2
STATE	COUNT	42101	11	KANSAS	5
STATE	COUNT	42101	11	KENTUCKY	7
STATE	COUNT	42101	11	LOUISIANA	3
STATE	COUNT	42101	11	MARYLAND	19
STATE	COUNT	42101	11	MASSACHUSETTS	5
STATE	COUNT	42101	11	MICHIGAN	3
STATE	COUNT	42101	11	MINNESOTA	3

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	42101	11	MISSOURI	10
STATE	COUNT	42101	11	NEBRASKA	1
STATE	COUNT	42101	11	NEVADA	1
STATE	COUNT	42101	11	NEW JERSEY	22
STATE	COUNT	42101	11	NEW MEXICO	1
STATE	COUNT	42101	11	NEW YORK	13
STATE	COUNT	42101	11	NORTH CAROLINA	2
STATE	COUNT	42101	11	OHIO	13
STATE	COUNT	42101	11	OKLAHOMA	4
STATE	COUNT	42101	11	OREGON	2
STATE	COUNT	42101	11	PENNSYLVANIA	2
STATE	COUNT	42101	11	RHODE ISLAND	2
STATE	COUNT	42101	11	TENNESSEE	4
STATE	COUNT	42101	11	TEXAS	1
STATE	COUNT	42101	11	UTAH	4
STATE	COUNT	42101	11	VIRGINIA	9
STATE	COUNT	42101	11	WASHINGTON	10
STATE	COUNT	42101	11	WEST VIRGINIA	1
STATE	COUNT	42101	11	WISCONSIN	1
POLUTCOD	COUNT	42101	11		223
STATE	COUNT	42101	12	OHIO	1
POLUTCOD	COUNT	42101	12		1
STATE	COUNT	42101	21	KENTUCKY	2
POLUTCOD	COUNT	42101	21		2

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	42401	11	ARIZONA	2
STATE	COUNT	42401	11	COLORADO	1
STATE	COUNT	42401	11	DELAWARE	6
STATE	COUNT	42401	11	DIST COLUMBIA	2
STATE	COUNT	42401	11	FLORIDA	3
STATE	COUNT	42401	11	ILLINOIS	1
STATE	COUNT	42401	11	KENTUCKY	5
STATE	COUNT	42401	11	MARYLAND	1
STATE	COUNT	42401	11	MASSACHUSETTS	4
STATE	COUNT	42401	11	MISSOURI	5
STATE	COUNT	42401	11	NEW JERSEY	22
STATE	COUNT	42401	11	NEW YORK	7
STATE	COUNT	42401	11	OHIO	4
STATE	COUNT	42401	11	PENNSYLVANIA	4
STATE	COUNT	42401	11	WASHINGTON	1
POLUTCOD	COUNT	42401	11		68
STATE	COUNT	42401	13	ARIZONA	2
STATE	COUNT	42401	13	CALIFORNIA	18
STATE	COUNT	42401	13	COLORADO	1
STATE	COUNT	42401	13	CONNECTICUT	1
STATE	COUNT	42401	13	DELAWARE	7
STATE	COUNT	42401	13	DIST COLUMBIA	2
STATE	COUNT	42401	13	FLORIDA	1
STATE	COUNT	42401	13	ILLINOIS	1
STATE	COUNT	42401	13	INDIANA	8

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	42401	13	MARYLAND	12
STATE	COUNT	42401	13	MINNESOTA	2
STATE	COUNT	42401	13	MISSOURI	2
STATE	COUNT	42401	13	NEW YORK	1
STATE	COUNT	42401	13	OHIO	7
STATE	COUNT	42401	13	OREGON	2
STATE	COUNT	42401	13	PENNSYLVANIA	2
STATE	COUNT	42401	13	VIRGINIA	2
STATE	COUNT	42401	13	WASHINGTON	9
POLUTCOD	COUNT	42401	13		80
STATE	COUNT	42401	14	ALABAMA	2
STATE	COUNT	42401	14	ARIZONA	8
STATE	COUNT	42401	14	DIST COLUMBIA	2
STATE	COUNT	42401	14	FLORIDA	2
STATE	COUNT	42401	14	GEORGIA	2
STATE	COUNT	42401	14	INDIANA	4
STATE	COUNT	42401	14	KANSAS	3
STATE	COUNT	42401	14	KENTUCKY	6
STATE	COUNT	42401	14	MASSACHUSETTS	2
STATE	COUNT	42401	14	MICHIGAN	22
STATE	COUNT	42401	14	MINNESOTA	4
STATE	COUNT	42401	14	MISSOURI	1
STATE	COUNT	42401	14	NEW YORK	12
STATE	COUNT	42401	14	NORTH CAROLINA	1

