

## Analysis of Nitrous Oxide in Air

GML Technical Procedure

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Date

Version	Effective Date	Author	Approval	Filename
2.2.0	Jun. 8, 2026	AMC	IV	TP_analysis_N2O_v2.2.0 docx

## 1. Purpose

This document provides the technical procedures for analysis of nitrous oxide (N<sub>2</sub>O) in air by Quantum Cascade Tunable Infrared Laser Direct Absorption Spectroscopy (QC-TILDAS).

## 2. Scope

NOAA/GML provides compressed gas standards (reference materials) to the WMO/GAW community. Natural air or modified natural air gas standards are analyzed for N<sub>2</sub>O. Nitrous oxide dry air mole fractions are determined by Quantum Cascade Tunable Infrared Laser Direct Absorption Spectroscopy (QC-TILDAS) since 2025 and gas chromatography with electron capture detection prior to 2025, relative to the WMO N<sub>2</sub>O mole fraction scale. The WMO N<sub>2</sub>O mole fraction scale is derived from gravimetrically-prepared primary standards (see TP\_primary\_gravimetry.pdf). The procedures described here only pertain to N<sub>2</sub>O analysis for which a certificate of analysis is issued.

## 3. Informative References

Hall, B.D., G.S. Dutton, and J.W. Elkins (2007), The NOAA nitrous oxide standard scale for atmospheric observations, *J. Geophys. Res.*, 112, D09305, doi:10.1029/2006JD007954.

Hall, B.D., G.S. Dutton, D.J. Mondeel, J. D. Nance, M. Rigby, J.H. Butler<sup>1</sup>, F.L. Moore, D.F. Hurst, and J.W. Elkins (2011), Improving measurements of SF<sub>6</sub> for the study of atmospheric transport and emissions, *Atmos. Meas. Tech. Discuss.*, 4, 4131-4163.

JCGM (2008), International vocabulary of metrology — Basic and general concepts and associated terms (VIM), JCGM 200:2008.

JCGM 100:2008 Evaluation of Measurement Data – Guide to the Expression of Uncertainty in Measurement (ISO GUM 1995 with minor corrections), Joint Committee for Guides in Metrology (2008);

[http://www.bipm.org/utls/common/documents/jcgm/JCGM\\_100\\_2008\\_E.pdf](http://www.bipm.org/utls/common/documents/jcgm/JCGM_100_2008_E.pdf)

Salameh, P.K., Scripps Institution of Oceanography, Unix-based Integrator and Chromatographic Database, personal communication, 1997.

## 4. Terms and Definitions

- **Analysis System:** Includes the gas chromatograph, associated hardware, and computer used to analyze N<sub>2</sub>O in compressed gas cylinders (synonymous with measuring system).

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- **Gas Standard:** A cylinder of compressed gas with mole fractions assigned by metrological methods or by comparison to higher-level standards. Used to characterize the response of an instrument for calibration or quality control purposes. For the purposes of this TP, primary, secondary, and tertiary standards are gas standards.
- **Mole Fraction:** The ratio of the number of moles of a particular compound to the total number of moles. Dry air mole fraction is the ratio of the number of moles of a particular compound to the total number of moles in dry air. Within the scope of this TP, all samples are analyzed for dry air mole fraction.
- **Primary Standard:** A measurement standard established using a primary reference measurement procedure, or created as an artifact, chosen by convention.
- **Reference Cylinder:** Cylinder of dry air designated for the calibration of other standards for quantities of the same kind. The instrument response curve is often determined from instrument response relative to the reference cylinder. The reference cylinder is also used to track instrument drift on short time scales.
- **Regulator:** A device used to reduce the pressure in a gas cylinder (input) to a lower pressure (output) during use. High-purity and ultra-high purity regulators are used.
- **Response Curve:** A function that relates the instrument response to amount of substance (mole fraction).
- **Secondary Standard:** A standard whose value is determined through analysis relative to primary standards, for a quantity of the same kind. These standards are used to calibrate the instrument response. Use of secondary standards for routine calibration prolongs the life of primary standards. For N<sub>2</sub>O, values for secondary standards may also be assigned by comparison to other secondary standards, with verification performed by comparison to primaries. It is acceptable in some cases to use a well-characterized tertiary standard in the role of secondary.
- **Target Tank:** A tertiary standard used for routine monitoring of system performance. The system should be capable of reproducing the assigned value of the target tank (within expected uncertainties).
- **Tertiary Standard:** A standard whose value is determined through analysis relative to secondary standards, for a quantity of the same kind.
- **WMO/GAW:** World Meteorological Organization, Global Atmosphere Watch.

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## 5. Procedures

### 5.1 Gas Handling

Cylinders to be analyzed are stored in a common location and moved to the N<sub>2</sub>O analysis lab when needed. Prior to analysis, a regulator is attached. Several regulator models are used. For N<sub>2</sub>O, regulator purity is generally not an issue, although high purity or ultra-high purity models are preferred to preserve the integrity of other trace gases. Upon connecting the regulator, the residual gas in the regulator is purged (flushed) with air from the cylinder. The analyst determines the amount of flushing and conditioning time required, as it depends on the history of the regulator and the mole fraction of the gas being analyzed. The cylinder to be analyzed is connected to one of the analysis ports on the analysis system. The outlet pressure of the regulator should be set to 10-20 psig.

A small amount of drying agent, Mg(ClO<sub>4</sub>)<sub>2</sub>, is typically used in the sample line. Gas from both the reference cylinder and sample cylinder are passed through the drying agent. The drying agent should be inspected after analysis of a series of moist air samples, and replaced as necessary. The drying agent will be exhausted after about 20 moist samples (80%-90% relative humidity). However, the vast majority of samples analyzed on this system are dry (dew point < -70 °C).

