Analysis of Nitrous Oxide in Air

GMD Technical Procedure

Contents

1. Purpose
2. Scope
3. References
4. Terms and Definitions
5. Procedures
   - 5.1 Gas Handling
   - 5.2 Analysis System
   - 5.3 Quality Control
6. Calculations
   - 6.1 Mole Fraction
   - 6.2 Uncertainties
7. Data Collection and Storage
8. Safety
9. Documentation
10. Appendix

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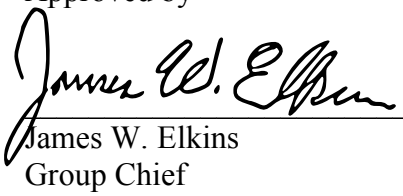

08/06/2019

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1. Purpose

This document provides the technical procedures for analysis of nitrous oxide (N_2O) in air by gas chromatography with electron capture detection.

2. Scope

NOAA/ESRL/GMD provides compressed gas standards (reference materials) to the WMO/GAW community. Natural air or modified natural air gas standards are analyzed for N_2O. Nitrous oxide dry air mole fractions are determined by gas chromatography with electron capture detection, relative to the WMO N_2O mole fraction scale. The WMO N_2O mole fraction scale is derived from gravimetrically-prepared primary standards (see TP_primary_gravimetry.pdf). The procedures described here only pertain to N_2O 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. Butler1, F.L. Moore, D.F. Hurst, and J.W. Elkins (2011), Improving measurements of SF_6 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/utils/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_2O in compressed gas cylinders (synonymous with measuring system**)**.

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 analyte to the total number of moles. Dry air mole fraction is the ratio of the number of moles of analyte 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 (refgas): 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_2O, values for secondary standards may also be assigned by comparison to other secondary standards, with verification performed by comparison to primaries.

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.

5. Procedures

5.1 Gas Handling

Cylinders to be analyzed are stored in a common location and moved to the N_2O analysis room when needed. Prior to analysis, a regulator is attached. Several regulators models are used. For N_2O, 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. It is left to the analyst to determine 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 flow rate should be set to ~100 mL min^{-1}. The flow rate of the reference cylinder should also be set to ~100 mL min^{-1}.

A small amount of drying agent, $Mg(ClO_4)_2$, 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 N_2O analysis system is described in Hall et al. (2007) and Hall et al. (2011). Briefly, gas samples are loaded into a fixed-volume, stainless steel sample loop by flushing the loop, and then injected onto a series of packed columns using a multi-port valve. N_2O and SF_6 are separated from other compounds and detected in the electron capture detector. To improve SF_6 results, we moved from a 2-column system to a 3-column system in 2006 (Hall et al., 2011). This did not impact the performance of N_2O.

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_2O mole fraction typical of the remote troposphere. A computer program controls the sample selection valve, the GC sample injection valve, and stores the data from the detector (via the electrometer). The N_2O results are sensitive to ECD temperature, carrier gas flow rate, CO_2 dopant level, and quality of the carrier gas. The CO_2 dopant level was set to maximize N_2O response and minimize the sensitivity to minor changes in the CO_2 dopant level. The GC operating conditions should not be changed without just cause and all changes should be recorded. The performance of the system should be verified following major changes.

Each unknown should be analyzed against the reference cylinder on at least two occasions (3 preferred). Each analysis episode should consist of at least 6 injections.

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_2O response of the reference cylinder, day-to-day variability of the baseline, repeatability of 6-10 repeat injections, peak shape, baseline noise, and variations in the response curve and residuals. Typically, the response curve is determined every 1-2 months by comparing the reference cylinder to five secondary standards. Experience has shown that it is not necessary to analyze secondary standards more often than this. However, it is up to the technical lead to determine 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_2O (previously analyzed on the system) can also be used to assess performance.

6.0 Calculations

6.1 Mole Fraction

The amount of N_2O is determined by comparing the peak area (or peak height) of the unknown sample to that of the reference cylinder. Peak height and peak area are determined using custom-built integration software (gcwerks.com; Salameh, 1997).