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	42401	14	OHIO	1
STATE	COUNT	42401	14	PENNSYLVANIA	1
STATE	COUNT	42401	14	TENNESSEE	1
STATE	COUNT	42401	14	VIRGINIA	2
POLUTCOD	COUNT	42401	14		76
STATE	COUNT	42401	15	TENNESSEE	1
POLUTCOD	COUNT	42401	15		1
STATE	COUNT	42401	16	MARYLAND	11
STATE	COUNT	42401	16	VIRGINIA	1
POLUTCOD	COUNT	42401	16		12
STATE	COUNT	42401	31	NEW YORK	38
POLUTCOD	COUNT	42401	31		38
STATE	COUNT	42401	33	MISSOURI	3
POLUTCOD	COUNT	42401	33		3
STATE	COUNT	42401	91	ALABAMA	13
STATE	COUNT	42401	91	ALASKA	1
STATE	COUNT	42401	91	ARIZONA	7
STATE	COUNT	42401	91	ARKANSAS	2
STATE	COUNT	42401	91	CALIFORNIA	16
STATE	COUNT	42401	91	COLORADO	2
STATE	COUNT	42401	91	CONNECTICUT	4
STATE	COUNT	42401	91	DELAWARE	3
STATE	COUNT	42401	91	DIST COLUMBIA	2
STATE	COUNT	42401	91	FLORIDA	34
STATE	COUNT	42401	91	GEORGIA	13
STATE	COUNT	42401			

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	42401	91	HAWAII	12
STATE	COUNT	42401	91	ILLINOIS	38
STATE	COUNT	42401	91	INDIANA	66
STATE	COUNT	42401	91	IOWA	2
STATE	COUNT	42401	91	KANSAS	30
STATE	COUNT	42401	91	KENTUCKY	98
STATE	COUNT	42401	91	LOUISIANA	17
STATE	COUNT	42401	91	MAINE	6
STATE	COUNT	42401	91	MARYLAND	49
STATE	COUNT	42401	91	MASSACHUSETTS	53
STATE	COUNT	42401	91	MICHIGAN	24
STATE	COUNT	42401	91	MINNESOTA	18
STATE	COUNT	42401	91	MISSISSIPPI	2
STATE	COUNT	42401	91	MISSOURI	4
STATE	COUNT	42401	91	MONTANA	1
STATE	COUNT	42401	91	NEBRASKA	4
STATE	COUNT	42401	91	NEVADA	3
STATE	COUNT	42401	91	NEW HAMPSHIRE	4
STATE	COUNT	42401	91	NEW JERSEY	8
STATE	COUNT	42401	91	NEW MEXICO	8
STATE	COUNT	42401	91	NEW YORK	34
STATE	COUNT	42401	91	NORTH CAROLINA	156
STATE	COUNT	42401	91	OHIO	67
				OKLAHOMA	27

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	42401	91	OREGON	1
STATE	COUNT	42401	91	PENNSYLVANIA	14
STATE	COUNT	42401	91	PUERTO RICO	4
STATE	COUNT	42401	91	RHODE ISLAND	18
STATE	COUNT	42401	91	SOUTH CAROLINA	38
STATE	COUNT	42401	91	SOUTH DAKOTA	1
STATE	COUNT	42401	91	TENNESSEE	37
STATE	COUNT	42401	91	TEXAS	13
STATE	COUNT	42401	91	UTAH	1
STATE	COUNT	42401	91	VIRGINIA	49
STATE	COUNT	42401	91	WASHINGTON	4
STATE	COUNT	42401	91	WEST VIRGINIA	15
STATE	COUNT	42401	91	WISCONSIN	3
STATE	COUNT	42401	91	WYOMING	2
STATE	COUNT	42401	91	GUAM	9
STATE	COUNT	42401	91	VIRGIN ISLANDS	3
POLUTCOD	COUNT	42401	91		1040
STATE	COUNT	42401	92	FLORIDA	1
STATE	COUNT	42401	92	MASSACHUSETTS	44
POLUTCOD	COUNT	42401	92		45
STATE	COUNT	42401	93	INDIANA	2
POLUTCOD	COUNT	42401	93		2
STATE	COUNT	42602	11	ALABAMA	2
STATE	COUNT	42602	11	ARIZONA	3
STATE	COUNT	42602	11	CALIFORNIA	50