### 5.2 Analysis System

The current N<sub>2</sub>O analysis system is combined with the CO calibration system. A QC-TILDAS analyzer is used to measure CO and N<sub>2</sub>O concurrently.

The older GC-ECD N<sub>2</sub>O analysis system is described in Hall et al. (2007) and Hall et al. (2011). It is used for SF<sub>6</sub> calibrations and we continue to monitor the N<sub>2</sub>O results to further our understanding of the agreement between the GC-ECD and QC-TILDAS methods.

Instrument responses are determined regularly using suites of standards (Primary or Secondary) analyzed during dedicated instrument calibration episodes. Typically, 30-60 second averages are used for each measurement point (the instruments typically have a 1 Hz data rate). Each measurement of a standard is bracketed by measurement of a reference gas used to normalize for span drift of the instruments. Typically, 6-8 replicate analyses are made for each standard. A 2<sup>nd</sup> order polynomial orthogonal distance regression (ODR) fit to the normalized response of the suite of standards is used to define the mole fraction vs instrument response of the instrument. These calibration curves (or response curves) are then used for converting subsequent sample analyses to mole fractions. New calibration curves are produced approximately bi-weekly to monthly, or whenever the reference cylinder is changed.

The cylinder to be analyzed is compared to a reference cylinder in an alternating, A-B-A-B-A... sequence. The reference cylinder consists of natural air with an N<sub>2</sub>O mole fraction typical of the

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remote troposphere. The normalized response for each sample aliquot is used with the most recent valid response curve to calculate N<sub>2</sub>O mole fractions.

### 5.3 Quality Control

It is critical that assignments made using the analytical system are reproducible. For a sample mole fraction that does not change with time, the system must be capable of reproducing the assigned value (within uncertainties) over the long term.

The experienced analyst can easily determine when the system is performing normally. Indicators of performance include, but are not limited to, the N<sub>2</sub>O response of the reference cylinder, repeatability of repeat injections, and variations in the response curve and residuals. Typically, the response curve is determined every 2-4 weeks by comparing the reference cylinder to the full suite of secondary standards. Experience has shown that it is not necessary to analyze secondary standards more often than this. However, the technical lead determines if this frequency is sufficient to define the response curve within the expected uncertainties. In addition, one or more target tanks are analyzed every few weeks. Target tanks are key indicators of system performance (assuming long-term changes in mole fraction due to drift are known). Additionally, cylinders with known N<sub>2</sub>O (previously analyzed on the system) can also be used to assess performance.

## 6.0 Calculations

### 6.1 Mole Fraction

The mole fraction of N<sub>2</sub>O in an unknown sample is determined by comparing the instrument response of the unknown sample to that of a suite of standards using common CCL procedures as described in TP\_analysis\_calculations.

The current WMO N<sub>2</sub>O scale was developed in 2006 and transferred to a set of secondary standards that year. A replacement set of secondary standards was installed in 2010. Values for the 2010 set of secondaries were determined relative to the 2006 set of secondaries, and verified by comparison to the primaries. The current set of N<sub>2</sub>O secondary standards are the same gas mixtures used as CO secondary standards. Value assignments for these are from comparisons to the 2010 secondaries on the GC-ECD system. Assigned values are stored in a MySQL database.

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## 6.2 Uncertainties

Two estimates of uncertainty are reported for each sample. The first is the expanded uncertainty associated with the value assignment (see TP\_primary\_gravimetry.docx), and is derived from uncertainties in the primary standards that define the scale, scale transfer, and any other significant uncertainties. Expanded uncertainties are calculated using the GUM (JCGM, 2008) as a guide.

The second term, referred to as scale transfer uncertainty, is the uncertainty of the measurement relative to the defined scale. This quantity is the relevant uncertainty estimate to use when propagating uncertainties to atmospheric measurements and comparing to other measurements traceable to the WMO scale.

The scale transfer uncertainty of a calibration episode, referred to as "episode uncertainty" in data distributions, and resulting value assignment is calculated using common CCL procedures as described in TP\_analysis\_calculations.

## 7.0 Data Collection and Storage

Processed data and metadata are stored on a centrally located computer in a relational database. The raw data (instrument responses) are archived in text files on a networked server. The database is backed up once a day. The raw data server has a full back up every 2 weeks and incremental back-ups every work day. The results (processed data) are also available from a web interface and can be accessed by users according to the cylinder serial number and fill code which together uniquely identify gas mixtures provided by the CCL.

## 8.0 Safety

It is GML policy to follow safe working practices when handling compressed gas cylinders and laboratory chemicals. Compressed gas cylinders should be secured when analyzed, transported, or stored. Personal protective equipment (PPE) should be used when working with hazardous chemicals or in a high noise environment.

## 9.0 Documentation

Notes pertaining to cylinder analysis are recorded on log sheets dedicated to the analysis system. For each analysis, the cylinder number, date, and time of analysis should be recorded, along with any variables likely to affect the result. The analyst to determine which, if any, additional data should be recorded.

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Significant notes relating to the performance and maintenance of the analytical system should be recorded using ELOG (an electronic record system).

### 10.0 Appendix

#### 10.1 Equipment

The following equipment is critical to the functions described in this TP.

Item	Manufacturer	Model Number
QC-TILDAS	Aerodyne	QC-TILDAS N2O/CO
Valves	Valco	multiple models of SD low pressure selector valves EC12WE, ECSD10MWE

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