



NARSTO Measurement Methods Compendium

Introduction to the Compendium

Accurate and reliable measurements provide the data essential for the advancement of ozone science. The NARSTO Measurement Methods Compendium serves as a clearinghouse of atmospheric measurement techniques, both standard ones such as those documented as Federal Reference Methods and those still in developmental stages. We believe that offering methods descriptions in this concise compendium format will serve the ozone and aerosol research community and the general public by facilitating discussion and exchange of information, providing signposts to key literature sources and intercomparison results, and identifying pitfalls associated with individual methods.

The techniques presented in the NARSTO compendium include those used for physical and chemical characterizations related to ozone and aerosols. Also included are the meteorological measurement techniques that provide data for understanding the transport, formation, and transformation mechanisms of the pollutants. The compendium is organized into three areas; gas-phase species, atmospheric aerosols, and meteorology.

- The measurement methods for gas-phase species are further divided into oxidants, nitrogen species, volatile organic compounds, and aerosol precursors.
- The aerosol section describes measurement methods specifically related to the physical and chemical characterization of atmospheric particulate matter that is closely linked to ozone. The physical characterization of particles generally includes the number, mass, size, shape, morphology, light scattering and absorptive properties, and refractive index. The chemical analysis typically involves the detection of the amount of chemicals associated with single particles or particles accumulated on filters.
- The meteorological section presents the standard and state-of-the-art measurement techniques currently used in ozone and aerosol research. The Methods Compendium includes sections that describe techniques used to assess wind field, the thermodynamic state of the atmosphere, radiation field, and cloud parameters at the surface, aloft, and in profiles.

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NARSTO Measurement Methods Compendium

Access Method Descriptions

- **Oxidants**
 - [Ozone \(O₃\)](#)
 - HO₂ and RO₂
 - H₂O₂ and other Peroxides
- **Nitrogen Containing Species**
 - NO
 - [NO₂](#)
 - PAN and other Peroxy Nitrates
 - Nitrate Radicals
 - HNO₃
 - NO_y
- **VOC**
 - [Sampling and Analysis Summary Information for PAMS VOC Target Species](#)
 - [NMOC](#)
 - HCHO
 - Alcohols and Higher Carbonyls
 - Organic Acids
- **CO**
- **R&D Ozone and Precursor Methods**
 - [Chemical Ionization Mass Spectrometry](#)
 - [Differential Absorption LIDAR \(DIAL\)](#)
 - [Differential Optical Absorption Spectrometry \(DOAS\)](#)
 - [Laser-Induced Fluorescence \(LIF\)](#)
 - [Matrix Isolation Electron Spin Resonance \(MIESR\)](#)
 - [Tunable Diode Laser Absorption Spectroscopy \(TDLAS\)](#)
- **Aerosol Precursors**
 - SO₂
 - Reduced Sulfur
 - H₂SO₄
 - Ammonia
- **Particulate Matter**
 - [PM₁₀](#)
 - [PM_{2.5}](#)

For definitions of method description terms see the [Annotated Method Description Outline and Definitions](#).

For more information, see the Ambient Monitoring Technology Information Center's home page at <http://www.epa.gov/ttnamti1>.

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NARSTO Measurement Methods Compendium

Ozone Methods

I. Ozone (O₃)

A. Chemiluminescence with Ethylene (C₂H₄) - (FRM)

1. Basis: Chemiluminescence is the technique used to measure an analyte by mixing it with a species with which it reacts to form light. The intensity of the light is proportional to the concentration of pollutant, and this intensity can be measured.
2. Range: 0.0-0.5 ppmv (FRM requirement)
3. Minimum Detection Level: 0.002-0.005 ppmv
4. Operating Temperature: N/A
5. Known Interference: Water vapor (3% H₂O by volume at 25°C, based on tests at O₃ concentrations of 0.085 to 0.32 ppmv and at H₂O concentrations of 1 to 3%)
6. Notes of Interest: Chemiluminescence with compounds other than ethylene can also be used to measure ozone (i.e., eosin-Y, Rhodamine B organic dye). Rhodamine B organic dye is the only other chemiluminescent compound to be named a Federal Equivalence Method (FEM).
7. Instruments - Manufacturer:
 - a. Beckman Model 950A Ozone Analyzer - [Beckman Coulter](#)
 - b. Bendix or Combustion Engineering Model 8002 Ozone Analyzer - Bendix Corporation (refer to [ABB Process Analytics](#))
 - c. Columbia Scientific Industries Model 2000 Ozone Analyzer - Columbia Scientific Industries
 - d. McMillan (MEC) Models 1100-1, 1100-2, and 1100-3 Ozone Meters - McMillan Electronics Corp. (a subsidiary of Columbia Scientific Industries)
 - e. Meloy Model OA325-2R and OA350-2R Ozone Analyzers - Meloy Instruments Inc.
 - f. Monitor Labs Model 8410E Ozone Analyzer - [Monitor Labs Inc.](#)
 - g. Phillips PW9771 O₃ Analyzer - Phillips Electronic Instruments Inc. (utilizes measurement by chemiluminescence with Rhodamine B)
 - h. Luminox Ozone Analyzer (LOZ-3) - Unisearch Associates, Inc. (utilizes measurement by chemiluminescence with eosin-Y. See Notes of Interest)
8. References: 3, 4, 5, 12, 23 ([Go to References](#))

B. Ultraviolet (UV) Photometry - (FEM)

1. Basis: Upon exposure to UV light, ozone will absorb some of the light and the intensity difference will be directly proportional to the concentration of ozone. Frequently the UV light source is a 254 nm emission line from a mercury discharge lamp.
2. Range: 0-1 ppmv
3. Minimum Detection Level: 2-5 ppbv
4. Operating Temperature: 10°C-40°C

5. Known Interference: Gaseous hydrocarbons with strong absorption at 254 nm, such as aromatic hydrocarbons (i.e., benzene and substituted benzene rings).
6. Notes of Interest: N/A
7. Instrument - Manufacturer:
 - a. Advanced Pollution Instruments, Inc. Model 400 Ozone Analyzer - Advanced Pollution Instruments, Inc.
 - b. Dasibi Models 1003-AH, 1003-PC, 1003-RS, 1008-AH, 1008-PC, and 1008-RS Ozone Analyzers - Dasibi Environmental Corp.
 - c. Envirionics Series 300 Ozone Analyzer - [Envirionics Inc.](#)
 - d. Environment S.A. Model O₃41M UV Ozone Analyzer - [Environment S.A.](#)
 - e. Horiba Instruments Model APOA-360 Ozone Monitor - [Horiba Instruments Inc.](#)
 - f. Monitor Labs Model 8810, ML9810, MI9810B, ML9811, and ML9812 Ozone Analyzers - [Monitor Labs Inc.](#)
 - g. Lear Siegler Model 8810 and ML9810 Ozone Analyzers - Lear Siegler Measurement Controls Corp. (available through [Monitor Labs Inc.](#))
 - h. Wedding & Associates Model 1010 Ozone Analyzer - Wedding & Associates Inc. (a subsidiary of [Thermo Environmental Instruments Inc.](#))
 - i. PCI Ozone Corporation LC-12 Ozone Analyzer - [PCI-WEDECO](#)
 - j. Thermo Electron Models 49 and 49C U.V. Photometric Ambient O₃ Analyzers - [Thermo Environmental Instruments Inc.](#)
8. References: 3, 4, 23 ([Go to References](#))

C. Differential Optical Absorption Spectrometry (DOAS) - (FEM)

1. Basis: The wavelength of light where a distinct absorption peak occurs is determined for an analyte. A wavelength (λ_1) on either side of the absorption peak is next determined. The intensity of a light source at wavelength (λ_1) is measured, and then the intensity is measured again after the light passes through the analyte. The difference of the intensities is proportional to the concentration of the analyte.
2. Range: 0-0.5 ppmv
3. Minimum Detection Level: 0.0015 ppmv
4. Operating Temperature: 20°C-30°C with -50°C to +50°C air temperature.
5. Known Interference: Anything that interrupts the path of the laser will cause some interference (i.e., animals, cars, planes, etc.).
6. Notes of Interest: DOAS is a long-path measuring technique. Measurements can be made in an optical pathway from 0.5 to 10 kilometers in length.
7. Instrument - Manufacturer:
 - a. OPSIS Model AR 500 System and System 300 Open Path Ambient Air Monitoring Systems for Ozone - manufactured by [OPSIS AB of Sweden](#) (available from [ABB Power Plant Controls, Inc.](#))
8. References: 3, 4, 14, 15, 23 ([Go to References](#))

For definitions of method description terms see the [Annotated Method Description Outline and Definitions](#).

For more information on FRM/FEM instrumentation, visit the [AMTIC home page](#).



NARSTO Measurement Methods Compendium

NO₂ Methods

I. NO₂

A. Chemiluminescence after NO₂ conversion to NO - (FRM)

1. Basis: Chemiluminescence is the technique used to measure an analyte by mixing it with a species with which it reacts to form light. The intensity of the light is proportional to the concentration of the analyte and can be measured. Ambient air is flooded with excess ozone, which reacts with NO to produce excited NO₂. The NO₂ emits a photon as it returns to ground state. The NO₂ in a second ambient air sample is then reduced to NO by a converter. The new NO concentration can again be measured by chemiluminescence. The difference of the concentrations is the concentration of NO₂.
2. Range: 0.25 - 25 ppmv
3. Minimum Detection Level: 0 .005 ppmv
4. Operating Temperature: N/A
5. Known Interference: Water vapor above 20 ppm concentration. NO₂ to NO converter specific interference:
 - a. *Catalytic reduction using heated molybdenum* - PAN (375°C, 450°C); ethyl nitrate; ethyl nitrite; HONO; HNO₃ (350°C, 375°C, 450°C); methyl nitrate, n-propyl nitrate, n-butyl nitrate, nitroresol (450°C)
 - b. *Catalytic reduction using heated stainless steel* (650°C) - NH₃, CH₃NH₂, HCN, N₂O
 - c. *Reaction with CO over a gold catalyst surface* - n-propyl nitrate; HNO₃, N₂O₅, PAN (3,000 ppm CO over 300°C gold surface); HCN, NH₃ (except in the presence of water vapor under 700°C)
 - d. *Reaction with iron sulfate (FeSO₄) at room temperature* - PAN, HONO, and other nitrogen-containing species (dry conditions)
 - e. *Reaction with carbon at 200°C* - PAN (285°C), HNO₃ (285°C), n-propyl nitrate, phosgene, trichloroacetyl chloride, chloroform, chlorine, hydrogen chloride,

photochemical reaction products of perchloroethylene-NO_x mixtures, photochemical reaction products of molecular chloride (Cl₂)-NO_x mixtures, photochemical reaction products of molecular chloride (Cl₂)-methanethiol mixtures, methanethiol, ethanethiol, ethyl sulfide, ethyl disulfide, methyl disulfide, 3-methylthiophene, H₂S, 2,5-dimethylthiophene, methyl sulfide, methyl ethyl sulfide