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	42602	11	CONNECTICUT	1
STATE	COUNT	42602	11	DIST COLUMBIA	1
STATE	COUNT	42602	11	FLORIDA	4
STATE	COUNT	42602	11	GEORGIA	1
STATE	COUNT	42602	11	KENTUCKY	8
STATE	COUNT	42602	11	MAINE	1
STATE	COUNT	42602	11	MARYLAND	6
STATE	COUNT	42602	11	MASSACHUSETTS	1
STATE	COUNT	42602	11	MINNESOTA	1
STATE	COUNT	42602	11	MISSOURI	8
STATE	COUNT	42602	11	NEVADA	1
STATE	COUNT	42602	11	NEW YORK	13
STATE	COUNT	42602	11	NORTH CAROLINA	1
STATE	COUNT	42602	11	OHIO	2
STATE	COUNT	42602	11	OKLAHOMA	1
STATE	COUNT	42602	11	OREGON	1
STATE	COUNT	42602	11	PENNSYLVANIA	1
STATE	COUNT	42602	11	TENNESSEE	1
STATE	COUNT	42602	11	VIRGINIA	2
POLUTCOD	COUNT	42602	11		110
STATE	COUNT	42602	12	COLORADO	1
STATE	COUNT	42602	12	DIST COLUMBIA	1
STATE	COUNT	42602	12	ILLINOIS	1
STATE	COUNT	42602	12	MISSOURI	1

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	42602	12	NEW JERSEY	5
STATE	COUNT	42602	12	OHIO	1
STATE	COUNT	42602	12	PENNSYLVANIA	1
STATE	COUNT	42602	12	RHODE ISLAND	2
STATE	COUNT	42602	12	VIRGINIA	2
POLUTCOD	COUNT	42602	12		15
STATE	COUNT	42602	13	KANSAS	2
STATE	COUNT	42602	13	MINNESOTA	1
STATE	COUNT	42602	13	NEVADA	1
STATE	COUNT	42602	13	TENNESSEE	1
POLUTCOD	COUNT	42602	13		5
STATE	COUNT	42602	14	ARIZONA	1
STATE	COUNT	42602	14	COLORADO	1
STATE	COUNT	42602	14	CONNECTICUT	1
STATE	COUNT	42602	14	DIST COLUMBIA	2
STATE	COUNT	42602	14	ILLINOIS	2
STATE	COUNT	42602	14	INDIANA	1
STATE	COUNT	42602	14	IOWA	1
STATE	COUNT	42602	14	KENTUCKY	3
STATE	COUNT	42602	14	MARYLAND	1
STATE	COUNT	42602	14	MASSACHUSETTS	1
STATE	COUNT	42602	14	MINNESOTA	1
STATE	COUNT	42602	14	MISSOURI	2
STATE	COUNT	42602	14	NEBRASKA	1
STATE	COUNT	42602	14	NEW MEXICO	1

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	42602	14	NEW YORK	2
STATE	COUNT	42602	14	OHIO	5
STATE	COUNT	42602	14	PENNSYLVANIA	5
STATE	COUNT	42602	14	TEXAS	2
STATE	COUNT	42602	14	UTAH	1
STATE	COUNT	42602	14	VIRGINIA	2
POLUTCOD	COUNT	42602	14		36
STATE	COUNT	42602	71	MINNESOTA	11
POLUTCOD	COUNT	42602	71		11
STATE	COUNT	42602	72	INDIANA	11
POLUTCOD	COUNT	42602	72		11
STATE	COUNT	42602	91	ALABAMA	13
STATE	COUNT	42602	91	ALASKA	1
STATE	COUNT	42602	91	ARIZONA	5
STATE	COUNT	42602	91	ARKANSAS	2
STATE	COUNT	42602	91	CALIFORNIA	16
STATE	COUNT	42602	91	COLORADO	2
STATE	COUNT	42602	91	CONNECTICUT	4
STATE	COUNT	42602	91	DELAWARE	3
STATE	COUNT	42602	91	DIST COLUMBIA	2
STATE	COUNT	42602	91	FLORIDA	22
STATE	COUNT	42602	91	GEORGIA	13
STATE	COUNT	42602	91	HAWAII	11
STATE	COUNT	42602	91	ILLINOIS	4

