National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material 2660

Oxides of Nitrogen (NO_X) in Air

(Nominal Concentration 100 μmol/mol)

This Standard Reference Material (SRM) is a primary standard to which the concentrations of secondary working standards may be related. The SRM is intended for the calibration of chemiluminescent type instruments used for oxides of nitrogen (NO_X) determinations and for other applications including the analysis of stationary source emissions.

This SRM is a mixture of nitrogen dioxide (NO_2) in air provided as a compressed gas in a DOT-approved aluminum cylinder equipped with a CGA-660 stainless steel valve at a nominal pressure of 12 MPa (1700 psig). This cylinder provides the user with 0.7 m^3 of useable mixture at normal temperature and pressure (NTP). Each SRM mixture has been individually analyzed for oxides of nitrogen (NO_X) which is defined for the purposes of this SRM as nitrogen dioxide (NO_2) and nitric acid (HNO_3). The concentration given below applies only to the cylinder identified by cylinder number and NIST sample number on this certificate.

NO_X Concentration:	±	μmol/mol
Cylinder number:	NIST Sample number:	

The uncertainty of the certified value includes the estimated uncertainty of the NIST primary analytical methods used to assign a concentration to this lot's control standard, and the imprecision of the intercomparisons of the lot control standard to the other cylinders in this lot. The uncertainty is expressed as an expanded uncertainty $U = k\,u_c$ with u_c being determined from experimental standard deviations and the coverage factor k being equal to 2. Since the concentration values of NIST gaseous SRMs are assumed to be normally distributed with an experimental standard deviation of u_c, the reported value for the NO_X concentration is asserted to lie in the interval defined by U with a level of confidence of approximately 95 percent.

The certified value on this certificate is valid for two (2) years from the date of shipment from NIST. A validation sticker is supplied with each gas cylinder to specify its certification period. This should be affixed to the cylinder upon receipt of the SRM.

The analytical measurements leading to the certification of this SRM lot were performed in the NIST Organic Analytical Research Division by W.R. Miller, W.D. Dorko, and P.A. Johnson.

The overall direction and coordination of the technical work required for this SRM's certification was performed in the NIST Organic Analytical Research Division by W.J. Thorn III, F.R. Guenther, and W.E. May.

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

Gaithersburg, MD, 20899
July 20, 1993

Thomas E. Gills, Acting Chief
Standard Reference Materials Program

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Stability: This SRM is considered to be stable. No significant losses of NO_X (total) concentration have been observed for similar samples contained in aluminum cylinders for periods of time greater than 2 years. However, some intraconversion of NO_X species may occur due to the reaction of nitrogen dioxide and surface adsorbed water to form gas phase nitric acid in-situ. Periodic reanalyses of SRMs from this lot will be performed at NIST to assure the ongoing stability for the lot. If significant changes in the concentration are observed, the purchaser will be notified.

Mixture Preparation: The gas mixtures were prepared under contract by a commercial specialty gas vendor, following NIST technical specifications for their preparation. These specifications stipulate that all of the mixtures be similar in concentration and are stable with time. This lot of oxides of nitrogen (NO_X) in air mixtures has been determined to have met all technical criteria.

Analytical Methods: Analyses of NO_X concentrations for this lot of cylinders were performed using a chemiluminescent NO/NO_X continuous monitor equipped with a stainless steel thermal ($NO_X \rightarrow NO$) converter operating above 625 °C. The NO_X output signal was processed by a signal averager under the control of a computer.

The two main components of the total NO_X signal are NO_2 and gas phase HNO_3. Nitrogen dioxide (NO_2) was measured directly on a chemiluminescent continuous monitor with the thermal converter; after scrubbing out the nitric acid (HNO_3). This HNO_3 removal was accomplished by passing the NO_X sample gas through a series of Gelman* Sciences "Nylasorb" membrane filters prior to the sample inlet. The HNO_3 response was calculated by subtracting the filtered signal (NO_2) from the unfiltered signal (total NO_X).

Lot Homogeneity: Each of the NO_X mixtures comprising the lot was analyzed using chemiluminescence with a lot control standard as a reference. A second homogeneity analysis was performed at NIST after a 1.3 year stability hold period had elapsed. The average NO_X concentration of the lot decreased 2% relative over the duration of the study and is an acceptable stability. Future decreases (if any) are expected to be smaller and should be well within the stated uncertainty for this SRM.

