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Standards and Traceability for Air Quality Measurements: Flow Rates and Gaseous Pollutants

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Abstract: Accurate and precise flow rate and gas concentration measurement standards are needed for comparable air quality measurements. Transfer standards are most often used for calibration, performance testing, and auditing of field monitors. These must be traceable to primary standards that are in turn derived from fundamental units of length, mass, temperature, and time. Flow rates and volumes are measured by devices based on positive displacement, pressure differences, and temperature increases or decreases. Stable gas concentrations are prepared in non-reactive pressurized containers by gravimetric and dilution methods. Reactive gases are generated from photochemistry and permeation devices. These standards are used to determine the accuracy, precision, and validity of air quality measurements, and these attributes should be reported with the measurement values.

1. Introduction

Air quality measurements are acquired for multiple purposes using a wide variety of physical and chemical methods. All of these methods require some sort of standardization that allows the values acquired to be compared with each other and with regulatory limits. As more air quality monitors are installed worldwide, and as the number of measured observables increases, there is a need to summarize and review the standardization process and available resources. Various standard-setting organizations, such as the International Standards Organization [1] and American Society of Testing and Materials [2], have issued procedures for creating and using measurement standards. Unfortunately, these procedures are available only at high cost, and several have not been updated to reflect current technology. Fortunately, summaries and reviews of the topic have been published, along with more specific literature on individual standards, and the most useful of these are identified here. The following discussion defines common terms related to air

quality standards, identifies their uses, and describes options available for flow rate/volume and gas concentration measurements. Suspended particulate matter (PM) standards will be addressed in a forthcoming publication.

2. Definitions

"Standards" and "standardization" refer to several different things in air quality science and are defined as follows:

- *Air quality regulatory standards* Ambient air quality standards (AAQS) have been established in many countries as a means to protect public health and welfare [3–8]. AAQS define a measured indicator (usually the criteria contaminants of carbon monoxide [CO]; nitrogen dioxide [NO_2]; sulfur dioxide [SO_2]; ozone [O_3]; and PM mass and lead [Pb]), an averaging time [e.g., 5 min; 1-h; 24-h; or 1 year], a statistical form [e.g., annual average; maximum value; or upper 98th percentile], and concentration limits for each averaging time. Emission standards are also set for large industrial sources and engine exhaust.

- *Air quality measurement standardization* Procedures and methods are defined for determining compliance with regulatory standards. This standardization can be:

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(1) performance-based, in which specifications are given for the measured quantities and tolerable deviations from the desired values, or (2) design-based, in which the dimensions and types of measurement equipment are defined [9, 10]. The U.S. EPA's [11] federal reference methods (FRMs) represent a combination of performance and design standardization. Figure 1 shows examples of performance- and design-based standards for $PM_{2.5}$ (mass of particles with aerodynamic diameter <2.5 μm) FRMs. The disadvantage of design-based methods are that newer, and possibly more accurate, technology must demonstrate equivalence with methods that may have been found to be less applicable to modern pollution situations. An example of this is standardization of the Method 5 stack test method [12] which draws effluent through a hot filter to measure PM, then through impinger solutions that are intended to capture condensable gases, but in reality collect soluble SO_2 and organic compounds [13]. Dilution sampling systems [14, 15], similar to those used for engine exhaust, provide more realistic PM emissions.

- *Air quality measurement standards* These are methods or materials of well-known properties used for measurement calibration, auditing, and performance testing, and are the subject of this paper. These are classified as:

  - *Primary Standard* Mixtures or substances or devices with properties or values derived from fundamental physical parameters of length, mass, temperature, and time as related to primary standards established by national and international metrology institutes. Primary standards are prepared and maintained under well-controlled environmental conditions.
  - *Transfer (Secondary) Standard* Mixtures or substances or devices with values based upon comparison with primary standards and traceable to them. Transfer standards may also be primary standards, but they are often less costly and available in larger quantities than primary standards. As several transfer standards are used in field applications without environmental control, and are often less costly to produce, transfer standards may be less accurate and precise than primary standards.
  - *Reference Materials* Substances representing different environmental matrices that have been analyzed by multiple laboratories and have had values assigned based on inter-laboratory agreement. These are sometimes used as primary standards, but they are more appropriate as audit standards. They are often used to evaluate the effect of interferences that are encountered in environmental measurements.