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	42602	91	INDIANA	41
STATE	COUNT	42602	91	IOWA	2
STATE	COUNT	42602	91	KANSAS	29
STATE	COUNT	42602	91	KENTUCKY	87
STATE	COUNT	42602	91	LOUISIANA	4
STATE	COUNT	42602	91	MAINE	1
STATE	COUNT	42602	91	MARYLAND	49
STATE	COUNT	42602	91	MASSACHUSETTS	54
STATE	COUNT	42602	91	MICHIGAN	6
STATE	COUNT	42602	91	MINNESOTA	3
STATE	COUNT	42602	91	MISSISSIPPI	2
STATE	COUNT	42602	91	MISSOURI	4
STATE	COUNT	42602	91	MONTANA	1
STATE	COUNT	42602	91	NEBRASKA	3
STATE	COUNT	42602	91	NEW HAMPSHIRE	4
STATE	COUNT	42602	91	NEW JERSEY	8
STATE	COUNT	42602	91	NEW MEXICO	7
STATE	COUNT	42602	91	NEW YORK	9
STATE	COUNT	42602	91	NORTH CAROLINA	155
STATE	COUNT	42602	91	OHIO	67
STATE	COUNT	42602	91	OKLAHOMA	19
STATE	COUNT	42602	91	OREGON	1
STATE	COUNT	42602	91	PENNSYLVANIA	14
STATE	COUNT	42602	91	PUERTO RICO	4
STATE	COUNT	42602	91	RHODE ISLAND	18

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	42602	91	SOUTH CAROLINA	38
STATE	COUNT	42602	91	SOUTH DAKOTA	1
STATE	COUNT	42602	91	TENNESSEE	41
STATE	COUNT	42602	91	TEXAS	13
STATE	COUNT	42602	91	UTAH	1
STATE	COUNT	42602	91	VIRGINIA	7
STATE	COUNT	42602	91	WASHINGTON	10
STATE	COUNT	42602	91	WEST VIRGINIA	1
STATE	COUNT	42602	91	WISCONSIN	3
STATE	COUNT	42602	91	WYOMING	2
STATE	COUNT	42602	91	GUAM	9
POLUTCOD	COUNT	42602	91		816
STATE	COUNT	42602	94	KENTUCKY	28
POLUTCOD	COUNT	42602	94		28
STATE	COUNT	44101	11	ARIZONA	1
STATE	COUNT	44101	11	COLORADO	1
STATE	COUNT	44101	11	DIST COLUMBIA	1
STATE	COUNT	44101	11	FLORIDA	2
STATE	COUNT	44101	11	ILLINOIS	1
STATE	COUNT	44101	11	INDIANA	2
STATE	COUNT	44101	11	IOWA	1
STATE	COUNT	44101	11	KANSAS	1
STATE	COUNT	44101	11	MISSOURI	1
STATE	COUNT	44101	11	NEW JERSEY	4

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	44101	11	NEW YORK	12
STATE	COUNT	44101	11	NORTH CAROLINA	2
STATE	COUNT	44101	11	OHIO	8
STATE	COUNT	44101	11	PENNSYLVANIA	1
STATE	COUNT	44101	11	TENNESSEE	4
STATE	COUNT	44101	11	TEXAS	1
STATE	COUNT	44101	11	VIRGINIA	4
STATE	COUNT	44101	11	WASHINGTON	1
STATE	COUNT	44101	11	WISCONSIN	1
POLUTCOD	COUNT	44101	11		49
STATE	COUNT	44101	13	KANSAS	3
STATE	COUNT	44101	13	NEVADA	1
STATE	COUNT	44101	13	NEW MEXICO	1
STATE	COUNT	44101	13	WASHINGTON	5
POLUTCOD	COUNT	44101	13		10
STATE	COUNT	44101	14	ALABAMA	1
STATE	COUNT	44101	14	ARIZONA	1
STATE	COUNT	44101	14	CALIFORNIA	56
STATE	COUNT	44101	14	COLORADO	1
STATE	COUNT	44101	14	KENTUCKY	1
STATE	COUNT	44101	14	MINNESOTA	1
STATE	COUNT	44101	14	MISSOURI	8
STATE	COUNT	44101	14	OHIO	2
STATE	COUNT	44101	14	OREGON	1
STATE	COUNT	44101	14	PENNSYLVANIA	1