The ratio of peak area between the unknown and the reference is used to calculate mole fraction. A response curve R = f(C), is determined from analysis of the secondary standards, where *C* is dry air mole fraction and *R* is the peak area ratio. Peak height could also be used, but peak area is preferred because the N_2O peak is asymmetric. The functional form is normally a 2nd order polynomial with coefficients a_0, a_1, a_2:

$$R = a_2C^2 + a_1C + a_0 \quad (1)$$

Equation (1) is solved for *C* with *R* determined from analysis.

The coefficients for the response function are determined using orthogonal distance regression, taking uncertainties (one standard deviation) of both independent and dependent variables into account. The mole fraction of an unknown is determined from the response curve (1) and the peak area ratio, *R,* determined for the unknown.

The current WMO N_2O 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. Assigned values are stored in a SQL database.

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 quantity reported is the long-term reproducibility of the system based on repeated analysis of multiple cylinders (95%ile) (see 10.3). Reproducibility is an estimate of our ability to propagate the scale over time periods of several years. It provides an estimate of our ability to detect possible drift in cylinders over time scales of typical use, and is useful for assessing the role of reference materials with respect to inter-laboratory compatibility. The expanded uncertainty of the WMO/GAW calibration scale, based on uncertainties associated with primary standards and scale transfer, is not useful for assessing possible drift or inter-laboratory compatibility among laboratories on a common scale. For the purposes of N_2O analysis within the WMO/GAW community, reproducibility is the key quantity.

Current estimates of expanded uncertainty and reproducibility, for N_2O in the ambient mole fractions range (~325 nmol mol^{-1}), are 0.4 nmol mol^{-1} and 0.22 nmol mol^{-1}, respectively.

7.0 Data Collection and Storage

Data are stored in both raw format (raw chromatograms) and in several processed forms (integrated peak areas and heights and response ratios) to facilitate efficient data processing and quality control. Data are stored on two computer systems: the analysis system computer and the data processing computer. Both the processing computer and the analysis system computer are backed up regularly.

Mole fractions assigned to secondary standards are stored in a MySQL database, and retrieved by the processing program. For final processing, data are stored as peak area ratios and peak height ratios in a single master file, which can be easily re-processed. In the unlikely event that raw chromatograms require re-integration, this can be done on a case-by-case basis.

Final sample mole fraction assignments are stored on the processing computer (backed up daily) and uploaded to a web server through which assigned mole fractions can be accessed by users according to cylinder serial number.

8.0 Safety

It is GMD policy to follow safe working practices when handling compressed gas cylinders and laboratory chemicals. Pressurized 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 in a notebook 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. It is left to the analyst to determine which, if any, additional data should be recorded.

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
Gas Chromatograph	Agilent Technologies	6890
Computer	Dell	
Electron Capture Detector	Agilent Technologies	G1533A
Valves	Valco	EC12WE, ECSD10MWE
Packed Columns	Alltech (custom length)	porapak Q, molecular sieve 5A
Temperature Controller	Omega	CN76000

10.2 Sample Calculations (mean mole fraction)

Sample calculations are shown here for a typical analysis, using area ratio to calculate dry air mole fraction (X_i). Port 2 is the reference cylinder, port 6 is the unknown. Here the unknown was analyzed three times over three days, 8 injections each day. Area and height ratios are determined from the response of the unknown and the average response of the reference cylinders immediately before and after the unknown. The mean area ratios for each period are recorded. The area mean ratio, R, from all samples is used to calculate dry air mole fraction, C, (in nmol mol^{-1}, abbreviated ppb) using the coefficients: a_2=-1.22210·10^{-6}, a_1 = 3.18890·10^{-3}, a_0 = 0.098730. Response curve coefficients were determined in a separate analysis of the secondary standards as described in section 6.1.

$$C = \frac{-a_1 + \sqrt{a_1^2 - 4a_2(a_0 - R)}}{2a_2} \quad (2)$$

Table A1: Data used to compute mean N_2O dry air mole fraction for an unknown gas cylinder.

