Preparation of Primary Standards by Gravimetric Methods

GMD Technical Procedure

Contents

Approved by

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1.   Purpose

This document provides the technical procedures for the preparation of primary standards (as compressed gas mixtures) by gravimetric methods. These procedures are valid for the following mixtures: carbon monoxide in air, methane in air, nitrous oxide in air, sulfur hexafluoride in air, and combinations of the above. Mixtures prepared by gravimetric methods are directly traceable to the SI unit, mass.

2.   Scope

This document provides general procedures for the preparation of primary standards using four different methods: 1) transfer of an analyte (liquid phase) from a glass capillary tube to a cylinder followed by dilution, 2) direct transfer of an analyte(s) (gas phase) to a cylinder followed by dilution, 3) transfer of an analyte (gas phase) to a weighing vessel and then to a cylinder using a flushing technique, followed by dilution, 4) transfer of an analyte to a weighing vessel and then to a cylinder without flushing, followed by dilution. Note that method (1) is not currently used for primary standards covered by this procedure. The methods are referred to as 1) capillary method, 2) direct transfer, 3) tube flush, and 4) tube expansion.

Methods used for preparation of primary standards by gravimetric methods follow closely those specified in ISO 6142. Differences from ISO 6142 are noted in this document.

3.   References

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4. Terms and Definitions

analyte: A substance whose chemical composition is to be determined by chemical analysis.

control volume: An object of similar mass and volume to that for which the mass is to be determined. The control volume is used to track relative changes in the mass of the primary object to be weighted (cylinder, transfer tube, capillary, etc.) and also to track drift in the balance.

diluent: The gas, usually ultra-pure or synthetic air, which is added to a gas standard to dilute the mole fraction of the analyte to the desired level.

mass piece: Weight (stainless steel or brass) from a calibration mass set, traceable to national standards (NIST).

mole fraction: The ratio of the number of moles of analyte to the total number of moles present. Commonly used abbreviations include: ppm = μmol mol^{-1}, ppb = nmol mol^{-1}, and ppt = pmol mol^{-1}.

primary standard: A measurement standard established using a primary reference measurement procedure, or created as an artifact, chosen by convention.

receptacle: Volume to which gas will be added (included cylinders, transfer tubes, and other devices used to store gas samples).

reference cylinder: Cylinder of dry air designated for the calibration of other standards for quantities of the same kind. The instrument response function 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.

scrubbing system: Various absorbents, packed in stainless steel volumes, used for removing impurities from diluent gas.

secondary standard: A standard whose value is determined through analysis relative to primary standards, or through comparison to other secondary standards with verification by comparison 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.

tertiary standard: A standard whose value is determined through analysis relative to secondary standards, for a quantity of the same kind.

transfer tube or transfer volume: A singled-ended or double-ended tube (usually stainless steel) with a valves on one or both ends, used for transferring an aliquot of gas to a cylinder.

5.   Procedures

5.1   Gas Blending

Gas blending is performed using a gas manifold, which consists of a vacuum pump, a series of valves, and a gas scrubbing system. Valves and other materials should be chosen to minimize "memory effects" when gases of different mole fraction are introduced. The gas scrubbing system consists of different absorbents or catalysts to remove trace contaminants from the diluent gas. The selection of absorbents/catalysts depends on the analyte of interest (e.g. section 5.6.5).

5.2   Cylinder Selection and Preparation

Primary standards are prepared in various types of cylinders; the choice of which depends on its ability to maintain the integrity of a particular gas mixture at a particular mole fraction during long-term storage. Cylinder size, materials, valves, and surface treatments vary depending on the stability characteristics. For example, N_2O and SF_6 standards are typically prepared in 5.9 L aluminum cylinders with brass pack-less valves, while carbon monoxide standards are prepared in 29.5 L cylinders owing to potential out-gassing of CO that may occur over time.   For standards prepared at mole fractions near those found in the remote troposphere, cylinders are typically conditioned to a gas mixture of similar mole fraction for several days or weeks prior to use.   Cylinders can be reused when contamination or surface losses are expected to be negligible (i.e., when cylinders are will be exposed to similar mole fractions and gas mixtures).