- f. *Photolysis at 320-400 nm* - HONO; NO₃; HO₂NO₂; N₂O₅

6. Notes of Interest: N/A

7. Instrument - Manufacturer:

- a. Advanced Pollution Instrumentation, Inc. Model 200 NO₂ Analyzer - Advanced Pollution Instrumentation, Inc.
- b. Advanced Pollution Instrumentation, Inc. Model 200A NO₂ Analyzer - Advanced Pollution Instrumentation, Inc.
- c. Beckman Model 952-A NO/NO₂/NO_x Analyzer - [Beckman Coulter](#)
- d. Bendix Model 8101-B Oxides of Nitrogen Analyzer - Bendix Corporation (refer to [ABB Process Analytics](#))
- e. Bendix/Combustion Engineering Model 8101-C Oxides of Nitrogen Analyzer - Bendix Corporation (refer to [ABB Process Analytics](#))
- f. Columbia Scientific Industries Models 1600 and 5600 Analyzers - Columbia Scientific Industries
- g. Dasibi Model 2108 Oxides of Nitrogen Analyzer - Dasibi Environmental Corp.
- h. Environnement S.A. Model AC31M NO Analyzer - Environnement S.A.
- i. Horiba Instruments Model APNA-360 NO-NO₂-NO_x Monitor - [Horiba Instruments Inc.](#)
- j. Monitor Labs Model 8440E Nitrogen Oxides Analyzer - [Monitor Labs Inc.](#)
- k. Monitor Labs Model ML9841B - [Monitor Labs](#)
- l. Monitor Labs/Lear Siegler Model 8840 and Model 8841 Nitrogen Oxides Analyzer - [Monitor Labs Inc.](#)
- m. Monitor Labs/Lear Siegler Models ML9841 and ML9841 - [Monitor Labs Inc.](#)
- n. Wedding and Associates Model 1030 NO₂ Analyzer - Wedding and Associates Inc. (a subsidiary of [Thermo Environmental Instruments Inc.](#))
- o. Phillips Model PW9762/02 NO/NO₂/NO_x Analyzer - Phillips Electronic Instruments, Inc.
- p. Thermo Electron/Thermo Environmental Instruments Model 14 B/E and Model 14 D/E - [Thermo Environmental Instruments Inc.](#)
- q. Thermo Environmental Instrument Model 42 and 42C NO/NO₂/NO_x Analyzer - [Thermo Environmental Instruments Inc.](#)

8. References: 1, 4, 5, 23 ([Go to References](#))

B. Differential Optical Absorption Spectrometry (DOAS) - (FEM)

1. Basis: The wavelength of light where a distinct absorption peak occurs is determined for an analyte. A wavelength (λ_1) on either side of the absorption peak is next determined. The intensity of a light source at wavelength (λ_1) is measured and then the intensity is measured again after the light passes through the analyte. The difference of the intensities is proportional to the concentration to the analyte.
2. Range: 0-500 ppbv
3. Minimum Detection Level: 4 ppbv
4. Operating Temperature: 20°C-30°C and an air temperature of -50°C-50°C
5. Known Interference: Anything that interrupts the path of the laser will cause some interference (i.e., animals, cars, planes, etc.).
6. Notes of Interest: DOAS is a long path measuring technique. Measurements can be made in

an optical pathway from 1 to 10 kilometers.

7. Instrument - Manufacturer:
 - a. OPSIS Model AR 500 and System 300 Open Path Ambient Air Monitoring System for NO₂ - manufactured by [OP SIS AB of Sweden](#) (available from [ABB Power Plant Controls, Inc.](#))
8. References: 1, 4, 8, 14, 15 ([Go to References](#))

C. Sodium Arsenite Method - (FEM)

1. Basis: Ambient air is bubbled with an orifice bubbler through a solution of sodium hydroxide (NaOH). The NO₂ is reduced to nitrite. The nitrite is reacted with sulfanilamide and N-1-naphthylethylenediamine (NEDA) in acid media to form an azo dye. The dye can be analyzed with a spectrophotometer at 540 nm.
2. Range: 30-150 ppbv
3. Minimum Detection Level: 5 ppbv
4. Operating Temperature: N/A
5. Known Interference: NO and CO₂ are known interferences but at concentrations far exceeding those found in ambient air. The role of SO₂ as an interference has not been determined.
6. Notes of Interest: The original manual FRM was the Jacobs-Hochheiser Method. The method was withdrawn in 1973 by the EPA and is now considered unacceptable for air sampling and analysis.
7. Instrument - Manufacturer: This is a manual method.
8. References: 1, 11 ([Go to References](#))

D. Sodium Arsenite Method Technicon II Automated Analysis System - (FEM)

1. Basis: Ambient air is bubbled with an orifice bubbler through a solution of sodium hydroxide (NaOH). The NO₂ is reduced to nitrite. The nitrite is reacted with sulfanilamide and N-1-naphthylethylenediamine (NEDA) in acid media to form an azo dye. The dye can be analyzed with a spectrophotometer at 540 nm. This method is considered a continuous method because hardware is used to make continuous measurements of the concentration of NO₂.
2. Range: 30-150 ppbv
3. Minimum Detection Level: 5 ppbv
4. Operating Temperature: N/A
5. Known Interference: NO and CO₂ are known interferences but at concentrations far exceeding those found in ambient air. The role of SO₂ as an interference has not been determined.
6. Notes of Interest: The original manual FRM was the Jacobs-Hochheiser Method. The method was withdrawn in 1973 by the EPA and is now considered unacceptable for air sampling and analysis.
7. Instrument - Manufacturer: No current information on Technicon could be located.
8. References: 1, 11 ([Go to References](#))

E. TGS-ANSA - (FEM)

1. Basis: Ambient air is bubbled with an orifice bubbler through a solution of triethanolamine, guaiacol, and sodium metabisulfite (TGS). The NO₂ is reduced to nitrite and then reacted with sulfanilamide and 8-amino-1-naphthalene-sulfonic acid ammonium salt (ANSA) to form an azo dye. The dye is analyzed with a spectrophotometer at 550 nm.
2. Range: 30-150 ppbv
3. Minimum Detection Level: 8 ppbv
4. Operating Temperature: N/A
5. Known Interference: No interference from NH₃, CO, formaldehyde, NO, phenol, O₃, or SO₂.
6. Notes of Interest: The original manual FRM was the Jacobs-Hochheiser Method. The method

was withdrawn in 1973 by the EPA and is now considered unacceptable for air sampling and analysis.

7. Instrument - Manufacturer: This is a manual method.

8. References: 1, 10 ([Go to References](#))

For definitions of method description terms see the [Annotated Method Description Outline and Definitions](#).

For more information on FRM/FEM instrumentation, visit the [AMTIC Designated Methods -- NO₂](#).

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Sampling and Analysis Summary Information for PAMS VOC Target Species

See Methods for VOCs on Next Page

Number of VOC Compounds = 60

Compound Name	IUPAC Name (if different)	Group Designation (note 1)	AIRS Parameter Number (note 1)	Boiling Point (degrees C) (note 2)	Volatility	CAS Number (note 2)	Sampling Method Alternatives (note 3)	Separator (note 4)	Detector (note 5)	EPA Ref. Desig. For Current Method (note 6)	Detection Limit (ppbv) (note 6)	Alternative Methods (possibly lower cost) (note 6)
1	Ethane		43202	-88.5	Very vol.	74-84-0	Multi-adsorbent	GC	MS	TO-17	0.2-25	No alternative
2	Propane		43204	-42	Very vol.	74-98-6	Multi-adsorbent	GC	MS	TO-17	0.2-25	No alternative
3	Isobutane	2-Methylpropane	43214	-12	Very vol.	75-28-5	Can+ads or Can	GC	MS/FID	TO-15	0.2-25	TO-14A
4	n-Butane		43212	0	Very vol.	106-97-8	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
5	Isopentane	2-Methylbutane	43221	28	Very vol.	78-78-4	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
6	n-Pentane		43220	36	Very vol.	109-66-0	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
7	Cyclopentane		43242	49	Very vol.	287-92-3	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
8	2,2-Dimethylbutane		43244	50	Med. vol.	75-83-2	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
9	2,3-Dimethylbutane		43284	58	Med. vol.	79-29-8	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
10	2-Methylpentane		43285	60	Med. vol.	107-83-5	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
11	3-Methylpentane		43230	63	Med. vol.	96-14-0	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
12	n-Hexane		43231	69	Med. vol.	110-54-3	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
13	Methylcyclopentane		43282	72	Med. vol.	96-37-7	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
14	Cyclohexane		43248	81	Med. vol.	110-82-7	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
15	2,4-Dimethylpentane		43247	81	Med. vol.	108-08-7	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
16	2-Methyl hexane		43263	90	Med. vol.	591-76-4	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
17	2,3-Dimethylpentane		43291	90	Med. vol.	565-59-3	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
18	3-Methylhexane		43249	92	Med. vol.	6131-24-4	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
19	2,2,4-Trimethylpentane		43250	99	Med. vol.	540-84-1	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
20	n-Heptane		43232	99	Med. vol.	142-82-5	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
21	Methylcyclohexane		43261	101	Med. vol.	108-87-2	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
22	2,3,4-Trimethylpentane		43252	114	Med. vol.	565-75-3	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
23	2-Methylheptane		43960	118	Med. vol.	592-27-8	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
24	3-Methylheptane		43253	119	Med. vol.	6131-25-5	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
25	n-Octane		43233	126	Less vol.	111-65-9	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
26	n-Nonane		43235	151	Less vol.	111-84-2	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
27	n-Decane		43238	174	Less vol.	124-18-5	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
28	n-Undecane		43954	196	Less vol.	1120-21-4	Can+ads/can	GC	MS/FID	TO-15	0.2-25	TO-14A
29	n-Dodecane		43141	217	Less vol.	112-40-3	Can+ads	GC	MS	TO-15	0.2-25	No alternative
1	Acetylene	Ethyne	43206	-85	Very vol.	74-86-2	Multi-adsorbent	GC	MS	TO-17	0.2-25	No alternative
1	Ethylene	Ethene	43203	-104	Very vol.	74-85-1	Multi-adsorbent	GC	MS	TO-17	0.2-25	No alternative
2	Propylene	1-Propene	43205	-48	Very vol.	115-07-1	Multi-adsorbent	GC	MS	TO-17	0.2-25	No alternative
3	1-Butene		43280	-6	Very vol.	106-98-9	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
4	trans-2-Butene		43216	1	Very vol.	624-64-6	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
5	cis-2-Butene		43217	4	Very vol.	590-18-1	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
6	1-Pentene		43224	30	Very vol.	109-67-1	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
7	Isoprene	2-Methyl-1,3-butadiene	43243	34	Very vol.	78-79-5	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
8	trans-2-Pentene		43226	36	Very vol.	646-04-8	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
9	cis-2-Pentene		43227	37	Very vol.	627-20-3	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
10	1-Hexene		43245	63	Med vol.	592-41-6	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
1	Benzene		45201	80	Med. vol.	71-43-2	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
2	Toluene	Methyl-benzene	45202	111	Med. vol.	108-98-3	Can+ads/can/CMS	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-2
3	Ethylbenzene		45203	136	Less vol.	100-41-4	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
4	meta-Xylene	1,3-Methyl-benzene	45109	139	Less vol.	108-38-3	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
5	para-Xylene	1,4-Methyl-benzene	45109	138	Less vol.	106-42-3	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
6	Styrene	Ethenyl-benzene	45220	145	Less vol.	100-42-5	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
7	ortho-Xylene	1,2-Methyl-benzene	45204	145	Less vol.	95-47-6	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
8	Isopropylbenzene (cumene)	1-Methyl-ethyl-benzene	45210	152	Less vol.	98-82-8	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
9	n-propylbenzene	Propyl-benzene	45209	159	Less vol.	103-65-1	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
10	m-Ethyltoluene	1-Ethyl-3-methyl-benzene	45212	161	Less vol.	620-14-4	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
11	p-Ethyltoluene	1-Ethyl-4-methyl-benzene	45213	162	Less vol.	622-96-8	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
12	1,3,5-Trimethylbenzene		45207	165	Less vol.	108-67-8	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
13	o-Ethyltoluene	1-Ethyl-2-methyl-benzene	45211	165	Less vol.	611-14-3	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
14	1,2,4-Trimethylbenzene		45208	169	Less vol.	95-63-6	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
15	1,2,3-Trimethylbenzene		45225	176	Less vol.	526-73-8	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
16	m-Diethylbenzene	1,3-Diethyl-benzene	45218	181	Less vol.	141-93-5	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
17	p-Diethylbenzene	1,2-Diethyl-benzene	45219	184	Less vol.	105-05-5	Can+ads/can/cryog.	GC	MS/FID	TO-15	0.2-25	TO-14A/TO-3
1	Acetaldehyde	Ethanal	43503	20	Very vol.	75-07-0	Cartridge/Liquid Impinger	HPLC	UV	TO-11A	0.5-100	TO-5
2	Acetone	2-Propanone	43551	56	Med. vol.	67-64-1	Cartridge/Liquid Impinger	HPLC	UV	TO-11A	0.5-100	TO-5
3	Formaldehyde	Methanal	43502	-20	Very vol.	50-00-0	Cartridge/Liquid Impinger	HPLC	UV	TO-11A	0.5-100	TO-5

