National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 1804

Eighteen Toxic Volatile Organic Compounds in Nitrogen

This Standard Reference Material (SRM) is intended for the calibration of instruments used for the determination of toxic volatile organic compounds (VOC's) in stationary source emissions. SRM 1804 is a mixture of eighteen toxic VOC's, collectively designated as EPA Group 5, in a nitrogen matrix. It should be useful for providing quality assurance and accuracy for measurements of VOC's in air monitoring and for the development and evaluation of methods used for such measurements.

The certified values for fifteen VOC compounds are given in Table 1. Non-certified values for the additional three VOC's are given in Table 2 for information only (see Stability section). The certified values given in Table 1 apply only to the cylinder identified by cylinder number and sample number given below in this certificate.

Cylinder Number: Sample Number:

SRM 1804 is supplied in an aluminum cylinder with a pressure of 12.4 MPa (1800 psi) with a deliverable volume of 3.6 m^3 (127 cubic feet) at normal temperature and pressure. The cylinder conforms to DOT specifications and is equipped with a stainless steel CGA-350 packless valve. When sold, the cylinder becomes the property of the purchaser.

The certified values in this certificate are valid for two years from the date of shipment from NIST. A validation sticker is supplied with the gas cylinder that specifies its certification period. Please affix this sticker to the cylinder upon receipt.

Caution: Care must be taken to avoid contamination of the SRM during its use with any gas handling system.

The development and technical measurements leading to the certification of this SRM were performed in the NIST Gas and Particulate Science Division by G.C. Rhoderick.

The statistical analysis of the certification data was performed by R.C. Paule of the National Measurement Laboratory.

The overall coordination of measurements leading to certification was under the direction of W.L. Zielinski, Jr., and R.A. Velapoldi, Chief of the Gas and Particulate Science Division.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the Office of Standard Reference Materials by T.E. Gills.

Gaithersburg, MD 20899
January 8, 1990

William P. Reed, Acting Chief
Office of Standard Reference Materials

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Background

This SRM was developed through joint support of the Quality Assurance Division of the Atmospheric Research and Exposure Assessment Laboratory of the U.S. Environmental Protection Agency in Research Triangle Park, NC (EPA/AREAL/RTP), and the NIST Gas and Particulate Science Division. The eighteen volatile organic compounds in this SRM were identified and selected for inclusion in this reference mixture in discussions with the staff of EPA/AREAL/RTP and state monitoring programs.

Materials Preparation

This SRM is one of a group or "lot" of twenty cylinders that was prepared commercially according to NIST specifications to ensure that the lot is homogeneous and stable. The cylinder gas mixtures were prepared by transferring equal portions of a higher concentration "master" mixture, containing the eighteen compounds, into each of the twenty cylinders. The cylinders were then pressurized with a pure, dry, nitrogen matrix gas.

Analysis

The eighteen organic compounds were determined and certified by comparison with gravimetric standards prepared at NIST. All measurements were made using gas chromatography (GC). Analytical conditions for bromomethane, trichlorofluoromethane, trichloromethane (chloroform), 1,1,1-trichloroethane, tetrachloromethane (carbon tetrachloride), trichloroethene, 1,2-dibromoethane, and tetrachloroethene follow. The measurements were made using a GC system equipped with an electron capture detector, a gas sampling valve having a 0.1 mL sample loop, and a 60 meter by 0.75 mm i.d. borosilicate wide-bore capillary column coated with SPB-1 operated at a column oven temperature of 45 °C and a nitrogen carrier gas flow rate of 10 mL/minute through the column and a nitrogen make-up flow of 25 mL/minute. A representative chromatogram obtained using this procedure is given in Figure 1.

For the remaining organic compounds, plus bromomethane and 1,2-dibromoethane, measurements were made using a GC system equipped with a flame-ionization detector, a cryogenic preconcentration gas sampling and automatic stream selection system, and a 2.4 meter by 3.2 mm i.d. stainless-steel column packed with 1% SP-1000 on 60/80 mesh Carbopack B operated at a column oven temperature of 45 °C for 3 minutes then raised to 160 °C at 8 °C/minute then to 240 °C at 12 °C/minute. A representative chromatogram obtained using this procedure is given in Figure 2.