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5.3   Balance Selection and Use

Weighings can be performed on a number of electronic and analytical balances. Balances should be selected to maximize weighing precision, unless other factors are deemed more important. Weighings are performed relative to a control object (cylinder, capillary, or transfer tube) of similar mass and volume. This allows for the tracking of drift and also eliminates the need for buoyancy corrections in most cases. Objects should be weighed multiple times relative to control objects. Linear drift correction is generally sufficient. Efforts to achieve optimal weighing precision should be pursued, including minimizing air drafts, floor vibrations, and rapid changes in room temperature.

For balances that are auto-calibrating, a calibration sequence should be performed on the day of use. For balances that are not auto-calibrating, the calibration should be checked and recorded prior to use. This can be done by either weighing a series of mass pieces from a mass set, or by adding the receptacle to be weighed to the balance, and then adding a mass piece approximately equal to the expected change in mass. This method ensures that the mass to be determined has been referenced to at least one standard mass piece at the appropriate span.

Standard mass pieces and control objects should be stored in a dust-free environment, and retained for future comparison to provide a history of relative calibrations. Prior to weighing receptacles, dust and other loosely attached objects such as labels or paper tags should be removed if these are likely to come off during preparation of the gravimetric standard. Objects should be at room temperature for weighing.

When using the mass comparator, users should be aware that the comparator is only accurate when comparing equal masses. A correction factor, to be used when comparing unequal masses, can be determined by using a gas cylinder as a tare weight, and adding 1 kg and 5 kg stainless steel weights to the tare. A custom-made aluminum cylinder cap is used to mount the 1kg and 5kg weights vertically on the tare cylinder. The correction factor, f, is ~1.00161 and is applied as follows: $\delta m(actual) = \delta m(apparent) * f$, where δm is the mass difference between two objects. The value of f has been confirmed by comparing δm determined using the mass comparator with that determined using floor balance E1210.

5.4   Traceability

Balances should be serviced and calibrated by an accredited organization on a yearly basis to ensure NIST traceability. In the event that a balance cannot be certified, weighings should be referenced to standard mass pieces. This applies in particular to a Voland HCE-10G dual-pan balance, which no longer functions as intended. Not all internal weights can be directed on and off the beam. Use of this balance requires a combination of mass pieces and internal weights.

Mass pieces should be calibrated regularly, with the schedule determined by considering the likely change in mass over a period of time and the effect of these changes on uncertainties

associated with preparing standards. Mass pieces can be calibrated independently (by an accredited laboratory) or by comparison (e.g. using recently-certified analytical balances). Records of mass piece calibration or comparison should be kept for reference.

Measurement of the oxygen mole fraction in dilution air is traceable to NIST SRM 2659A ($20.863 \pm 0.021\%$ O_2).

5.5   Reagent Gases

High-purity reagent gases should be obtained whenever possible. An assay of reagent gases used to prepare primary standards should be performed, if possible. The purity of the reagent (determined either from in-house assay, or manufacturer's report) should be recorded along with any purity corrections applied.

5.6   Transfer Procedures

Aliquots of liquid or gas are transferred to cylinders in a variety of ways. A common aspect of the transfer and dilution is that the trace contaminants in the diluent gas can affect the mole fraction of the standard. Normally, trace contaminants are removed from the diluent gas using a combination of scrubbers. It is important to verify the purity of the diluent gas as it exits the manifold either by preparing blank standards, or by taking grab samples off the manifold during the dilution process. An alternative method is to measure the mole fraction of analyte in the diluent gas and perform the dilution without scrubbing. Standards should be adjusted for the amount of analyte introduced into the standard from the diluent gas when this can be reliably measured. However, it can be difficult to determine the amount of analyte in the diluent gas because it is typically at trace levels, much lower that the target mole fraction of the standard, and near the detection limit of analytical methods.