note 1: See lists and discussion in " Technical Assistance Document for Sampling and Analysis of Ozone Precursors" EPA/600/R-98/161 (USEPA, Human Exposure and Atmospheric Sciences Division, Research Triangle Park, North Carolina. September, 1998, Section 2, pp. 5-7.

note 2: Boiling Points and CAS numbers are found in "CRC Handbook of Chemistry and Physics," 79th Edition, D. R. Lide, ed., Boca Raton, January, 1998, Section 3, pp. 3-1 ff.

note 3: At a simple level, sampling procedures fall into either canister techniques or adsorbent techniques. But the five methods, TO2,3,14A,15 and 17, provide for alternatives within these two categories. In addition, adsorbents vary with respect to breakthrough limits and VOC volatilities. The abbreviations shown include: Can = canister of any type, CMS = carbon molecular sieve adsorbent, Cry = cryogenic concentration technique (types vary), Ads = adsorbent of type other than CMS, including multisorbent tubes. Generally, it is assumed that most canister sampling methods are more costly than most adsorbent methods. However, complex multi-adsorbent cartridges can be costly.

note 4: Gas chromatograph is the designated separation method for both mass spectrometer and flame ionization methods.

note 5: Although mass spectrometer is the method of detection given for the most recent EPA methods, flame ionization is shown as an alternative detector for Methods TO-14A and TO-2.

note 6: Detailed descriptions of methods TO-1 through TO-17 are shown at <http://www.epa.gov/ttn/amtic/airtox.html>.

METHODS FOR PAMS VOCs (note 1)

See VOC Species Information on Previous Page

Method Designation	Collector	Analyzer	Detector	Volatility category that method best matches (note 2)	Boiling pt. range (C) (note 1)	Most Appropriate Compounds	Detection limit (ppbv)	Cost comments and ratings: 1 = least costly (note 3)	Procedural Steps in Methods				
									1. Sample Collection	2. Sample Treatment	3. Sample Transfer	4. Separation	5. Detection, Identification, and Measurement
TO-1	Tenax cartridge	GC	MS	Less volatile	80 to 200	aromatic hydrocarbons, benzene, toluene, and xylene	0.01 to 100	2: MS is costly, but no canister required	1. Collect sample by drawing ambient air through Tenax cartridge.	2. Return to lab. Heat cartridge and purge with inert gas.	3. Transfer VOCs to cryog. trap, then heat trap for insertion of VOCs into GC.	4. Hold GC column at low temperature, then heat as VOCs are introduced.	5. Separate by GC and identify and measure by MS. ECD and FID are mentioned, but not identified as part of this method.
TO-2	Carbon molecular sieve cartridge	GC	MS FID	Medium volatile	-15 to 120	benzene, toluene	0.1 to 200	1: FID not as costly as MS, and no canister req.	1. Collect sample by drawing ambient air through CMS cartridge.	2. Return to lab and purge water vapor from cartridge with dry air and heated helium.	3. Transfer VOCs to cryog. loop (trap), then heat trap for insertion of VOCs into GC.	4. Hold GC column at low temperature, then heat as VOCs are introduced.	5. Separate by GC and identify and measure by MS. FID is identified as a possibly preferable for this method.
TO-3	Cryogenic canister	GC	FID	Medium volatile	-10 to 200	many VOCS	0.1 to 200	2: Cryog. canister system raises cost, but FID cheaper than MS	1. Collect sample by drawing ambient air through cryog. trap (container), e.g., immersed in liquid argon.	2. May use Nafion or other dryer before air goes into cryog. container.	3. No intermediate transfer.	4. Cryog. cont. intake valve is switched to GC column injection, possibly on site. Cont. is heated to 150 deg C.	5. Identify and measure compounds by FID (provides det. limits of 1 to 5 ng for many compounds).
TO-5	DNPH liquid impinger	HPLC	UV	Very volatile	-20 to 56	aldehydes and ketones	1 to 50	2: Uses HPLC	1. Draw ambient air into midget impinger containing 10 ml DNPH reagent	2. Place solution in vial and return to lab. Remove isooctane layer, extract aq.	3. Evaporate organic layers and dissolve residue in methanol.	4. Inject into HPLC.	5. Determine derivatives using UV detector at 370 nm.
TO-11A	DNPH Cartridge	HPLC	UV	Very volatile	-20 to 56	aldehydes and ketones	0.5 to 100	2: Similar to TO-5, but use of cartridge might be more costly	1. Draw ambient air into DNPH coated cartridge. Place cartridge in glass vial and seal.	2. Return to lab. Remove cartridge and wash with acetonitrile.	3. No further processing needed.	4. Acetonitrile solution is diluted and injected into HPLC.	5. Determine derivative by UV detection at 350 nm.
TO-14A	Canister / cryog. trap	GC	FID/ECD or MS	Medium volatile (covers almost all VOCs)	-29 to 213	non-polar VOCs	0.2 to 25	2: Canister system req., FID optional	1. Draw ambient air into canister (e.g. 6L) equipped with flow control device.	2. Return to lab. Dry with Nafion dryer or alternative.	3. Transfer VOCs to cryog loop (trap), then heat trap for insertion of VOCs into GC.	4. Separation in GC for transfer either to MS or to combination-detector system.	5. TO-14A describes either a two-way MS system (SCAN versus SIM) or a three-way FID-PID).
TO-15	Canister / sorbent trap	GC	MS	Medium volatile (covers almost all VOCs)	-50 to 240	polar/non-polar VOCs	0.2 to 25	3: Canister plus solid adsorbent with MS	1. Draw ambient air into canister (e.g. 6L) equipped with flow control device.	2. Return to lab. Pass sample through multisorbent packed tube. Purge water vapor with helium.	3. Cryog. trap concentrator optional.	4. Separation in GC.	5. identify and measure compounds by MS
TO-16	none	FTIR, open path	Infra-red spectrom.	Less volatile (covers med. also)	25 to 500	polar/non-polar VOCs		2: No sampling system req., but complex field equip.	1. No specific sampling system. All of the air in the line of the FTIR is "sampled".	2. none	3. none	4. none	6. Identify and measure compounds in open air by FTIR.
TO-17	Adsorbent tube	GC	MS	Very volatile (covers med. also)	-60 to 200	polar/non-polar VOCs	0.2 to 25	3: Uses multisorbent cartridge and MS	1. Draw ambient air through a multisorbent packed tube.	2. Seal and pack tube. Return to lab. Tube may be stored before analysis.	3. Transfer VOCs to intermediate adsorbent trap or directly to GC, by heating sampling tube.	4. Separation in GC.	5. Identify and measure compounds by MS.

Note 1 Most of the information in this table is from the EPA * Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, 2nd Edition, EPA/625/R-96/010b, January 1999, available at the AMTIC webpage <http://www.epa.gov/ttn/amtic/airtox.html>, or from descriptions of the individual Methods, available at the same webpage.

Note 2 Temperature ranges for the methods are found in the Compendium referenced above, Table 2, pages 5-10, or in the descriptions of the Methods, where the temperature range for the Method is inferred from tests for detection of VOCs Boiling Points and CAS numbers are found in "CRC Handbook of Chemistry and Physics," 76th Edition, D. R. Lide, ed., Boca Raton, January 1995, Section 3, pp.3-1ff.

Effective temperature ranges for adsorbents are found in the description for TO-17, Table 1, pp. 17-33 to 17-44

FOR VERY VOLATILE VOCs: (BP < 50) Choose an adsorbent (multisorbent) with capability of adsorbing in the required BP range. Then choose a TO Method with an adsorbent sampling procedure.

FOR MEDIUM VOLATILE VOCs: (50 < BP < 120) Choose either a canister or an adsorbent system which covers the BP range as precisely as possible, so as to avoid the cost of excess capability.

FOR LESS VOLATILE VOCs: (120 < BP) Choose either a canister or an adsorbent system of lowest possible cost.

Note 3 The assumptions underlying the cost comments are, that in general, canister sampling is more costly than adsorbent because of the equipment required for field air intake, and that MS is a more costly method than FID because of the higher equipment cost. However, there are always tradeoffs, for example, between equipment cost and personnel training costs. And some sorbent cartridges may well be as costly as the comparable canister equipment.