Date	Time	Port	HEIGHT	AREA	BC	height ratio	area ratio	Xi	Avg ratio	std dev
20110707	1107	2	1211861	33642796	B-B					
20110707	1120	6	1222567.6	33969016	B-B	1.00840	1.00908	**326.27**	1.00895	0.00044
20110707	1132	2	1212896.6	33683976	B-B					
20110707	1144	6	1222772	33965788	B-B	1.00835	1.00843	**326.00**		
20110707	1156	2	1212384.5	33679684	B-B					
20110707	1208	6	1223668.2	34002444	B-B	1.00870	1.00918	**326.31**		
20110707	1220	2	1213848.1	33706620	B-B					
20110707	1232	6	1224698.8	34011800	B-B	1.00854	1.00904	**326.26**		
20110707	1244	2	1214813.8	33707300	B-B					
20110707	1421	2	1216846.5	33773840	B-B					
20110707	1433	6	1228058	34084384	B-B	1.00939	1.00919	**326.32**		
20110707	1445	2	1216424.6	33774152	B-B					
20110707	1457	6	1225603.1	34047016	B-B	1.00798	1.00849	**326.03**		
20110707	1509	2	1215365	33746424	B-B					
20110707	1521	6	1225780.4	34030368	B-B	1.00858	1.00851	**326.03**		
20110707	1534	2	1215337.6	33740172	B-B					
20110707	1546	6	1226543.5	34070760	B-B	1.00890	1.00967	**326.52**		
20110707	1558	2	1216101.9	33748428	B-B					
20110708	1010	2	1222947.2	33927368	B-B					
20110708	1022	6	1234244.2	34189768	B-B	1.00902	1.00820	**325.90**	1.00880	0.00037
20110708	1034	2	1223476.5	33896128	B-B					
20110708	1046	6	1234229	34213068	B-B	1.00885	1.00921	**326.33**		
20110708	1058	2	1223318.5	33905228	B-B					

20110708	1110	6	1234551.1	34212628	B-B	1.00888	1.00892	**326.20**			
20110708	1122	2	1224060.8	33915084	B-B						
20110708	1134	6	1235079.8	34231036	B-B	1.00882	1.00908	**326.27**			
20110708	1146	2	1224507.1	33930672	B-B						
20110708	1323	2	1226116.9	33973464	B-B						
20110708	1335	6	1236722.9	34285768	B-B	1.00834	1.00882	**326.16**			
20110708	1347	2	1226865.4	33998448	B-B						
20110708	1359	6	1238703.6	34324012	B-B	1.00924	1.00920	**326.32**			
20110708	1412	2	1227855.8	34023892	B-B						
20110708	1424	6	1238707.1	34320932	B-B	1.00873	1.00855	**326.05**			
20110708	1436	2	1228114.8	34035968	B-B						
20110708	1448	6	1237901.8	34321396	B-B	1.00832	1.00844	**326.00**			
20110708	1500	2	1227252.9	34032196	B-B						
20110712	1234	2	1215328.5	33725236	B-B						
20110712	1246	6	1226630.2	34030540	B-B	1.00948	1.00928	**326.35**	1.00914	0.00026	
20110712	1258	2	1214884	33710104	B-B						
20110712	1310	6	1226772.6	34038448	B-B	1.00990	1.00919	**326.32**			
20110712	1322	2	1214611.1	33746964	B-B						
20110712	1334	6	1226130.4	34050792	B-B	1.00888	1.00880	**326.16**			
20110712	1346	2	1216075.9	33760304	B-B						
20110712	1359	6	1225982.1	34071980	B-B	1.00848	1.00927	**326.35**			
20110712	1411	2	1215279.6	33757704	B-B						
20110712	1547	2	1215189.2	33759168	B-B						
20110712	1559	6	1225730.2	34060308	B-B	1.00815	1.00883	**326.16**			
20110712	1611	2	1216460.8	33765540	B-B						
20110712	1624	6	1227208.1	34067112	B-B	1.00888	1.00897	**326.23**			
20110712	1636	2	1216346.2	33762644	B-B						
20110712	1648	6	1227650.9	34106056	B-B	1.00895	1.00959	**326.48**			
20110712	1700	2	1217184.5	33801620	B-B						
20110712	1712	6	1228385	34097972	B-B	1.00904	1.00916	**326.31**			