5.6.1   Capillary Method

Note, the capillary method is not applicable to primary standards prepared in conjuction with GMD's role as WMO/GAW CCL. It is included here for reference.

A liquid reagent is transferred to an evacuated gas cylinder using the glass capillary method. A glass capillary, sealed on one end, is first weighed relative to a control object. Then, a pure reagent or known liquid mixture is transferred to the capillary (either by cryogenic trapping on a vacuum manifold, or by inserting the capillary into a test tube with the open end submerged in liquid and drawing liquid into the capillary by pulling a slight vacuum on the test tube (Schmidt and Rook, 1983)). The condensed phase is moved to the sealed end by centrifuge or cryogenic cooling and the open end of the capillary is sealed in a flame. Liquid can also be drawn into the capillary using cryogens when the transfer is done on a vacuum manifold. If the procedure is performed on a vacuum manifold, sealing the capillary under vacuum cuts the capillary in two

pieces (a sealed piece containing liquid, and a residual piece). After equilibrating to room temperature, the capillary piece(s) are weighed again relative to a control. The mass of liquid is determined from the difference between the relative weighings, corrected for any additional changes in mass (buoyancy, density, mass added/lost upon sealing, etc). Typically these corrections are very small (~0.03%).

The aliquot is transferred to an evacuated cylinder by inserting the capillary in a Teflon tube, and attaching the Teflon tube to the cylinder and to a supply of diluent gas. Room air is flushed out of the tube by flowing diluent gas to vent. Then the cylinder valve is opened and a flow of diluent gas is established. The capillary is broken and gently heated to vaporize the aliquot and transfer all aliquot to the cylinder. Finally, the cylinder is pressurized with diluent gas.

5.6.2   Direct Transfer Method

This method involves the transfer of gas, either in pure or diluted form, directly to a cylinder followed by addition of dilution gas.

>   a) An evacuated cylinder is weighed relative to a control volume.
>   b) An aliquot of gas is transferred to the cylinder.
>   c) The cylinder is weighed relative to a control volume.
>   d) Dilution gas is added to the cylinder.
>   e) The cylinder is weighed a final time relative to a control volume.

5.6.3   Tube Expansion Method

This method involves the transfer of an aliquot of gas (pure or diluted) to a transfer volume (tube) and then to the cylinder. This method can be advantageous in that large dilution ratios (.e.g. 4000:1) can be achieved with relatively high precision, thus reducing the number of steps needed to reach ppb and ppt levels. Further, the cylinder is exposed to a high concentration of analyte for only a short time, since dilution gas can be added immediately to the cylinder without reweighing.

>   a) An evacuated cylinder is weighed relative to a control volume.
>   b) An aliquot is transfered to an evacuated transfer tube on the vacuum manifold.
>   c) The transfer tube is weighed relative to a control volume.
>   d) The aliquot is allowed to expand into an evacuated cylinder.
>   e) The valve on the transfer tube is closed.
>   f) Residual aliquot in the transfer line is pushed into the cylinder using dilution gas.
>   g) The transfer tube is weighed again relative to a control volume.
>   h) Dilution gas is added to the cylinder.
>   i) The cylinder is weighed relative to a control volume.

5.6.4   Tube Flush Method

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This method involves the transfer of an aliquot or gas (pure or diluted) to a transfer volume (tube) and then to the cylinder. Here the aliquot is transferred to the cylinder not by simple expansion, but by repeated pressurization and expansion using dilution gas. This method has the advantage that the cylinder need not be under vacuum for analyte transfer.