  - *Calibration Standards* Transfer standards at various concentration levels used to relate the output of a measurement method to a concentration level.
  - *Performance Test Standards* Transfer standards at various concentration levels used to evaluate instrument calibration during normal operation. These are often the same as the calibration standards. They are often used in "zero/span" tests.
  - *Audit Standards* Transfer standards with traceability independent of those used for calibration and performance testing. Performance audits are performed periodically to evaluate the accuracy of a method calibration and are performed by someone other than the person who normally operates the instrument.

3. Flow Rate/Volume Measurement Standards

The product of volumetric flow rate (F_v) and sampling time (t) equals the volume (V) passing through the measurement device:
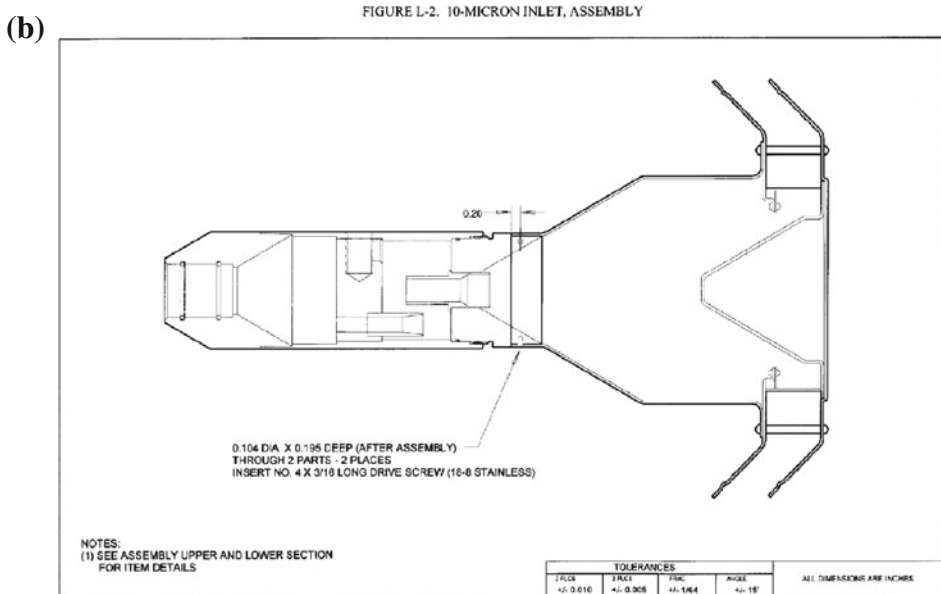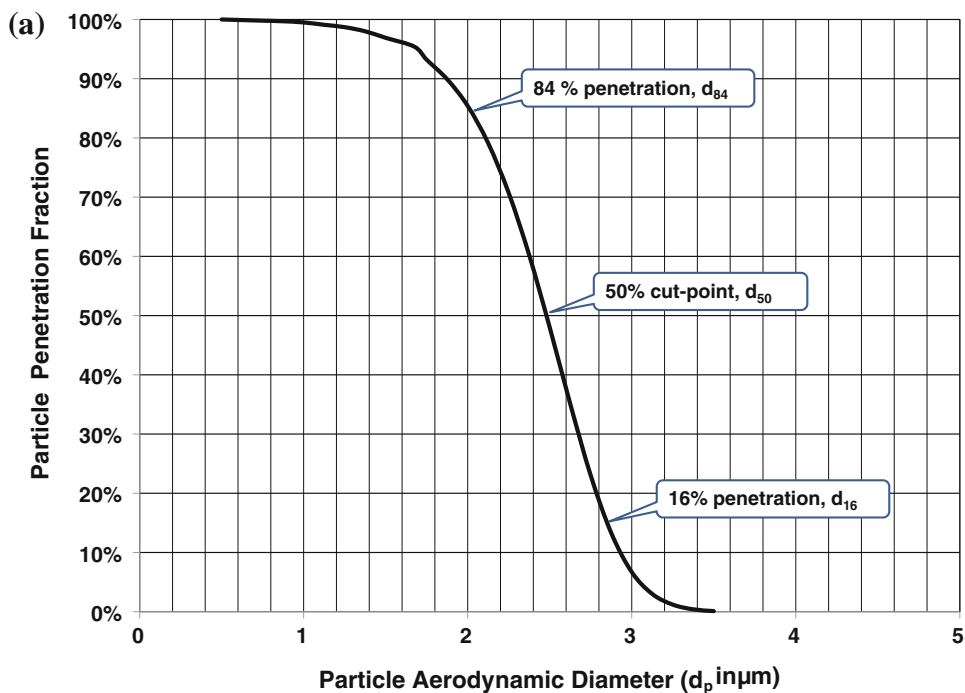
$$V = F_v t \tag{1}$$