Stability

This SRM is contained in an aluminum cylinder. Based on experience with these and similar cylinder mixtures of these compounds, the certified concentration values assigned to fifteen of the eighteen organic compounds in SRM 1804 should be stable within their stated uncertainties for a period of at least two years from date of shipment from NIST. The remaining three compounds, bromomethane, 1,2-dibromoethane and 1,3-butadiene, are not certified due to observed instability of these compounds in this cylinder lot. The concentration values for these compounds may be actually lower than that listed in Table 2. Periodic analyses of representative samples from this lot will be performed at NIST, and if significant changes are observed in the certified values within the two year period, purchasers of the SRM will be notified.

Similar gas mixtures in aluminum cylinders have exhibited changes in concentration when the cylinder pressure fell below 1.4 MPa (200 psi). Therefore, it is recommended that the sample not be used after the pressure has fallen below 2.8 MPa (400 psi).

Impurities

Several impurities are present in this SRM. The largest impurity elutes last, as seen in Figure 2, and its concentration varies from cylinder to cylinder in the lot. Using GC/MS, the compound was identified as octamethylcyclotetrasiloxane and the analysis indicates that its concentration may be as high as 15 nmol/mol (ppb) when compared to the 1,2-dimethlybenzene (ortho-xylene) signal. The other impurities in the SRM have a total concentration of less than 1 nmol/mol (ppb) when compared to the benzene signal. Another impurity that may be found with time is 1,1,2-trichloro-trifluoroethane (CFC-113) which is a common degreasing solvent used in the manufacturing of the valves. Although these valves were specially cleaned, there may be residual CFC-113.

Although minimal CFC-113 was found, less than 0.1 ppb, it is recommended that 1-2 liters of gas should be purged from the cylinder before it is used to reduce the possibility of large amounts of CFC-113 impurity in the gas stream coming from the cylinder. (This procedure will flush the valve area of high concentrations of CFC-113).

Reanalysis

The NIST will reanalyze this SRM for the original purchaser at a cost not to exceed the cost of similar SRM's available at the time of the request for reanalysis. If reanalysis indicates that the concentrations of the compounds have not changed from the original certified values, the certification period will be extended for an additional two year period from the time of reanalysis. The Gas Metrology Research Group in the NIST Gas and Particulate Science Division should be contacted to arrange for reanalysis.

Table 1. Certified Volatile Organic Compounds in SRM 1804

Compound	Concentration nmol/mol(ppb)[a,b]
Chloroethene (Vinyl chloride); CH_2:CHCl	5.3 ± 0.2
Trichlorofluoromethane; CCl_3F	5.1 ± 0.1
Dichloromethane; CH_2Cl_2	5.0 ± 0.3
Trichloromethane (Chloroform); $CHCl_3$	5.0 ± 0.2
1,2-Dichloroethane; $ClCH_2CH_2Cl$	5.0 ± 0.2
1,1,1-Trichloroethane; CH_3CCl_3	5.1 ± 0.1
Benzene; C_6H_6	5.0 ± 0.1
Tetrachloromethane (Carbon tetrachloride); CCl_4	5.0 ± 0.1
1,2-Dichloropropane; $CH_3CHClCH_2Cl$	5.0 ± 0.2
Trichloroethene (Trichloroethylene); ClCH:CCl_2	5.0 ± 0.2
Methylbenzene (Toluene); $C_6H_5(CH_3)$	4.9 ± 0.2
Tetrachloroethene (Tetrachloroethylene); Cl_2C:CCl_2	5.0 ± 0.2
Chlorobenzene; C_6H_5Cl	5.0 ± 0.2
Ethylbenzene; $C_6H_5(C_2H_5)$	4.7 ± 0.2
1,2-Dimethylbenzene (ortho-Xylene); $C_6H_5(CH_3)_2$	5.0 ± 0.2

[a]The certified value of each compound is the average of the measured concentrations. The uncertainty of the certified value is two standard deviations of the certified concentration for each compound plus allowances for known sources of possible error.