	HIGHLY VOLATILE	MEDIUM VOLATILE	LESS VOLATILE
SAMPLING: canister adsorbent cann/ads	TO-14A(?) TO-17 TO-15 (?)	TO-14A TO-2 TO-15	none TO-3 TO-1
DETECTION: mass spec flame ion.	TO-15, TO-17 TO-14A (?)	TO-2, TO-14A TO-2, TO-14A	TO-1 TO-3
	(?) = not optimal match of ranges.		



NARSTO Measurement Methods Compendium

NMOC Methods

I. Non-methane Organic Carbons (NMOC) Group

A. Cryogenic Preconcentration and Direct Flame Ionization Detection

1. Basis: The basis of the method described here, which is intended to obtain an aggregate measure for NMOCs, is, first, to separate methane, oxygen, and nitrogen from the sample by a cryogenic technique using liquid argon. Next, the entire sample can then be evaluated in a flame ionization detector (FID) to obtain a total value for NMOCs. Basis for commonly known EPA Method TO-12 (Ref. 30, p. TO12-2).
2. Range: 0.1 to 200 ppmvC (Ref. 30, Project Summary, Table 2)
3. Minimum Detection Level: 10 ppb (Ref. 31), 50 ppb, using propane standard (0.15ppmvC, using propane standard) (Ref. 32)
4. Operating Temperature: 0 to 45°C (Ref. 31)
5. Known Interference: (See Ref. 30, Project Summary, Table 2, and Ref. 30, p. TO12-5).
 - a. High moisture levels in ambient air cause ice formation in the cryogenic trap process; can also require adjustment of FID baseline when calculating NMOC value.
 - b. If need arises to determine specific proportions of one or more species, must change to different process.
 - c. If unusual types of organic compounds, outside the VOC category, are in the sample, the FID measurement loses reliability (precision).
 - d. Other gasses, such as oxygen, nitrogen, and methane, if present in large amounts, and also interfere with this method, and some devices will specify the limits of the range of these gasses, for example: CH₄, 0.0 to 2500 ppm (Ref. 31).
6. Notes of Interest:
 - a. Simple standard procedures are used, and automated canister equipment is available to reduce personnel field time.
 - b. Adsorbent materials can be used with TO-12, but are not defined as part of the method. Contaminants and reactions that occur with adsorbents may be a problem. Storage of samples in the canisters is possible.
 - c. Low background noise problem helps improve sensitivity (LDL). The method suggests that sampling canisters be considered free of contamination if they contain less than 0.02 ppmC hydrocarbons (Ref. 30, p. TO12-14).
 - d. Total NMOC values are useful as a screening variable for sites or areas where no other monitoring equipment is installed.
 - e. Analysis is much faster and cheaper because GC not used.
 - f. State of the art of ambient air quality modeling has not clarified whether specific (individual) volatile organic compound (VOC) measurements will be absolutely necessary as input variables for models which predict ambient air quality, rather than total non-methane organic compounds (NMOC). Further model development may indicate that NMOC values will be useful ozone predictors for some conditions.

- g. The term volatile organic compounds generally refers to gaseous organic compounds that have a vapor pressure greater than 0.15 mm and generally have a carbon content ranging from C1 through C12 (Ref. 22, p. 3-107). Reference 22 also describes how the terms nonmethane organic carbons (NMOCs) and nonmethane hydrocarbons (NMHCs) have come into use. Interest in a simple method for some large group of VOCs has led to the current definition of EPA method TO-12 as a method for all NMOCs, including the NMHC, carbonyl, and polar subgroups.
 - h. EPA has defined two separate methods, TO-5 and TO-11A, both of which use a UV detector, for specifically measuring the carbonyls. Furthermore, three newer methods, TO-15 (GC/MS), TO-16 (FTIR), and TO-17 (GC/MS), are intended to separate and to measure every VOC, including those in polar and non-polar groups. Descriptions of all of these methods are contained in Reference 30 (Project Summary).
 - i. Regarding "lower detection limit": The VOCs are expected to occur in urban ambient air at concentrations possibly less than 0.1ppbC. This level, given by Reference 33 (Section 2.3.1, page 9), is much lower than the level given in the discussion for TO-12 (5 to 7 ppmC, page TO12-3), because this very low level refers to levels of individual compounds.
 - j. The units ppmC, sometimes given as ppmvC, means that the volume concentration of the gas is multiplied by the number of carbon atoms in the molecule.
7. Instruments - Manufacturer:
- a. Model 51 Flame Ionization Detector (heated total hydrocarbon analyzer) - Thermo Environmental Instruments Inc. <http://www.thermoei.com/>
 - b. Model 55C Direct Methane, Non-Methane Analyzer (uses combined gas chromatography and flame ionization detector, can separate methane without cryogenic preconcentration) - Thermo Environmental Instruments Inc. <http://www.thermoei.com/>
 - c. Model NGA 2000 McFID Methane, Non-Methane Hydrocarbon Analyzer (uses combined gas chromatography and flame ionization detector, cryogenic preconcentration not required) - Rosemount Analytical Inc. <http://www.frco.com/proanalytic/>
8. References: 30, 31, 32, 22, 33 ([Go to References](#))

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NARSTO Measurement Methods Compendium

CO Methods

I. CO

A. Non-Dispersive Infrared Photometry (NDIR) - (FRM)

1. Basis: Infrared light from a conventional source passes through two parallel cells. The reference cell contains a gas that will not absorb the radiation. The sample cell is continuously pumped with ambient air. The CO in the sample cell will absorb radiation at $\sim 4.6 \mu\text{m}$. The difference in the intensities of the light beams passing through the cells is used to determine the concentration of CO.
2. Range: 0-100 ppmv
3. Minimum Detection Level: 0.1-0.4 ppmv
4. Operating Temperature: Relatively independent of normal ambient air temperature changes.
5. Known Interference: Water vapor and CO₂
6. Notes of Interest: There are two major varieties of NDIR analyzers: Luft-type detector and Gas-Filter Correlation (GFC) monitors. GFC monitors are smaller, eliminate interference from CO₂, and greatly reduce water vapor interference.
7. Instrument - Manufacturer:
 - a. Advanced Pollution Instrumentation, Inc. Model 300 CO Analyzer - Advanced Pollution Instrumentation, Inc.
 - b. Beckman Model 866 CO Monitoring System - [Beckman Coulter](#).
 - c. Bendix/Combustion Engineering Model 8501-5CA CO Analyzer - Bendix Corporation (refer to [ABB Process Analytics](#))
 - d. Dasibi Model 3003 and 3008 CO Analyzers - Dasibi Environmental Corp.
 - e. Environnement S.A. Model CO11M CO Analyzer - [Environnement S.A. Inc.](#) (refer to [Thermo Environmental Instruments Inc.](#))
 - f. MSA/LIRA Model 202S CO Analyzer System - [Mine Safety Appliances Company](#)
 - g. Thermo Electron/Thermo Environmental Instruments Models 48 and 48C - [Thermo Environmental Instruments Inc.](#)
8. References:

For definitions of method description terms see the [Annotated Method Description Outline and Definitions](#).

For more information on FRM/FEM instrumentation, visit the [AMTIC Designated Methods -- CO](#).

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NARSTO Measurement Methods Compendium

R&D Ozone and Precursor Methods

I. R&D Ozone and Precursor Methods

A. Chemical Ionization Mass Spectrometry

1. Basis: The ambient air sample is mixed with an ionized reagent, and the resulting mixture is introduced directly into a mass spectrometer, where ions are focused with ion optics (magnetic lenses), analyzed by a magnetic quadrupole and detected with a commercial ion multiplier. The multiplier connects to a discriminator/preamplifier which converts ion signals into TTL pulses. A computer is required to convert the signals to a graphic spectrum presentation (See Figure 1) (Ref. 34).

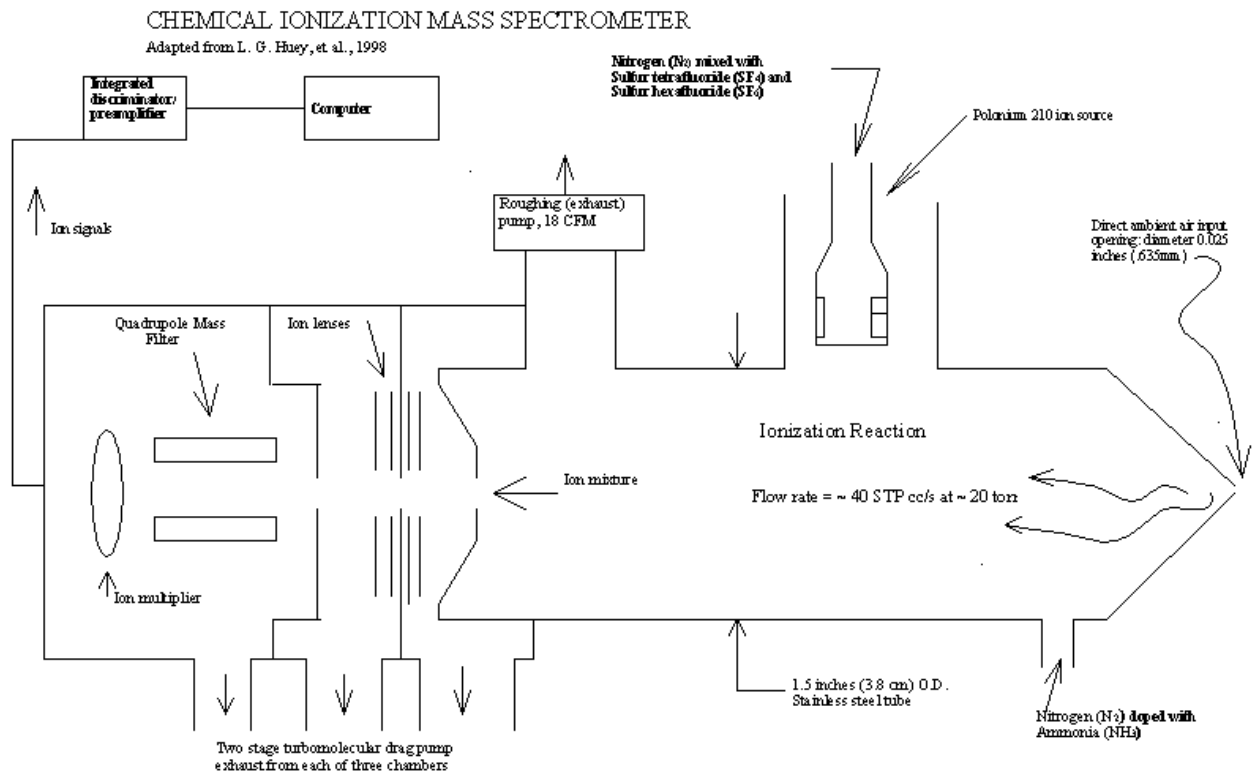


Figure 1: Chemical Ionization Mass Spectrometer.