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	44101	14	TENNESSEE	1
STATE	COUNT	44101	14	VIRGINIA	1
POLUTCOD	COUNT	44101	14		75
STATE	COUNT	44101	15	CALIFORNIA	12
STATE	COUNT	44101	15	VIRGINIA	1
POLUTCOD	COUNT	44101	15		13
STATE	COUNT	44101	51	OKLAHOMA	5
POLUTCOD	COUNT	44101	51		5
STATE	COUNT	44101	81	MINNESOTA	7
STATE	COUNT	44101	81	NORTH CAROLINA	7
STATE	COUNT	44101	81	OKLAHOMA	13
STATE	COUNT	44101	81	SOUTH CAROLINA	37
POLUTCOD	COUNT	44101	81		64
STATE	COUNT	44101	82	KANSAS	3
STATE	COUNT	44101	82	KENTUCKY	76
STATE	COUNT	44101	82	OHIO	6
POLUTCOD	COUNT	44101	82		85
STATE	COUNT	44201	11	ALABAMA	2
STATE	COUNT	44201	11	COLORADO	1
STATE	COUNT	44201	11	DIST COLUMBIA	1
STATE	COUNT	44201	11	FLORIDA	4
STATE	COUNT	44201	11	GEORGIA	1
STATE	COUNT	44201	11	HAWAII	1
STATE	COUNT	44201	11	ILLINOIS	1

TABLE II

		POLLUTANT CODE	METH CODE		NUMBER OF SITES
STATE	COUNT	44201	11	INDIANA	1
STATE	COUNT	44201	11	KANSAS	2
STATE	COUNT	44201	11	KENTUCKY	2
STATE	COUNT	44201	11	LOUISIANA	3
STATE	COUNT	44201	11	MARYLAND	6
STATE	COUNT	44201	11	MICHIGAN	1
STATE	COUNT	44201	11	MISSOURI	1
STATE	COUNT	44201	11	NEBRASKA	3
STATE	COUNT	44201	11	NEW YORK	12
STATE	COUNT	44201	11	NORTH CAROLINA	2
STATE	COUNT	44201	11	OHIO	7
STATE	COUNT	44201	11	OKLAHOMA	2
STATE	COUNT	44201	11	PENNSYLVANIA	1
STATE	COUNT	44201	11	SOUTH CAROLINA	1
STATE	COUNT	44201	11	TENNESSEE	1
STATE	COUNT	44201	11	TEXAS	1
STATE	COUNT	44201	11	VIRGINIA	5
POLUTCOD	COUNT	44201	11		62
STATE	COUNT	44201	13	OREGON	1
POLUTCOD	COUNT	44201	13		1

APPENDIX A.*

FEDERAL REFERENCE METHODS

UNAPPROVED METHODS

UNACCEPTABLE METHODS

APPENDIX B.

RATIONALE FOR RANKING THE METHODS

AS UNACCEPTABLE

*Extracted from Guideline Document OAQPS 1.2-017, A Description of the Analytical Techniques and Associated SAROAD Method Codes Used in Storing Data in the National Aerometric Data Bank.

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 µm 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 $\mu g/m^3$. 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, "APTD-0741, APTIC, Research Triangle Park, North Carolina, 1971, p. 17.

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

The non-dispersive infrared instrument has a sample cell, a rereference 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 reach the two compartments 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.

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 ($-NH_3^+$) form a red violet compound called pararosaniline methylsulfonic acid which is measured spectrophotometrically. The method is described 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. 28, 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, "APTD 0741, APTIC, Research Triangle Park, N. C., 1971, p. 20.

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 flow rates 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.

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 Proceedings, U. S.Department of Commerce, (May 5-June 4, 1971), p 217.

42401 11 SULFUR DIOXIDE-INSTRUMENTAL-WEST GAEKE-COLORIMETIC

A continuous analyzing system is set up 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 hr 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 oxdizes 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 Acralyzer 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 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 33 SULFUR DIOXIDE-DAVIS INSTRUMENT-SEQUENTIAL-CONDUCTIMETRIC

Water is deionized by passage through an amberlite resin column; then its conductivity is measured. 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.

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. $NO/NO_x/NO_2$ Analyzer Bulletin, Bulletin 4133, Beckman Instruments, Inc., Fullerton, Calif.

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

The method is much like method 42602 71 except for the absorber (1.0g 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 94 NITROGEN DIOXIDE-GAS BUBBLER-NASN-SODIUM ARSENITE-FRIT

This method is identical to method 42602 71 except that 1.0g/l 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, 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.
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.