[b]Each of the certified compounds of the gas mixture is reported as the molar ratio of that compound relative to the total of all other constituents.

Appendix to SRM Certificate 1804

The noncertified values listed in Table 2 are supplied for the convenience of the user of this SRM. The information provided does not meet the requirements for certification by the National Institute of Standards and Technology. NIST does not recommend that this information be used for calibration, bias evaluation, or similar purposes for which certified values are used.

Table 2. Non-certified Compounds in SRM 1804

Compound	Concentration nmol/mol(ppb)
1,3-Butadiene; CH_2:CHCH:CH_2	(4.7)
Bromomethane; CH_3Br	(5.5)
1,2-Dibromoethane; $BrCH_2CH_2Br$	(4.8)

Figure 1. Wide-bore capillary column; ECD.

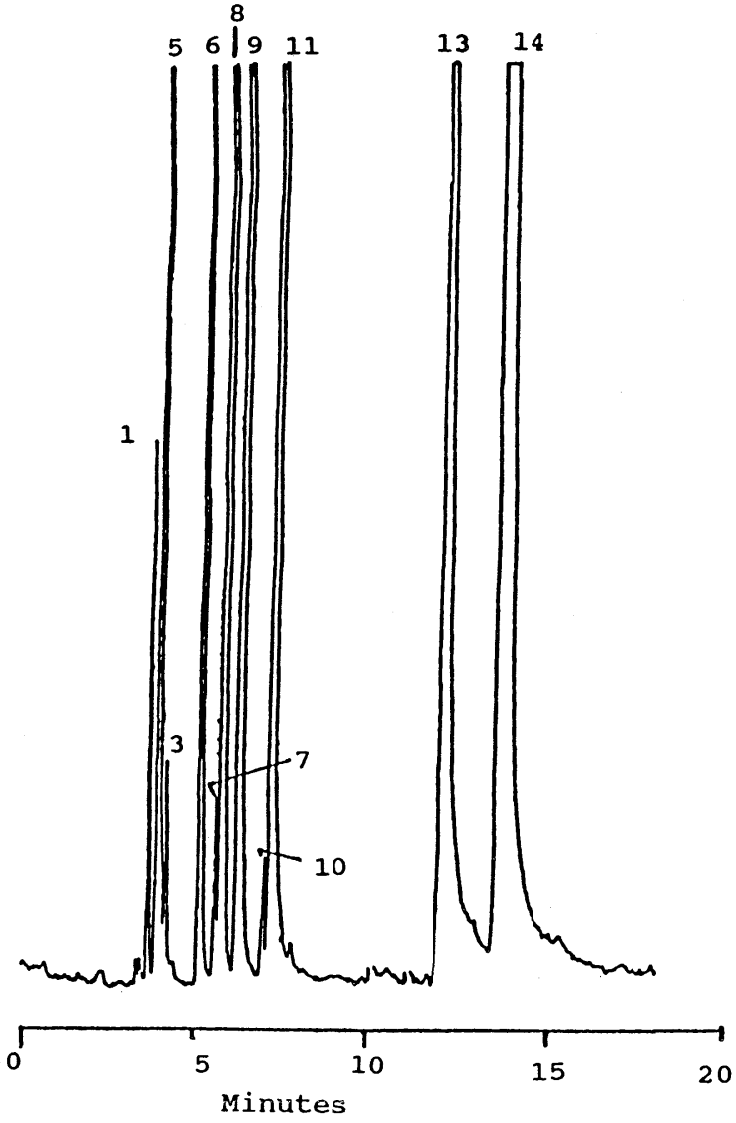
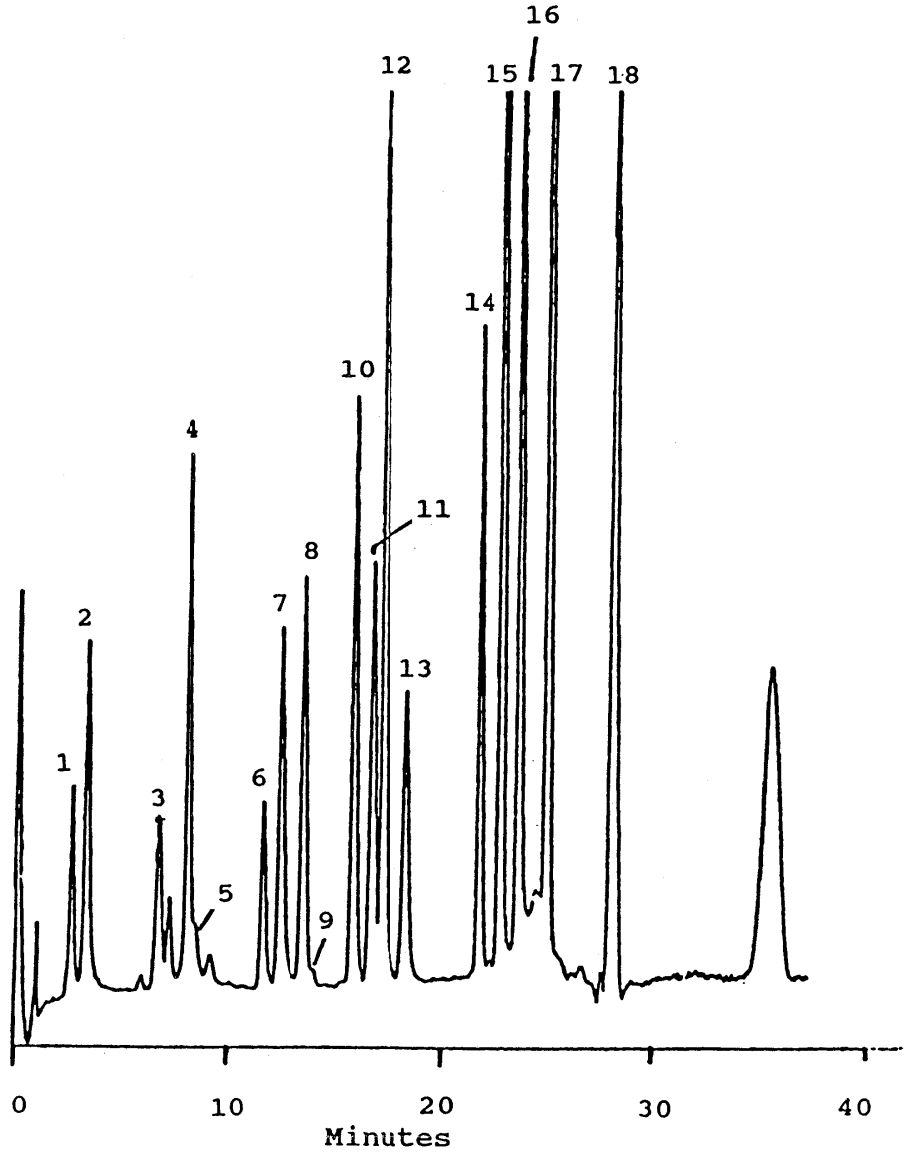


Figure 2. Packed column; FID.



(1) Bromomethane; (2) Chloroethene; (3) Dichloromethane; (4)1,3-Butadiene;
(5) Trichlorofluoromethane; (6) Trichloromethane; (7) 1,2-Dichloroethane;
(8) 1,1,1-Trichloroethane; (9) Tetrachloromethane; (10) 1,2-Dichloropropane;
(11) Trichloroethene; (12) Benzene; (13) 1,2-Dibromoethane; (14) Tetrachloroethene;
(15) Methylbenzene; (16) Chlorobenzene; (17) Ethylbenzene; (18) 1,2-Dimethylbenzene