Since t can be accurately measured, quantification of V and F_v are interchangeable. Many modern air quality measurement devices contain some form of flow measurement and timing device. Accurate flow rates are essential for all air quality monitoring devices and for preparing their measurement standards. Collocated comparisons of monitoring devices often show near-perfect correlations between the reported concentrations, but slopes differing from unity by ±10 % or more. The first suspect in these cases is differences in the flow rate or sample volume.

Given the importance of flow rate and volume values, there is a surprisingly small literature describing and comparing the different measurement and standardization options. Baker and Pouchot [16, 17] provide the most concise, accurate, and accessible summary of flow and volume measurement standards while Bean [18] contains a more comprehensive treatment. These methods can be classified into the following categories:

- Positive displacement systems have precise internal volumes that can be filled and emptied as a function of time. Since these volumes are relatable to the primary meter standard in Paris, most of these are suitable as primary standards.
- Head devices restrict the flow with an obstruction, thereby changing the flow speed and reducing the pressure. The pressure reduction can be related to the flow rate as determined by a primary standard.

Fig. 1 Examples of performance and design standards for PM$_{2.5}$ (mass of particles with aerodynamic diameter <2.5 μm) federal reference methods (FRMs, [128, 129]. *Top panel* performance-based sampling effectiveness curve [130, 131] for a PM$_{2.5}$ size-selective inlet. *Bottom panel* design-specification for a PM$_{10}$ (particles with aerodynamic diameters < 10 μm) size-selective inlet used to measure compliance with ambient air quality standards (AAQS). Rotate 90° counterclockwise for ambient FRM monitoring

(a)

(b)

FIGURE L-2. 10-MICRON INLET, ASSEMBLY

- Gravitational resistance variable area devices allow the flow to raise a weight within an annulus that varies with height. These are calibrated to primary standards.
- Rotational devices consist of turbines or fans that spin at higher rates when flow rates increase. These are calibrated to primary standards.
- Thermal cooling devices measure the temperature lost from a heated wire with a constant electrical current as the gas passes over it or the increase in gas temperature as it passes over a surface maintained at a constant

temperature. These quantify mass as opposed to volumetric flow rates and are calibrated to primary standards.

Table 1 describes some of the primary and transfer standards for flow rate/volume commonly used for air quality purposes, and Fig. 2 illustrates some of their appearances.