A NO_X response ratio for each of the SRM mixtures was determined from the NIST homogeneity analyses by dividing the NO_X response of each SRM unit by the corresponding response for this lot's control standard. The estimated uncertainty for each response ratio measurement was 0.3% relative. A mean value for the NO_X response ratio for the 25 SRM mixtures was computed along with the standard deviation of the mean. The 1.3 percent standard deviation of the mean indicates that there was a significant cylinder to cylinder variability within the lot and consequently each of these twenty-five SRM 2660 cylinders were individually assigned a concentration value.

NO_X Concentration Value Assignment: NIST assigned the concentration value for the oxides of nitrogen (NO_X) for this lot's control standard by two methods:

Method 1. Nitrogen dioxide permeation tubes were maintained at 25 °C under continuous flow of air controlled by a calibrated mass flow controller. The permeation rates were determined by weekly weight loss measurements on a microbalance. The permeation NO_2/air standard was intercompared over several weeks to the lot control standard by chemiluminescence in the total NO_X mode. The average NO_X concentration determined by method 1 was 99.6 $\pm$ 0.5 μmol/mol.

Method 2. A NIST SRM 1684b lot control standard containing 96.7 μmol/mol nitric oxide (NO) in nitrogen was intercompared several times over a period of weeks with SRM 2660 lot control standard by chemiluminescence in the total NO_X mode. The apparent NO_X concentration measured was then corrected for inefficiency of the thermal converter and for significant response effects due to the air matrix. The average NO_X concentration determined for the SRM 2660 lot control standard by method 2 was 99.2 $\pm$ 0.6 μmol/mol.

The final assigned value for the concentration, 99.4 $\pm$ 0.6 μmol/mol for the control from this lot of SRMs is the average of the two methods. The assigned concentration value for this control combined with the independent measured NO_X output ratio for each SRM 2660 cylinder resulted in the final assigned concentration value reported as the NIST certified value.

Other Analyses: Additional analyses performed during the certification procedure are given below. The concentrations reported are not certified values but are given for information purposes only.

a) Nitrogen Dioxide (NO_2) was measured to be _____ percent of the certified NO_X concentration reported on page 1 by chemiluminescence after nitric acid removal.

b) Nitric Acid (HNO_3) was calculated to be _____ percent of the certified NO_X concentration reported on page 1 by subtracting the measured percent NO_2 above from one hundred percent.

c) Argon (Ar), oxygen (O_2), and nitrogen (N_2) were not determined; but are present at concentrations of their normal abundance in dry ambient air (0.93 mole percent Ar; 20.95 mole percent O_2; 78.08 mole percent N_2).

d) Carbon dioxide (CO_2) was scrubbed from the air used to prepare SRM 2660 mixtures. However analysis of SRM 2660 by fourier transform infrared spectroscopy (FTIR) has detected CO_2 at a concentration of 5 ± 4 μmol/mol.

e) Water concentration: < 5 μmol/mol by phosphorus pentoxide electrochemical method.

Cylinder and Gas Handling Information: This SRM is supplied in a DOT 3AL specification (6061 alloy) aluminum cylinder with a water volume of 6 liters. Mixtures are shipped with a nominal pressure exceeding 12 MPa (1700 psig) which provides the user with 0.85 m^3 of useable mixture. The cylinder is the property of the purchaser and is equipped with a stainless steel CGA-660 valve which is the recommended outlet for this oxides of nitrogen (NO_X) mixture. NIST recommends that this cylinder not be used below 0.8 MPa (100 psig).

NIST recommends the use of a high-purity, stainless steel, two-stage pressure regulator with stainless steel diaphragm; and CGA-660 inlet to safely reduce the pressure; and to deliver this SRM mixture to the instrument. The regulator should be purged several times to prevent accidental contamination of the sample.

Recertification: NIST will recertify an SRM for an established fee. Sufficient SRM gas pressure should remain to make certification cost effective. Contact the NIST Organic Analytical Research Division at (301) 975-3108 to arrange for this service.

*The use of a trademark in this certificate is for identification only and does not imply endorsement of the product by the National Institute of Standards and Technology.