20110712	1724	2	1217578.9	33775192	B-B				
			summary	**N=24**	**mean**	**1.00878**	**1.00896**	**326.22**	**ppb**
					std dev	**0.00044**	**0.00038**	**0.16**	**ppb**

10.3 Reproducibility

Reproducibility was estimated from repeated analysis of a large number of tertiary standards. Several cylinders (Figure A1) have been analyzed numerous times from 2006-2019 under similar measurement conditions, but relative to different reference cylinders and two different sets of secondary standards. For results shown in Figure A1, the mean standard deviation of residuals is 0.09 ppb, and the reproducibility (k=2) is ~0.18 ppb.
We also examined differences between an initial measurement and a second measurement (occurring several months to 10 years later). From these data we find that reproducibility is a function of mole fraction, so we separated these data into two groups: (1): $310 < N_2O < 340$ ppb, and (2): $260 < N_2O < 310$, $340 < N_2O < 360$ ppb. The mean difference for near-ambient mole fractions (group 1) is -0.01 ppb (N=227). The 95th percentile of absolute differences is 0.19 ppb for group 1 and 0.3 ppb for group 2 (N=59). The previous estimate for reproducibility in the ambient range was 0.22 ppb. This has been lowered to 0.20 ppb.

Data shown in Figures A2 and A3 are consistent with those in A1. Therefore, we estimate reproducibilities, as 95thile:

(1) ±0.2 ppb, for N_2O 310-340 ppb

(2) ±0.3 ppb, for $260 < N_2O < 310$, $340 < N_2O < 360$ ppb

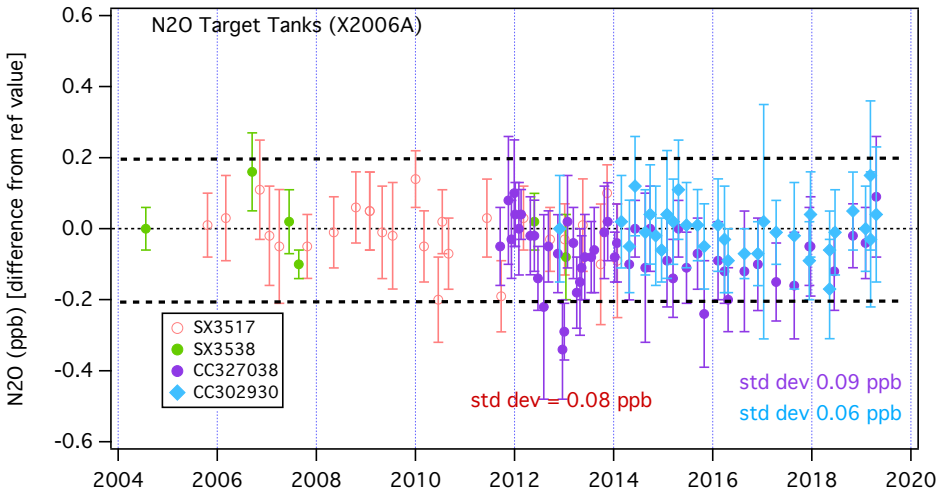

Figure A1: Deviation from assigned values for several cylinders analyzed between 2004-2019. Standard deviations for cylinders SX-3517 (317.1 ppb), SX-3538 (318.1 ppb), CC327038 (324.6 ppb), and CC302930 (326.0 ppb) are 0.08, 0.09, 0.09, 0.07 ppb respectively. Dashed lines are +/- 0.2 ppb for reference.