2. Range: Ambient air levels of .30 pptv (one part in 1012) to 1000 pptv (1000 parts in 1012, or one part in 109) (Ref. 34).
3. Minimum Detection Level: in ambient air .15 pptv in one second of integration (Ref. 34).
4. Operating Temperature: February to May in Boulder, Colorado, including temperatures above 20°C (Ref. 34).
5. Known Interference:
 - a. High levels of formic acid (HCO₂H) from on site sources were found to be a possible source of interference if measurement of formic acid as an ambient air pollutant were to be attempted.
 - b. Internal (within instrument) levels of nitric acid were high enough (10 to 20 percent of ambient air levels) to interfere with measurement. Interference was solved with a nylon wool scrubber.
 - c. Sensitivity to nitric acid is a function of temperature within the instrument because the reaction is in equilibrium, and the equilibrium constant is sensitive to temperature changes. A large flow of dry N₂ is used to bring the incoming ambient air to the internal temperature
6. Notes of Interest:
 - a. This method was developed to measure gas phase nitric acid, but can also be used to measure formic acid. Nitric acid is not only an abundant pollutant, but also acts as a sink for NO_x in the troposphere, so that its role is complicated, and probably important in air quality modeling (Ref. 35).
 - b. Huey et al. (Ref. 34) report that typical uncertainty for ambient air monitoring is +/- 35 percent for any given measurement. A 25 percent error occurs in the calibration for, which arises from fluctuations in the permeation rate and the temperature of the flow tube.
 - c. The method described is an in situ method but it is intended for use in the field where ambient air is drawn directly into the measurement equipment, avoiding canister storage. However, as described, a computer is directly connected to the mass spectrometer, and some type of protective housing is necessary for the complete system.
 - d. Terms pertinent to the description of CIMS and the instrument schematic in Figure 1:
 - Ion multiplier -- an ion multiplier senses (detects) highly focused ions from a quadrupole mass filter. The output of the ion multiplier is an electrical signal which can feed into electronic equipment for conversion to recording or display (Ref. 36, Vol. 6, Page 204).
 - Ion lenses -- both electrostatic and magnetic lenses provide either converging or refracting action on charged particles. The power of these lenses is a function of their electrostatic or magnetic field and their accelerating voltage (Ref. 36, Vol. 6, Page 204).

- TTL pulses -- refers to bipolar transistor-to-transistor logic, where the first transistor performs an "AND" operation on the inputs and the second transistor performs an inversion. TTL transistor pairs are operated in the saturation mode, and this overdriving helps to limit noise in the output signal (Ref. 36, Vol. 10, Page 181).
 - Quadrupole mass filter -- a strong focusing magnetic lens where the converging action on the particle stream is directly proportional to the strength of the magnetic field (Ref. 36, Vol. 6, Page 204)
7. Instruments - Manufacturer:
- a. Kimball Physics, Inc. - <http://www.kimphys.com/>
 - b. Colutron Research Corp. - <http://www.colutron.com/products>
 - c. Ion Tech Inc. - <http://www.iontechinc.com/>
8. References: 34, 35, 36 ([Go to References](#))

NARSTO COMPENDIUM

R&D METHODS FOR PAMS/VOCS OZONE PRECURSORS

5. Differential Absorption LIDAR - DIAL

[[Basis](#) | [Range](#) | [Min. Detection Level](#) | [Operating Temp.](#) | [Interferences](#) | [Notes of Interests](#) | [References](#)]

1. Basis: LIDAR stands for Light detection and ranging. DIAL is an application of LIDAR but using powerful lasers directed into the atmosphere to measure content of the air in aerosols, dust, and gases. This is achieved by the direct impingement of the laser beam on these materials, and its subsequent reflection and scattering. Since the target substances vary in concentration along the axis (optical path) of the transmitted beam, the receiving telescope equipment analyzes the strength of the returning (reflected) beam continually during its reception (Ednar et al., 1995). This reflected beam strength is reduced from the original transmission strength by some level which is proportional to the concentration of the target matter.

The DIAL technique is used to measure species concentrations in the lower few kilometer of the atmosphere. The DIAL equipment uses two parallel laser beams, either from two separate lasers tuned slightly differently, or from a pulsing or switching system which separates a single beam into two beams with slightly different wavelengths ([Fig. 1](#)). Fig. 1 is after Browell (1989). One of the two beams is tuned to the absorption wavelength of the target chemical species, and the other beam is tuned to a slightly different wavelength so that it is not absorbed. In other words, DIAL consists of two coordinated lidar beams. The assumption is made that the difference in the strength of the two reflected beams will be a measure of the concentration of the target species (McGraw Hill, 1992).

2. Range: The analysis range refers to the typical span of species concentrations that are measured by lidar/DIAL instruments. Various applications report the following concentrations, but they are NOT the concentration span that the instruments may be capable of.

a. Lidar: single ozone 15 to 75 ppbv 0 to 2700 m, laser with multi-beams, ground based (Zhao and Hardesty, 1996)

b. DIAL, ozone 20 to 65 ppbv at 950 m by aircraft (Senff et al., 1998)

c. UV-DIAL, ozone 42 to 82 ppbv, 450 to 1825 m by aircraft (Alvarez et al., 1998)

e. DIAL, SO₂ approx. 100-200 µg/m³, 0 - 150 m by ground based equipment (Ednar et al., 1995)

f. DIAL, NO₃ 133 - 211 pptv, 0 - 7.5 km by ground based equipment (one part in 10¹²) combined with DOAS (Povey et al., 1998)

3. Minimum detection limit: Ozone, 15 ppbv (Alvarez et al., 1998); SO₂, 100 µg/m³ (Ednar et al., 1995); NO₃, 133 - 211 pptv (Povey et al., 1998)

4. Operating temperature: The LIDAR equipment including DIAL optical housing, electronics, computer equipment, etc. typically is within an climate control enclosure (a trailer or an aircraft), therefore, the operating temperature is controlled to human comfort level ~ 70-72°F.

5. Known Interference:

- a. Use of a CO₂ laser relies on existence of sufficient aerosols in the atmosphere to provide useful backscatter. Visible and UV wavelengths must be used by molecular backscatter. The tuning difficulties of the CO₂ laser make the task of searching among and eliminating non-target species difficult (Grant et al., 1992).
- b. Chemical species absorption wavelengths may be temperature and pressure dependent, making it necessary to check these variables before tuning laser (Grant et al., 1992).
- c. Wind speed and direction will also cause measurements to change rapidly, since the target mass could be shifting location and mixing ratio (concentration) rapidly (Ednar et al., 1995).

6. Notes of Interest:

- a. The development of lidar and DIAL represents the hope that constituents of ambient air can become precisely measurable in some simple, remote sensing manner, over a wide range of altitudes, with greater convenience than any of the traditional techniques, such as the Fourier Transform Infrared (FTIR) open path technique which requires two pieces of equipment, one at each end of the beam pathway, or Laser Induced Fluorescence (LIF), which has not advanced beyond in situ applications.
- b. The application of lasers has been seen as the key to the use of spectroscopic principles in achieving the goal of remote sensing. Single laser beams with receivers (i.e., lidar alone) have been used to measure amounts of aerosols, dust, and molecular masses if they are dense enough to provide detectable reflection of the laser, called "backscatter" in the case of large volume substances (McGraw Hill, 1992).
- c. DIAL has been used since the mid-1960 s to measure atmospheric constituent species, including O₃, SO₂, Cl₂, NO, NO₂, and Hg (Grant et al., 1992).
- d. Due to advances in laser technology, lidars have also ramified into more or less distinct laser applications and design variations: Atmospheric lidars are sometimes divided into either aerosol/dust lidars and gas molecule lidars (Senff et al., 1998).
- e. Other lidar variations include:
 - Rayleigh lidars: designed to measure molecular scattering and thus determine atmospheric density and temperature profiles.
 - Resonance fluorescence lidars: intended to identify atomic or molecular substances by the level of fluorescence detected at specific wavelengths.
 - Raman lidars: intended to measure shifts in wavelength between the transmitted signal and the scattered signal, and have been used in the lower atmosphere to measure water vapor.
 - Doppler lidars: designed to measure Doppler shifts in frequency in order to determine velocity of tropospheric winds.

7. References:

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NARSTO COMPENDIUM

R&D METHODS FOR PAMS/VOCS OZONE PRECURSORS

Differential Optical Absorption Spectrometry (DOAS)

A. Basic Principles

Spectrometry is a chemical analysis technique that makes use of the features of electromagnetic radiation, including light. This radiation proceeds through space in a form which has a measurable wavelength, and a measurable energy or intensity. When the radiation passes through a substance such as the atmosphere it is modified and distorted by the molecules of the many chemical components which are mixed together in the substance.

Differential optical absorption spectrometry (DOAS) measures the absorption through an atmospheric path (typically 0.5 to 1.5 km) of two closely spaced wavelengths of light from an artificial source. One wavelength is chosen to match an absorption line (wavelength) of the compound of interest, and the other is close to but off that line, and is used to account for atmospheric effects. (EPA/600/P-93/004aF, p.3-98).

The term "absorption line" is used to mean a wavelength that a given atom or molecule absorbs more than it does other wavelengths. Thus, if a compound of interest were ozone, a wavelength would be identified which ozone - and ozone especially - absorbs more than other wavelengths.

A light beam containing this particular wavelength would be directed at a segment of the atmosphere, and the amount of the wavelength absorbed would be measured. This result would indicate how much ozone was present in that segment. A separate wavelength, varying slightly from the first, would be directed through the same segment, and its absorption would be compared with the first wavelength results to determine inadvertent absorption probably not due to ozone. This technique provides a comparison absorption level to improve accuracy in measuring the amount of radiation absorbed by the target molecule.

B. Range:

Span of species concentration measured by various DOAS instruments that were found in the literature are, for example:

SPECIES	LOW (ppbv)	HIGH (ppbv)	REFERENCE
p-xylene	2	280	Axelsson et al. (1995), p1259
ethylbenzene	4	450	Axelsson et al. (1995), p1259
1,2,3-trimethylbenzene	2	2700	Axelsson et al. (1995), p1259
NO ₂	9	135	Biermann et al. (1988), p1551

NO ₃	0.02	70	Biermann et al. (1988), p1551
Ozone (O ₃)	10	22	Stevens et al. (1993), p233
SO ₂	10	50	Stevens et al. (1993), p233

C. Minimum Detection Level:

Minimum Detection Level is defined as the lowest concentration of a species that DOAS devices can distinguish from background noise.