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 14 TOTAL OXIDANT-INSTRUMENTAL-COLORIMETRIC-NEUTRAL KI

Air to be measured is contacted with nuetral phosphate buffered potassium iodide. Oxidants convert the KI to I_2 or KI_3 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 CrO_3 prescrubber, 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 SO_2 in Analysis of Atmospheric Oxidant" Anal. Chem. 37, 779.

44101 15 TOTAL OXIDANT-INSTRUMENTAL-COULOMETRIC-NEUTRAL KI

Air to be measured is passed though 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 through 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.

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.

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 31 SULFUR DIOXIDE-DAVIS INSTRUMENT-HYDROGEN PEROXIDE

The Davis instrument is a conductimetric instrument, and, as such, this method is much like method 42401 13.

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 tetrachloromercurate; the starch which is used for standardization is made with 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.

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; cannot be used for sampling period over 30 minutes.

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.

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.

44101 82 TOTAL OXIDANT-GAS BUBBLER-FERROUS OXIDATION

Air to be measured is filtered through a Whatman No. 4 paper at 1 ft^3/min; 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.

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 SO_2 in **Analysis of Atmospheric Oxidant**" Anal. Chem. 37, 779.

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.

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 Ozone Sensing," Instrument Soc. of Amer. Trans., 1, 375.

2. Bufalini, J. J., (1968), "Gas Phase Titration of Atmospheric Ozone," Environ Sci Technol 2, 703.

3. Wartburg, A. F., and B. E. Saltzman, (1965), "Absorption Tube for Removal of Interfering SO_2 in Analysis of Atmospheric Oxidant" Anal. Chem. 37, 779.

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.

APPENDIX B

Rationale for Ranking the Methods as Unacceptable

CO 42101 12 COULOMETRIC

Interferences with this method include mercaptans, hydrogen sulfide, olefins, acetylenes, and water vapor. In addition, the slow response, need for careful column preparation, and the need for well controlled temperatures and flow rates make this an unreliable procedure.

SO_2 42401 15 THOMAS AUTOMETER

This is a conductimetric analyzer. Data collected using this analyzer should be reported as 42401-13.

SO_2 42401 31 DAVIS INSTRUMENT

This is a conductimetric analyzer. Data collected using this analyzer should be reported as 42401-13.

SO_2 42401 92 WEST-GAEKE BUBBLER

This method differs only slightly from 42401-91 and offers no substantial advantages. Method 42401-91 should thus be used for uniformity.

SO_2 42401 93 CONDUCTIMETRIC BUBBLER

The method lacks specificity; Method 42401-91 should be used to obtain better measurements.

NO_2 42602-71 J-H BUBBLER (orifice)

NO_2 42602 91 J-H BUBBLER (frit)

The objections to these methods have been detailed in 38 FR 15174 (June 8, 1973): The collection efficiency is a function of NO_2 concentration and the presence of NO introduces a positive interference.

NO_2 42602 72 SALTZMAN

This manual method suffers from interferences from SO_2, ozone, PAN, and prolonged exposure to light, and cannot be used for periods over 30 minutes.

TOTAL O_x 44101 11 ALKALINE KI-INSTRUMENTAL

The alkaline KI method produces such variable results in different hands that data from one site cannot be compared with data from another.

TOTAL O_x 44101 13 MAST MODEL 742-Z

This method is identical to method 44101-15. Data collected using this analyzer should be reported as 44101-15.

TOTAL O_x 44101 51 PHENOLPHTHALIN

Results of this method do not agree with those obtained by other total oxidant methods.

TOTAL O_x 44101 81 ALKALINE KI BUBBLER

The alkaline KI method produces such variable results in different hands that data from one site cannot be compared with data from another.

TOTAL O_x 44101 82 FERROUS OXIDATION

Results of this method do not agree with those obtained by other total oxidant methods.

OZONE 44201 13 COULOMETRIC

This method is identical to method 44101-15. Data collected using this method should be reported as 44101-15.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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16. ABSTRACT

This report contains a designation of the acceptability of various analytical measurement methods currently in use. Each monitoring method is placed into one of three categories i.e., approved-Federal Reference Method (FRM) or equivalent; unapproved - not yet determined to be equivalent to the FRM; and unacceptable - known to yield measurements of poor accuracy and reliability and in most cases obsolete.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Federal Reference Methods Unapproved Methods Unacceptable Methods SO_2 TSP CO NO_2 and Photochemical Oxidants		

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