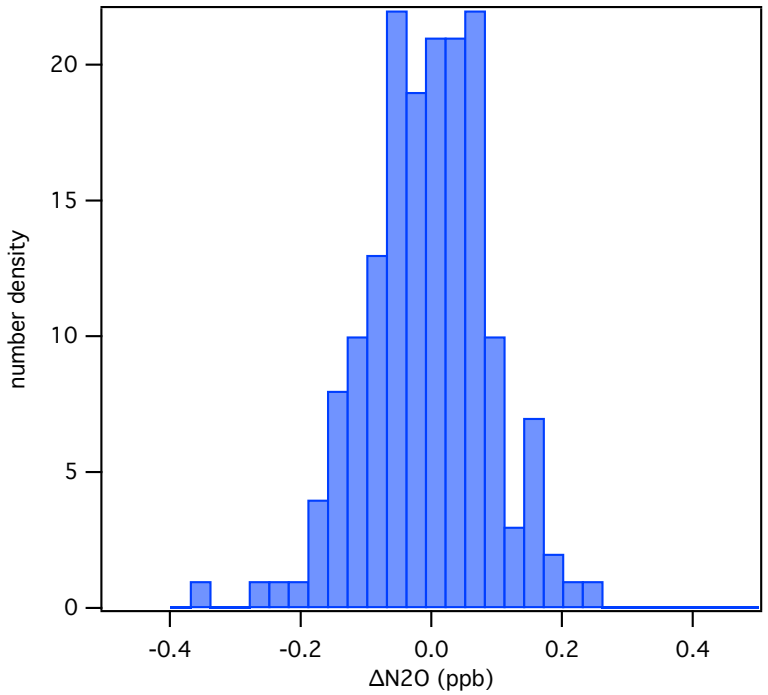

Figure A2: Histogram of differences between initial and subsequent N_2O measurements (occurring several months to 10 years apart, from 2006-2019) for N_2O in the range 310-340 ppb; 227 paired measurements.

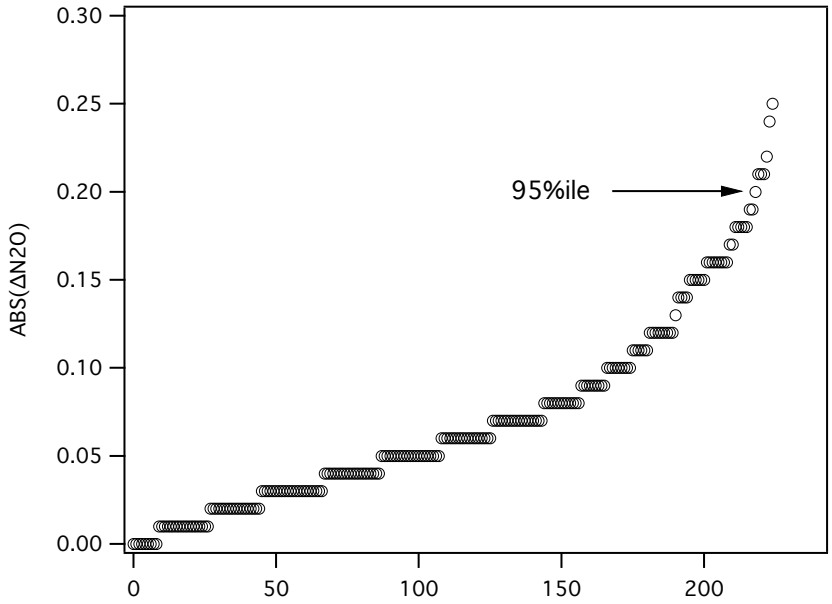

Figure A3: Absolute differences between initial and subsequent N_2O measurements, subject to the same restrictions as in figure A2. Note that updates to the reproducibility analysis may occur and not be documented here.