SPECIES	Minimum Detection Limit (ppbv)	REFERENCE
p-xylene	0.3	Axelsson et al. (1995), p1258
ethylbenzene	2	Axelsson et al. (1995), p1258
1,2,3-trimethylbenzene	6	Axelsson et al. (1995), p1258
NO ₂	4	Biermann et al. (1988), p1551
NO ₃	0.02	Biermann et al. (1988), p1551
Ozone (O ₃)	3	Stevens et al. (1993), p234
SO ₂	10	Stevens et al. (1993), p234

D. Operating Temperature:

An ambient air DOAS system was operated at an altitude of 15 meters above ground level in Lubbock, Texas (Vecera and Dasgupta, 1991). The average monthly temperature for April at Lubbock is about 18°C (Rudloff, 1981). In September and October, a DOAS light transmitter and receiver were operated on the roofs of EPA buildings, 20 meters above ground level in Research Triangle Park, North Carolina (Stevens et al., 1993). The average monthly temperature is estimated at 23°C and 18°C for those two months (Rudloff, 1981). In Jonkoping, Sweden, twelve months of continuous ozone monitoring were performed using a 750 meter retroreflector path, giving a total path length of 1500 meters (Axelsson et al., 1990). The average monthly temperatures range between -3°C to 16°C (Rudloff, 1981).

E. Known Interferences:

a. In open path DOAS applications, interference by miscellaneous atmospheric constituents is likely to be a problem. For example, in detecting ozone, oxygen is likely to interfere in the region below 270 nm. Sulphur dioxide has a strong absorption effect in the vicinity of 300 nm, and also presents interference, although weak, at 283 nm (Axelsson et al., 1990). Another example of species interference would be NO and NO₂ interfering with detection of HONO (Vecera and Dasgupta, 1991).

b. Heavy rain and fog, and even high humidity, have been found to interfere with the xenon lamp beam propagation, and to make absorption measurements impossible. The use of heaters on the lenses did not entirely solve this problem. However, it only becomes serious in very extreme conditions (Stevens et al., 1993).

c. In long path uses of UV light beams, atmospheric turbulence, such as that from thermal-induced effects, can distort reflections. One approach to solving this problem has been to use an extensive array of photodiode type receivers, but these arrays must all be calibrated, and can suffer from differences in surface coatings. Turbulence can be approached with other strategies, such as slotted disks, and new systems can be developed with these strategies (Edner et al., 1993). With advent of solid-state CCD and/or CMOS detectors, it is possible that a more robust detector can be built.

F. Notes of Interest:

a. In selecting any long path pollution monitoring strategy, DOAS should be compared with DIAL (Differential Absorption Lidar), a technique using pulsed lasers, either with wavelength switching, or with two separate wavelength laser sources. Although UV DOAS has problems with atmospheric interference, as noted above, it has not been abandoned in favor of the laser approach.

b. The DOAS approach has probably benefitted by the relatively simple applications which investigators have favored. In the meantime, DIAL and LIF (Laser induced fluorescence) may well have suffered from attempts to develop airborne and other mobile equipment. All of these techniques are still in the developmental stage, but the DOAS should continue to enjoy the advantage of an established beam source, the arc lamp, while laser sources include the tunable diode and the YAG, and may require the use of pumping and other ancillary technology.

G. References:

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NARSTO COMPENDIUM

R&D METHODS FOR PAMS/VOCS OZONE PRECURSORS

Laser-Induced Fluorescence (LIF)

A. Basic principle:

Fluorescence spectroscopy is widely used these days in environmental monitoring, clinical chemistry, DNA sequencing, genetic analysis, and many other applications. In excited singlet states, the electron in the excited orbital is paired (of opposite spin) to the second electron in the ground-state orbital. Consequently, return to the ground state is spin-allowed and accompany by emission of a photon. This process is called the "fluorescence emission" (Lakowicz, 1999; Garden et al., 1992; West, 1992). The emission light can be detected by using a device such as a photomultiplier tube, a diode array, and/or a charge-coupled device. The amount of analyte present in the sample is proportional to the intensity of the emission light (e.g., as in photon counts) of a specific wavelength and quantification is possible by using calibration data.

[Figure 1](#) shows a conceptual schematic of the laser-induced fluorescence process. Fluorescence measurements can be broadly divided into two types of measurements, steady-state and time-resolved. Steady-state measurements are those performed with constant illumination and observation. This is the most common type of measurement. The sample is illuminated with a continuous beam of light, and the intensity of emission spectrum is recorded. Because of the nanosecond timescale of fluorescence, most measurements are steady-state measurements. Time-resolved measurement is used for measuring intensity decays. For these measurements, the sample is exposed to a pulse of light, where the pulse width is typically shorter than the decay time of the sample. This intensity decay is recorded with a high-speed detection system that permits the intensity to be measured on the nanosecond timescale. A time-resolved system is generally more complex than the steady-state system, but the former offers the possibility of measuring much of the molecular information available from fluorescence that the steady-state time-averaging process does not. In atmospheric research, LIF method has been used mostly in the measurement of hydroxyl and hydroperoxyl radicals.

B. Operating Range: Strongly dependent upon individual instrument.

N/A

C. Detection Limit: Strongly dependent upon individual instrument.

An example is that Holland et al. (1995), Brune et al. (1992), and Bailey et al. (1997) inferred $\sim 10^5$ OH molecules cm^{-3} was the detection limit at the signal-to-noise ration greater than 2 for 1-minute data integration time.

D. Operating Temperatures: Instrument dependent.

LIF instruments are typically operated inside a climate-controlled housing (e.g., at normal room conditions) such that operating temperature, humidity, and so on remain at a stable level.

E. Known Interferences:

(a) Laser power modulation - laser excitation could generate OH radicals biasing the measurement (Wennberg et al., 1994)

(b) Chemical modulation - collision quenching of OH by ambient air molecules (Bailey et al., 1997)

F. Notes of Interest:

Use of LIF on measurement of ozone precursors such as OH and HO₂, primary oxidants in photochemical ozone production processes, has been done extensively. Use of LIF in the measurement of volatile organic compounds of interest to PAMS is under development.

G. Vocabulary Review:

(a) Hydroxyl radical: OH, an oxidant which plays a role in the conversion of trace gases to CO₂ or to water soluble components. It is typically shorter-lived in the troposphere than ozone, and its overall role in tropospheric chemistry is still under investigation.

(b) PAMS : Photochemical Assessment Monitoring Stations, defined in 40CFR, Part 58.1 (1998 edition). Part 58.41 describes the PAMS network, consisting of stations to collect data in ozone non-attainment areas. PAMS stations are required to report data on volatile organic carbons, as defined by EPA, and meteorological variables.

H. References:

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NARSTO COMPENDIUM

Research and Development Methods

Matrix Isolation Electron Spin Resonance

(MIESR)

A. Basic Principle:

The theory of electron spin and the related concept of magnetic dipole moment of the electron were postulated in 1925 in order to explain observed effects in the magnetic and x-ray spectra of certain atoms (Rich, 1992). The spectra appeared in the form of distinctive wavelength features of emitted resonance electromagnetic radiation when the molecules or atoms were subjected to magnetic flux conditions using magnetic flux instruments. Although theories use concepts such as "orbit" and "axis" to graphically describe the atomic structure, no similar theory exists that enables a simple pictorial depiction of electron spin. Nevertheless, application of spin resonance instruments and techniques enables the identification of atoms (and molecules, including radicals) and comprehension of their precise structure (Weissman, 1992).

Electron spin resonance analysis begins with the insertion of the atoms or molecules in a liquid solvent or cryogenic material (the matrix), and the use of a wide range of materials and temperatures has been reported. For example, o-Terphenyl was used at 275°C (Lewis and Singer, 1981), deuterium oxide (D₂O) at 77 K (Mihelcic et al., 1993), and Tetrahydrofuran at 203 K (Gescheidt, 1994). Then, the matrix is fed into a spectroscopic detector that detects the magnetic resonance emission. The term "matrix isolation electron spin resonance" refers to the two stages of the ESR technique. Thus MIESR is not generally considered a remote sensing method. Nevertheless, its capability for precise atomic analysis has led to the transportation of equipment to remote areas and use in programs as a comparison method with other technologies (Zenker et al., 1998). Comparison of this method with other instruments are given by Crosley (1995) and Werst and Trifunac (1998).

B: Range:

The range is the typical span of species concentration that would be measured by the MIESR technique. The concentration ranges shown in following table are the atmospheric concentrations that had been measured previously; they are not the span of a specific MIESR instrument.

LOCATION	DATE	CONDITIONS	SPECIES	CONCENTRATION RANGE (pptv)	REFERENCE
Schauinsland,	July '86	sunny day	NO ₂	<.001 - 100	Mihelcic et al., 1990
Germany		19°C (estimated)	RO ₂	10 - 600	Mihelcic et al., 1990
Canary Islands	Aug, '93	19-25°C (estimated)	RO _x	10 -60	Zenker et al., 1998; & Fischer et al., 1998

		19 -21°C (estimated)	NO ₂	650 - 820	
		48 -56% Rh	NO ₃	5.0 ± 2 - 10 ± 2	
			HO ₂	5 ± 3 - 10 ± 3	
			Sum (RO ₂)	5 ± 3 - 40 ± 5	

C: Minimum Detection Level:

The minimum detection level is the lowest concentration of a species that instruments using MIESR technique can detect. MIESR detection limits are typically in parts-per-trillion by volume level.

LOCATION	SPECIES	DETECTION LEVEL (pptv)	REFERENCE.
Schauinsland	NO ₂	5	Mihelcic et al., 1993
	RO ₂	5	Mihelcic et al., 1993
	NO ₃	3	Mihelcic et al., 1993
	HO ₂	5	Mihelcic et al., 1993

D. Operating Temperature:

The application of MIESR for analysis of ambient air has been developed as a two-stage process: First, ambient air is sampled by reduction to a very cold temperature; then, the frozen sample is transferred to the input state of the spectrometer. Ambient air is drawn into a vacuum chamber where it comes in contact with a very cold surface at about 77K. As the free radicals in the air sample adhere to the cold surface, a separate supply of some liquid such as water or D₂O is allowed to build up on the cold surface.

The cold surface is then stored cryogenically, while transported to the MIESR spectrometer. Since the radicals are extracted from the incoming ambient air onto the cold surface, the incoming air can be at any temperature. The air sampling instrument can operate in ambient air conditions, but the spectroscope need not do so. Ambient air sampling has been conducted at Schauinsland during the nighttime in August, where the estimated ambient air would be 8°C, average minimum (Rudloff, 1981), and at Tenerife (Canary Island) in August where the minimum average ambient air temperature would be around 19°C (Rudloff, 1981).

E. Known Interference:

Interferences are factors or conditions, either chemical, meteorological, or instrumental, which could be responsible for introducing error into the measurement results from use of MIESR.

1. MIESR method involves "freezing" (i.e., isolation) of many of the species mentioned above in a non-reactive matrix enabling their relative concentrations to be determined (Werst and Trifunac, 1998). One problem in the procedure is the matching of probable reactions to measured concentrations, sometimes called the "fake NO", which requires the assumption of more or less of some species than found by actual measurement (Mihelcic et al., 1993)
2. Even with the matrix isolation technique and the development of numerical techniques for MIESR spectral analysis, the separation for some species, e.g., the alkylperoxy radicals, has not been successful because of the close similarities of their spectra (Mihelcic et al., 1990).
3. Variability of MIESR was found to be about 50 percent in the measurement of peroxy radicals (RO_x) (Zenker et al., 1998).