   a) A cylinder is weighed relative to a control volume.
   b) An evacuated transfer tube is weighed relative to a control volume.
   c) An aliquot is transferred to the transfer tube on the vacuum manifold.
   d) The transfer tube is weighed relative to a control volume.
   e) The aliquot is allowed to expand into the cylinder. It is helpful if the gas pressure in the transfer tube is higher than the initial pressure of the cylinder, but this is not strictly required. If $P_{tt} < P_{cyl}$, the aliquot can be expanded into an evacuated section of the manifold, pressurized to $P > P_{cyl}$, and then expanded into the cylinder.
   f) The transfer tube is repeatedly pressurized with dilution gas ($P > P_{cyl}$) and expanded into the cylinder. The tube is typically flushed 10 or more times in this manner.
   g) The valve on the transfer tube is closed.
   h) Dilution gas is added to the cylinder.
   i) The cylinder is weighed relative to a control volume.

The transfer efficiency can be estimated by adding a known amount of additional diluent to the transfer tube after the analyte has been transferred to a cylinder using the method in 5.6.4, measuring amount of analyte in the transfer tube, and comparing that to the amount of analyte initially added to the tube. Experiments with N_2O and CFC-12 indicate a transfer efficiency greater than 99.998%.

5.6.5 Diluent Gas Considerations

The quality and composition of the dilution gas need to be considered. The presence of significant quantities of the component of interest could be important. The presence or absence of other trace gases could also impact the measurement if significant measurement artifacts exist. For example, argon could be important if standards are to be analyzed using single-line spectroscopic instruments.

The choice to use synthetic or scrubbed natural air for dilution gas depends on the analytical technique and the relative purity of the dilution air. In general, scrubbed natural air has been used for CH_4 and CO, and synthetic air has been used for N_2O and SF_6.

The choice to use dilution air as received from the vendor (without additional purification) or after additional purification should be considered with respect to the gas of interest. For example, N_2O standards made in the early 2000s were made using synthetic air with additional scrubbing to remove ~ 1-5 nmol mol^{-1} N_2O present in the dilution air. This introduced ~0.5 nmol mol^{-1} uncertainty due to variable purification efficiency, which was difficult to control.

Consequently, more recent N_2O standards were prepared without additional purification, as better quality dilution air became available ($N_2O < 0.1$ nmol mol^{-1}).

If additional purification is desired, the following materials should be considered
    a) molecular sieve 13x to remove N_2O (at -78 °C)
    b) activated carbon to remove SF_6 (at -78 °C)
    c) sofnocat 420 or 514 to remove CO

5.7 Data Collection and Storage

Data with respect to the preparation of the primary standards are kept in a notebook or in electronic form. Deviation from the procedures noted in 5.6.1-5.6.4 should be recorded and their potential effects explained. Values assigned to primary standards used to propagate the scale to secondary standards, are stored in a MySQL database.

5.8 Verification of Primary Standards

Verification of primary standards is accomplished by comparing a number of primary standards to each other using appropriate instruments. The relative responses of various primary standards should agree, to first order, with the expected response of the instrument. For example, standards should show a linear relationship on an instrument with an inherently linear response. Additional verification can be performed by preparing standards using a variety of techniques (5.6.1-5.6.4) and a variety of cylinder sizes or types.

6. Calculations

6.1 Dry Air Mole Fraction

Primary standards are reported as dry air mole fraction. Molecular weights (MW) are calculated using recent values for atomic weights, including estimates for the natural abundance of various isotopologues (Wieser and Coplen, 2011). The molecular weight of synthetic air (O_2+N_2) or natural air ($O_2+N_2 +Ar$) is determined by measuring the oxygen content. The mole fraction of argon in scrubbed natural air is assumed constant at 0.934%. Ranges for molecular weights were calculated from data in Wieser and Coplen (2011), and included in the uncertainty analysis.

The mole fraction of a component *(χ_i)* is calculated as the number of moles of that component (*m_i*) divided by total number of moles (*m*).

$$\chi_i = \frac{m_i}{\sum m}$$

For a single component standard in air,

$$\chi_i = \frac{\dfrac{M_i}{MW_i}}{\dfrac{M_i}{MW_i} + \dfrac{M_{air}}{MW_{air}}} + \chi_{i\_air}$$

where M is mass, MW is molecular weight, and χ_{i_dil} is the mole fraction of component *i* present in the dilution air (if known).