Most gas flow measurement devices are calibrated for air to standard conditions, which are usually 1 atm of pressure, but with standard reference temperatures of 0, 20, or 25 °C. Flow rates must be adjusted from the ambient
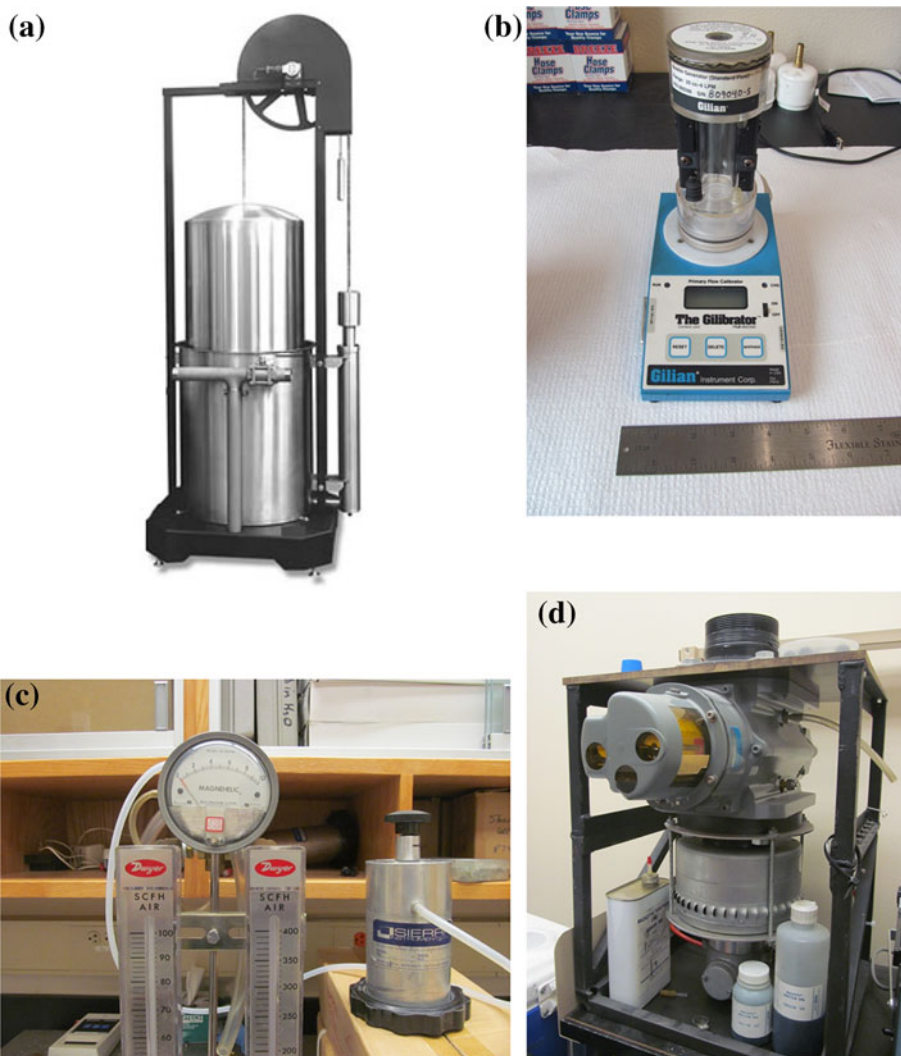
Table 1 Primary and transfer standards for flow rate/volume commonly used in air quality measurements