F. Notes of Interest:

The following notes of interest are possibly useful facts in the development of any strategy involving MIESR:

1. The notion of matrix isolation has typically implied very cold surfaces on which the radicals are trapped in a rare gas or halocarbon matrix, such as the Freon. However, halocarbon matrices which are liquids at room temperatures have also been used (Werst and Trifunac, 1998).
2. One of the conclusions of the intercomparison report by Zenker, et al. (1998) is that the comparison of methods measuring NO_2 gives some confidence that accurate measurements in the 50 - 700 pptv range can be achieved. The three methods compared were MIESR, chemilumescence, and tunable diode laser absorption spectroscopy. The differences were in the range of 4-13%.
3. Although the numerical analysis of the MIESR spectra has not resolved all of the problems, the principle has also been applied in the analysis of heavy metal pollutants in the atmosphere (Iosefzon-Kuyavskaya et al., 1993).

G. References:

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2. Fischer, H., et al., Trace gas measurements during the oxidizing capacity of the tropospheric atmosphere campaign at Izana: *J. Geophys. Res.*, 103(D11):13505-13518, 1998.
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13. Zenker, T., et al., Intercomparison of NO, NO₂, NO_y, O₃, and RO_x measurements during the oxidizing capacity of the tropospheric atmosphere (OCTA) campaign 1993 at Izana: *J. Geophys. Res.*, 103(D11): 13615-13634, June 1998

NARSTO COMPENDIUM

R&D METHODS FOR PAMS/VOCS OZONE PRECURSORS

4. Tunable Diode Laser Absorption Spectroscopy - TDLAS

[[Basis](#) | [Range](#) | [Min. Detection Level](#) | [Operating Temp.](#) | [Interferences](#) | [Notes of Interests](#) | [References](#)]

1. **Basis:** "Absorption spectroscopy" is a chemical analysis technique made possible by the phenomenon that a given molecule absorbs light at selected wavelengths. The wavelengths absorbed are characteristic of each molecule's atomic features (Southwest Sciences, 1999). The amount of light radiation absorbed by a substance depends on two factors: the number of molecules in the path of the light, and the characteristics of the molecule (e.g., absorption cross-section). Measurement of changes in the light intensity as it passes through the molecules, and the use of calibration and reference data, enable the determination of the number of molecules encountered.

Tunable Diode Laser Absorption Spectroscopy ([TDLAS](#)) uses a diode laser as the excitation light source for the absorption spectroscopic measurement. "Diode lasers" contain a small "diode" which is constructed of bits of various elements in crystalline form. When electrical current or heat, or both, are applied to the diode, it emits the laser light beam. The wavelength of the light beam is highly specific with respect to the material of the diode. This wavelength can be tuned over a small spectral window by varying the electrical and heat forces applied. Adjusting the wavelength is called "tuning" the diode, giving the laser the name "tunable diode laser" (Schiff, 1996; Werle, 1998).

TDLAS has been used typically in the measurement of trace gases in the lower and upper atmosphere. This technique has been applied to greenhouse gases such as CF₄ and C₂F₆, vehicular exhaust gas such as CO and CO₂, in-stack HF emission (e.g., Schiff, 1996).

2. **Range:** The measurement range is the typical span of species concentration that is measurable by a TDLAS device.

3. **Minimum Detection Level:** Typically, if the molecular absorption cross sections or absorption coefficients are known, the detection sensitivity for a gas species can be calculated. Smaller detection limits correspond to more sensitive detection. The following data were available at <http://www.swsciences.com/sensors.html> using an 1 meter optical path, lead-salt diode except HF, assuming 1E-5 absorbance, and 1 Hz bandwidth.

Species	Wavelength (nm)	Detection Limit (ppbv)
Water	5940	2.0
Nitric oxide	5250	5.8
Carbon dioxide	4230	0.13
Carbon monoxide	4600	0.75
Nitrogen dioxide	6140	3.0
Formaldehyde	3550	8.4
Ozone	9500	11
Ammonia	10300	0.80

Sulfur dioxide	7280	14
Hydrogen fluoride (HF)	1310 (Near-IR)	10

The sensitivity of TDLAS can be improved significantly by using a multipass cell (see [Notes of Interests](#)).

4. **Operating Temperature:** Tunable diode laser spectrometers have been used both *in-situ* and remote-sensing modes. For *in-situ* applications, the operating temperatures would be those of the laboratory, vehicle, or aircraft where the equipment is installed and operated. Lead-salt tunable diode lasers are the most widely used for atmospheric trace gas monitoring. A major disadvantage of the lasers is that they operate at temperatures generally below 100K and thus require cryogenic cooling (Kolb et al., 1995).

5. **Known Interferences:** Optical filtering, beam shaping, and collimating adjustment is generally required to ensure the TEM₀₀ beam quality during the operation (Kolb et al., 1995). In spite of the tunable feature of the diodes, their actual tunable wavelength range is generally limited. The property of the semiconductor diode laser thus represents a major limiting factor for a wide application of this technique.

6. Notes of Interest:

a. There are many reports on the use of TDLAS. Traditional single-path laser absorption techniques are not capable of 1.0 ppbv level of detection. Detection improvements can be achieved by using multi-pass cells (Pustogov, 1994); however, the cost of such devices is significant (See MayComm Research Inc. and New Focus, Inc. at the [References](#) Section).

b. Although at least five types of diodes are available on the market these days (Southwest Sciences, 1999), InGaAsP, AlGaAs, AlGaInP, Lead-salt lasers, and Antimonide lasers, the most commonly used diode laser in TDLAS is the lead-salt diode. It has a wide tunable range, over wavelengths from 3.3 μm to 30μm (Kolb et al., 1995), compared to other diode lasers.

c. TDLAS is a fast detection technique, and is specific to the analyte of interest. Multiple lasers can be multiplexed to design of an instrument capable of measuring multiple gas species in one box. The complexity and cost of TDLAS instrument are the major disadvantages of the technique.

7. References:

1. Kolb, C. E., et al., "Recent Advances in Spectroscopic Instrumentation for Measuring Stable Gases in the Natural Environment". Chap. 8 in: *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, ed. P. A. Matson and R. C. Harris, Blackwell Sci. Ltd., London, 1995.

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6. Southwest Sciences, Inc., "Diode Laser Gas Sensing". <http://www.swsciences.com/sensors.html> Santa Fe, New Mexico, June, 1999.
7. Werle, P., "A Review of Recent Advances in Semiconductor Laser Based Gas Monitors". *Spectrochimica Acta Part A*, 1998. 54:197-236,



NARSTO Measurement Methods Compendium

Particulate Matter Methods

I. Particulate Matter - size less than or equal to 10 micrometers (PM10)

A. Gravimetric Methods - exchangeable filters (FRM)

1. Basis: An air pump draws ambient air at a constant flow rate into a specially shaped inlet where particulate matter is separated into size fractions. Particulate matter is then collected on a filter. Each filter is weighed before and after use, to determine the net mass gain due to collected matter. The total volume of air filtered is known from the constant air flow, and the difference in filter weights is used to calculate the particulate matter concentration in micrograms per cubic meter ($\mu\text{g}/\text{m}^3$) of air.
2. Range: The concentration range is 30 to 300 $\mu\text{g}/\text{m}^3$ for test conditions. (Ref. 24, Para. 53.34, Table C-4)
3. Lower detection limit, or lower quantifiable limit: This limit is not set but is permitted to vary according to filter technology. (Ref. 25, Para. 3.1)
4. Temperature tolerance: Samplers must operate over a -30° to $+45^\circ\text{C}$ temperature range (Ref. 28, Para. 7.4.7). Some devices are offered with temperature protection features, which are optional.
5. Known Interference:
 - a. Particulate matter may be lost during filter handling and weighing procedures, especially if filter is exposed to warming.
 - b. Gaseous species may contaminate filters.
 - c. Humidity and absorbed water may be difficult to control both during operations and when handling filters.
 - d. Removing filters and transporting to a lab for analysis may affect results.
 - e. Meteorological conditions may affect flow rate.
6. Notes of Interest:
 - a. Precision (means agreement among successive measures of equal samples) is defined by EPA as follows: must be 5 $\mu\text{g}/\text{m}^3$ for PM10 concentrations below 80 $\mu\text{g}/\text{m}^3$ and 7 percent for PM10 concentrations above 80 $\mu\text{g}/\text{m}^3$ (Ref. 25, Para. 4.1), but the wording probably means "at least 5 $\mu\text{g}/\text{m}^3$." This requirement is simplified in Reference 26 (Para. 53.40, Table D-1) to 5 $\mu\text{g}/\text{m}^3$ or 7 percent for three collocated samplers.
 - b. Comparability: A procedure for testing comparability of PM10 methods is provided. This procedure requires operation of the various devices in the same context (immediate vicinity and time), and a subsequent statistical analysis of measurements. The results are required to correlate 0.97 with previously established reference, with respect to sample masses measured over 24 hours (Ref. 24, Para. 53.34, Table C-4).
 - c. Upper capacity limit: All samplers should be capable of measuring 24-hour mass concentrations of at least 300 micrograms per standard cubic meter of air (Ref. 25,

- Para. 3.1). Filter exchange features can extend the upper capacity for some devices, which use various automatic filter replacement mechanisms to overcome limitations of excess matter collecting on one filter. Thus a given device might be pre-loaded with several filters which will be used sequentially.
- d. Accurate air flow measurement is crucial to the determination of concentration of particulate matter, and sampling devices employ various systems for flow determination. For example, a mass sensor sends a signal to a microprocessor, which makes a determination and either increases or decreases fan speed. Appendix J requires that flow rate be accurate to within 2 percent of a preselected standard over a range of (potential) ambient conditions (Ref. 25, Para. 8.2.2).
7. Instrument - Manufacturer:
 - a. Partisol 2000 - [Rupprecht-Patashnick](#)
 - b. GMW-1200 - [Andersen Instruments, Inc.](#)
 - c. Model 600 - [Thermo-Environmental Instruments](#)
 - d. Model PQ100 Portable - [BGI Incorporated](#)
 - e. Model 241 series dichotomous sampler - [Andersen Instruments, Inc.](#)
 - f. Model Partisol-FRM 2000 - [Rupprecht - Patashnick](#)
 - g. Partisol-Plus Model 2025 - [Rupprecht - Patashnick](#)
 - h. Model PQ200 - [BGI Incorporated](#)
 8. References: 24, 25, 26 ([Go to References](#))