A purity correction may be applied to individual components when known.

6.2   Uncertainties

Two types of uncertainties can be calculated for primary standards. The first is based only on weighing repeatability. Relative weighing uncertainties are summed in quadrature, following procedures outlined in JCGM (2008). This uncertainty estimate includes only statistical uncertainties and is useful when comparing standards during verification.

A deviation from ISO 6142 is noted here. Currently, covariance between daughter standards and parents is not considered (see ISO 6142:2001(E), sec. 5.1.3). Analysis of N_2O and SF_6 primary standards suggests that covariance is a minor contributor to uncertainty compared to (a), (b), (c), (i), and (j) below.

To estimate the total, expanded uncertainty, uncertainties are summed according to methods outlined in JCGM (2008).
Uncertainties may include:
  a. weighing repeatability
  b. reagent purity, including cross contamination from multiple reagents
  c. impurities in the dilution gas
  d. transfer efficiency
  e. loss of metal, paint, or labels from cylinders or receptacles
  f. leakage from transfer tubes
  g. memory effects in transfer lines
  h. physical or chemical interactions with cylinder surfaces
  i. molecular weight
  j. scale transfer from primary-to-secondary and secondary-to-tertiary levels

Typically (a), (b), (c), (i), and (j) above are the most important.

It is also possible to sum uncertainty contributions differently, if uncertainties are likely to be one-sided (eg. contribute only in one direction),

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$$\mu^+ = \sqrt{\Sigma\mu_{m,j}^2 + \mu_c^2} + B^+$$

$$\mu^- = \sqrt{\Sigma\mu_{m,j}^2 + \mu_c^2} + B^-$$

where $\mu_{m,i}$ are relative weighing uncertainties, μ_c is the relative uncertainty in the parent standard when the standard is prepared by dilution of a higher-level standard (parent), and B^+ and B^- are bias estimates that would lead to overestimation or underestimation of the mole fraction. The final result is expressed as χ_i ($-\mu^-$, $+\mu^+$). For example, if the component of interest is present in the diluent gas and is neglected, it can only contribute in a positive way, and would lead to an underestimation of the mole fraction. If the existence of a component in the diluent gas is known, and can be estimated from analysis or other means, then the uncertainty associated with this estimate is included as a random error rather than as a bias error. This is the preferred method for estimating uncertainties associated with the dilution gas.

7.0   Calibration Scales - (does not apply to CO_2)

The preparation of primary standards ultimately leads to the establishment of a calibrations scale. Here we define a calibration scale, and how it is updated. Within GMD, an assignment of mole fraction by analysis is not typically made with reference to one primary standard. Instead, a suite of primary standards is prepared and related to a reference cylinder through analysis. The gravimetrically prepared values are used to establish a "response function" on a particular instrument. The response function can have different forms. Typically, the instrument response relative to a reference cylinder (R) is expressed as a linear or polynomial function of the mole fractions (C) of primary standards, R = f(C). The best-fit function is then used to "assign" new values to each primary standard in the suite, as well as to the reference cylinder. The assignments are typically done over a period of time, such that multiple assignments can be averaged and statistics computed. The primary standards and their assigned values constitute the calibration scale. Scales are named according to the year in which they are adopted. For example, the nitrous oxide scale consists of 13 primary standards analyzed on an Agilent 6890 gas chromatograph with electron capture detector, and is referred to as the WMO N_2O X2006A scale. The scale is then transferred to secondary standards for routine use. If a primary standard is added or removed from the suite, this results in the formation of a new scale, or includes a statement of equivalency. A new scale can be related to an older scale via secondary or tertiary standards.