B. Beta Attenuator Methods (FEM)

1. Basis: Beta particles (electrons with energies in the 0.01 to 0.1 MeV range) are attenuated according to an approximate exponential function when they pass through particulate deposits on a filter tape. Automated samplers (analyzers) use a continuous filter tape, first measuring the attenuation by the unexposed tape, and then measuring the attenuation after the tape has passed through the ambient air flow. The attenuation measurement converts to a measure of the mass on the filter, so that the filters do not require later laboratory analysis for the mass variable. For some devices, the beta particle source is ^{14}C .
2. Range: The concentration range is 30 to 300 $\mu\text{g}/\text{m}^3$ for test conditions. (Ref. 24, Para. 53.34, Table C-4)
3. Lower detection limit, or lower quantifiable limit: This limit is not set but is permitted to vary according to filter technology. (Ref. 25, Para. 3.1). An approximate value of 5 $\mu\text{g}/\text{m}^3$ is given in Ref. 27.
4. Temperature tolerance: Samplers must operate over a -30° to $+45^\circ\text{C}$ temperature range (Ref. 28, Para. 7.4.7). Some devices are offered with temperature protection features, which are optional.
5. Known Interference:
 - a. Particulate matter may be lost due to filter tape advance and vibration, especially if filter is exposed to warming.
 - b. Gaseous species may contaminate filters.
 - c. Humidity and absorbed water may be difficult to control during operations.
 - d. Meteorological conditions may affect flow rate.
 - e. Although on-site real-time mass measurement offers significant improvements over the filter removal and laboratory analysis process, the beta emission and detection process present additional on-site maintenance requirements.
6. Notes of Interest:
 - a. Precision (means agreement among successive measures of equal samples) is defined by EPA as follows: must be 5 $\mu\text{g}/\text{m}^3$ for PM10 concentrations below 80 $\mu\text{g}/\text{m}^3$ and 7 percent for PM10 concentrations above 80 $\mu\text{g}/\text{m}^3$ (Ref. 25, Para. 4.1), but the wording probably means "at least 5 $\mu\text{g}/\text{m}^3$." This requirement is simplified in Reference 26 (Para. 53.40, Table D-1) to 5 $\mu\text{g}/\text{m}^3$ or 7 percent for three collocated samplers.
 - b. Comparability: A procedure for testing comparability of PM10 methods is provided. This procedure requires operation of the various devices in the same context (immediate vicinity and time), and a subsequent statistical analysis of

measurements. The results are required to correlate 0.97 with previously established reference, with respect to sample masses measured over 24 hours (Ref. 24, Para. 53.34, Table C-4).

- c. Upper capacity limit: All samplers should be capable of measuring 24-hour mass concentrations of at least 300 micrograms per standard cubic meter of air (Ref. 25, Para. 3.1).
 - d. Because of the characteristics of the Beta particles emitters, which emit particles in irregular intervals, or bursts, the accuracy of the devices improves with longer periods of sampling, during which the emission frequency approaches a mean value, and thus detects the "true" ambient concentration, as deposited on the filter. By this same phenomenon, the detection of the "true" ambient concentration will be detected earlier, and more accurately for higher concentrations.
7. Instrument - Manufacturer:
- a. BAM/GBAM series - [Met One Instruments](#)
 - b. Model 650 - [Thermo-Environmental Instruments, Inc.](#)
 - c. Model FH-621-N - [Andersen Instruments Inc.](#)
8. References: 24, 25, 26, 27, 28 ([Go to References](#))

C. Tapered Element Oscillating Microbalance (TEOM) Methods (FEM)

1. Basis: Air is drawn through a tapered glass element with a filter attached. The element oscillates according to a characteristic frequency, that decreases as mass accumulates on the attached filter. Measurement of the change in frequency converts to measurement of the accumulated mass.
2. Range: The concentration range is 30 to 300 $\mu\text{g}/\text{m}^3$ for test conditions. (Ref. 24, Para. 53.34, Table C-4).
3. Lower detection limit, or lower quantifiable limit: This limit is not set but is permitted to vary according to filter technology. (Ref. 25, Para. 3.1). An approximate value of 5 $\mu\text{g}/\text{m}^3$ is given in Ref. 27.
4. Temperature tolerance: Samplers must operate over a -30° to $+45^\circ\text{C}$ temperature range (Ref. 28, Para. 7.4.7). Some devices are offered with temperature protection features, which are optional.
5. Known Interference:
 - a. Particulate matter may be lost due to vibration, especially if exposed to warming.
 - b. Gaseous species may contaminate filters.
 - c. Humidity and absorbed water may be difficult to control during operations.
 - d. Meteorological conditions may affect flow rate.
 - e. Although on-site real-time mass measurement offers significant improvements over the filter removal and laboratory analysis process, the TEOM equipment presents additional maintenance requirements.
6. Notes of Interest:
 - a. Precision (means agreement among successive measures of equal samples) is defined by EPA as follows: must be 5 $\mu\text{g}/\text{m}^3$ for PM10 concentrations below 80 $\mu\text{g}/\text{m}^3$ and 7 percent for PM10 concentrations above 80 $\mu\text{g}/\text{m}^3$ (Ref. 25, Para. 4.1), but the wording probably means "at least 5 $\mu\text{g}/\text{m}^3$." This requirement is simplified in Reference 26 (Para. 53.40, Table D-1) to 5 $\mu\text{g}/\text{m}^3$ or 7 percent for three collocated samplers.
 - b. Comparability: A procedure for testing comparability of PM10 methods is provided. This procedure requires operation of the various devices in the same context (immediate vicinity and time), and a subsequent statistical analysis of measurements. The results are required to correlate 0.97 with previously established reference, with respect to sample masses measured over 24 hours (Ref. 24, Para. 53.34, Table C-4).
 - c. Upper capacity limit: All samplers should be capable of measuring 24-hour mass concentrations of at least 300 micrograms per standard cubic meter of air (Ref. 25, Para. 3.1).
7. Instrument - Manufacturer

- a. Model 1400 - [Rupprecht-Patashnick](#)
- 8. References: 24, 25, 26, 27, 28 ([Go to References](#))

II. Particulate Matter - size less than or equal to 2.5 micrometers (PM2.5)

A. Gravimetric Methods - exchangeable filters (FRM)

1. Basis: An air pump draws ambient air at a constant flow rate into a specially shaped inlet. Suspended particulate matter is then collected on a filter. Each filter is weighed before and after use, and moisture content of filters is controlled. The total volume of air filtered is known from the constant air flow, and the difference in filter weights is used to calculate the particulate concentration micrograms per cubic meter of air ($\mu\text{g}/\text{m}^3$).
2. Range: The concentration range is 10 to 200 $\mu\text{g}/\text{m}^3$ for test conditions. (Ref. 24, Para. 53.34, Table C-4)
3. Lower detection limit, or lower quantifiable limit: FRM samplers should be able to detect a 24 hour average concentration of 2 $\mu\text{g}/\text{m}^3$ (Ref. 28, Para. 3.1).
4. Temperature tolerance: Samplers must operate over a -30° to $+45^\circ\text{C}$ temperature range (Ref. 28, Para. 7.4.7). Some devices are offered with temperature protection features, which are optional.
5. Known Interference:
 - a. Particulates may be lost during filter handling and weighing procedures especially if filter is exposed to warming.
 - b. Gaseous species may contaminate filters.
 - c. Humidity and absorbed water may be difficult to control both during operations and when handling filters.
 - d. Removing filters and transporting to lab for analysis may affect results.
 - e. Meteorological conditions may affect flow rate.
6. Notes of Interest:
 - a. Precision for PM2.5 samplers is specified as a 10 percent coefficient of variation or better (Ref. 28, Para. 5). A separate method of calculating precision for particulate samplers is given in Ref 26 (Para. 53.43(c)).
 - b. An upper limit for filter mass loading is not given. All samplers are probably able to measure an ambient air concentration of at least 200 micrograms per cubic meter over a 24 hour period (Ref. 28, Para. 3.2).
7. Instrument - Manufacturer:
 - a. Partisol Model FRM 2000 - [Rupprecht - Patashnick](#)
 - b. Partisol-Plus Model 2025 - [Rupprecht and Patashnick](#)
 - c. RAAS2.5-100 - [Andersen Instruments, Inc.](#)
 - d. RAAS2.5-300 - [Andersen Instruments, Inc.](#)
 - e. PQ200 - [BGI, Incorporated](#)
8. References: 24, 26, 28 ([Go to References](#))



NARSTO Measurement Methods Compendium

Annotated Method Description Outline and Definitions

Method Description Outline

The descriptions of measurement methods in this Compendium include the following types of information in an outline form.

- I. **Species** - The analyte whose concentration is to be determined.
 - A. **Method** - An analytical technique used to measure the concentration of the species.
 1. **Basis** - The basic chemical and/or the physical principles on which the method is founded.
 2. **Range** - The typical span of species concentration that is measured by instruments employing the method. Note that many of the instruments discussed in the text may exceed this range by varying levels.
 3. **Minimum Detection Level** - The lowest concentration of a species that an instrument employing the method can distinguish from the background noise.
 4. **Operating Temperature** - The typical temperature span in which an instrument employing the method can effectively measure the concentration of the species. Note that some instruments exceed this range to varying levels.
 5. **Known Interference** - Any factor (e.g., chemical species in the sample, physical conditions such as a power outage) that could introduce error and/or bias toward the measured concentration of the species using the method.
 6. **Notes of Interest** - Any additional information that would be useful when employing the method or that gives more insight into the method.
 7. **Instrument - Manufacturer** - The names of instruments and the manufacturers of the instruments. A web link is included, if it is available, at the end of this category to provide access to more information about the instruments and their manufacturers.
 8. **References** - The literary sources of the information given for each method.

Terms

The following terms are used in the descriptions of measurement methods.

- **Federal Reference Method (FRM)** - An instrument that employs a method specified in Title 40, Code of Federal Regulations, Part 50 (40 CFR Part 50). Appendices for measuring a certain species and meets the requirements specified in Title 40, Code of Federal Regulations, Part 53 (40 CFR Part 53), subchapter B.
- **Federal Equivalence Method (FEM)** - An instrument that employs a method other than the Federal Reference Method but meets the requirements for measuring a species specified in 40 CFR Part 53, subchapter B.

- **N/A** - Information is not available at present.

Links to Relevant Documents

(updated December 10, 2008)

- [Link to 40 CFR Part 50 \(with Appendices\) and to Part 53](#)

40 CFR Part 50 is National Primary and Secondary Ambient Air Quality Standards. It includes designation of FRMs. The Appendices are also of interest.

40 CFR Part 53 is Ambient Air Monitoring Reference and Equivalent Methods. It includes requirements for FEMs. HINTS: To find these documents in the Link above, select "Title 40 - Protection of Environment" and click "Go" Then "Browse Parts" 50-51 or 53-59 to find 40 CFR Part 50 or 40 CFR Part 53 (respectively)

See also the Ambient Monitoring Technology Information Center's home page at <http://www.epa.gov/ttnamti1>.

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