8.0   Safety

It is NOAA/GMD policy to follow safe working practices when handling compressed gas cylinders and laboratory chemicals. Pressurized cylinders should be secured (except when they are being weighed). Personal protective equipment (PPE) should be used when working with hazardous chemicals or in a high noise environment. Personnel working with radio nuclides (electron capture detectors) must be trained according to NOAA/GMD policies.

9.0   Documentation

The calculated mole fractions and molecular weight of each primary standard is recorded in a database. A paper label is created and attached to the cylinder. The label identifies the mole fractions and their uncertainties for each component of interest, the creator, and the notebook page on which more information can be found. Calibration certificates are not prepared for primary standards.

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10.0   Appendix

10.1   Uncertainties

weighing uncertainties
The uncertainties associated with mass determinations on analytical balances are determined from multiple weighings, relative to a control object, corrected for drift. Uncertainties depend both on the resolution of the balance and the weighing technique. Typical weighing sequences are ABABA …, ABBABBA…, and ABBBABBBA. Uncertainties, expressed as one standard deviation, are as follows:

Balance	Capacity	Typical Repeatability
Sauter E1216	60 kg	1 g
Sartorious CCE40K3	40 kg	2, 10 mg*
Voland	10 kg	10 mg
Mettler PR1200	1200 g	0.7 mg
Mettler AT201	200 g	0.05 mg
Mettler XP6	6 g	2 µg
Mettler UM3	3 g	1 µg

for N30 (small) and N150 (large) aluminum cylinders, respectively

Uncertainty Example (N_2O):
The typical standard uncertainty for a single primary standard contributing to the WMO-N_2O-X2006A scale, at 325 nmol mol^{-1}, is 0.5 nmol mol^{-1}. Relative contributions of various uncertainty components are shown below.

Typical Primary Standard (N_2O)	μ_i (fractional)	Relative Contribution	Type	distribution
reagent purity	5.774E-05	2%	B	rectangular
MW N_2O	1.312E-05	< 1%	B	rectangular
transfer efficiency	5.774E-05	2%	B	rectangular
MW dilution gas (synthetic air)	5.893E-04	22%	B	rectangular
weighing	1.077E-03	40%	A	normal
N_2O in dilution gas	8.882E-04	33%	B	rectangular

Analysis of a suite of primary standards and subsequent determination of a response function by orthogonal distance regression leads to an uncertainty estimate for the response function, which can then be combined with uncertainties associated with scale transfer from primary to secondary standards, and then secondary to tertiary standards. For N_2O, this leads to a total expanded uncertainty of 0.5 nmol mol^{-1} (k=2) at 325 nmol mol^{-1}. Primary standards and scale transfer contribute roughly equally to the expanded uncertainty in this case.

buoyancy effects

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Because all mass determinations are made relative to an object of similar density, buoyancy effects will only influence the standards when (a) the air density changes between weighings, or (b) the air density differs from the nominal 20°C and 1.20 kg m^{-3} (standard conditions to which weights are already referenced). The time scales for variations in humidity and room temperature and pressure are typically long compared to the time scales of weighing. The contribution of buoyancy is approximately 0.015% of the weights used, and weights are normally already corrected for buoyancy at an air density of 1.2 kg m^{-3}.   The error introduced by not correcting for air density in Boulder (1.0 kg/m^{-3}) is 0.0026% and is ignored. Buoyancy corrections are applied to the capillary method because comparisons are made between objects of different density.

10.2   Equipment

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

Item	Manufacturer	Model Number
Gas blending manifold (2)	Custom	
Analytical balance	Mettler-Toledo	UM3
Analytical balance	Mettler-Toledo	XP6
Analytical balance	Mettler-Toledo	AT201
Analytical balance	Mettler-Toledo	PR1200
Analytical balance	Sauter	E1216
Analytical balance	Voland	10kg
Mass comparator	Sartorious	CCE40K3
Oxygen analyzer	Beckman	E2
Transfer tubes (5, 10, 50 cm^3)	Custom	
Vacuum Pump	Varian	Tri-scroll

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