Flow measurement device (References)	Operating principles	Comments
Bell prover [76–80]	Positive displacement. The open end of a large cylindrical "bell" is immersed in a low-volatility oil and counterbalanced by a weight. Gas flow is introduced through a tube that extends above the oil surface, and the change in elevation of the cylinder above the oil is measured as a function of time. Pressure and temperature are monitored within the bell for adjustment to standard conditions	Primary standard, originally used by natural gas suppliers to calibrate dry gas meters. Was commonly used to calibrate high-volume sampler transfer standards, but is not practical for the lower flow rates of modern air quality monitors. When water is used instead of oil as a sealant, a correction is needed for saturated water vapor in the trapped gas
Piston meter [81]	Positive displacement. A plug with a mercury seal is tightly-fitted into a precisely-dimensioned glass tube. The piston rises as gas is introduced into the tube, and its change in elevation as a function of time quantifies the flow rate	Primary standard, in which adjustments are needed to correct for increased pressure owing to resistance of the plug
Bubble meter [82–85]	Positive displacement. Gas flows through a soap-saturated water solution, creating a bubble that clings to the sides of a vertical cylinder. The bubble rises and indicates the volume passing through the system as a function of time	Primary standard, in which the bubble provides minimal resistance to the air flow, but adjustments are needed to account for the water vapor added to the gas stream after passing through the soap-solution. Modern implementations pulse the gas through the cylinder and count the number of pulses per unit time
Roots meter [86]	Positive displacement. Two rotating lobes move in response to flow being drawn through the meter. The lobes seal to create a constant volume that moves the flow to the outlet. The number of revolutions, along with the gas volume displaced, gives an accurate measurement of the total gas volume	Transfer standard, because an empirical discharge coefficient depending on the rotational resistance of the lobes. The discharge coefficient remains constant for a given meter, so it is often used as a primary standard
Wet test meter [87]	Positive displacement. A compartmentalized inner cylinder with slits cut into it is located in an outer drum half filled with water. The measured gas is pumped into one of the submerged compartments on the inner drum, displacing the water and turning the drum. The number of rotations is related to the flow	Transfer standard, owing to the need to determine a discharge coefficient based on the drum geometry and resistance to rotation. Since the discharge constant remains the same after standardization to a primary source, this is often used as a primary standard
Dry gas meter [88]	Positive displacement. Internal bellows inflate and deflate as the measured gas passes through the meter	Transfer standard, commonly used in buildings to measure natural gas consumption. Smaller units are also used in some air quality samplers to measure integrated sample volumes. Several filling and emptying cycles are needed as the volume is not constant within a cycle and measurement does not necessarily stop at the beginning portion of the cycle
Orifice meter [89]	Head device. One or more orifices of known area are placed at the inlet to a sampling system and the pressure drop is measured across the orifice. These can also be located in a sample flow line, most often in the form of a venturi with pressure drop measured at the narrowest point. The pressure drop is related to the flow measured by a primary standard using a calibration curve	Transfer standard, a simple, inexpensive and accurate flow device. A water anemometer can be used to measure pressure drop, though Magnehelics are more practical. The orifice is commonly used to set the mass flow controller for the high-volume sampler used to measure total suspended particulate (TSP) for lead quantification
Critical orifice/ throat [90–101]	Head device. When the ratio of downstream to upstream pressure for flow through an orifice drops below 0.53 (i.e., for air, slightly different for other gases), the velocity stabilizes at the speed of sound and does not increase. Flat plates with a small hole and hypodermic needles have been used as critical orifices. The critical throat is a variation that reduces the 0.53 downstream/upstream ratio, thereby requiring less energy for the flow mover	Transfer standard, although theoretically a primary standard, it is treated as a transfer standard calibrated against a primary standard to account for imprecise dimensions of the orifice. These are often used behind a substrate that collects gases and/or particles, but a high capacity pump is needed to retain the desired pressure difference
Laminar flow meter [18, 102]	Head device. It consists of a tube through which the gas flows under laminar conditions. The pressure drop across the tube is directly proportional to the volumetric flow rate and gas viscosity	Transfer standard, a simple, inexpensive and accurate flow device. It has lower pressure drop and particle losses than orifice meters and is therefore suitable for in-line flow measurement. The pressure drop can be measured by a Magnehelic gauge, and related to a primary standard by a calibration curve

Table 1 continued

Flow measurement device (References)	Operating principles	Comments
Rotameter [103–109]	Gravitational resistance/variable area device. A float is located in a tapered tube that increases its area with vertical distance from the flow entry point. The flow raises the float in the tube until the upward aerodynamic force equals the weight of the float. Floats of different sizes and densities can be used in the same tube to cover a wide range of flow rates	Transfer standard, calibrated against a primary standard. The scale is non-linear unless the tapered tube follows a complex pattern that is difficult to manufacture. Most rotameters have slightly angled bores in the shape of an inverted and truncated cone. For a spherical float, readings are taken at the middle of the ball. Non-spherical floats should have the reading position well-marked
Turbine meter [110, 111]	Rotational device. A propeller is located in a tube through which the flow is directed. The number of rotations per unit time is related to the flow rate	Transfer standard, in which a discharge coefficient is determined by calibration against a primary standard
Mass flow meter [97, 112–114]	Thermal cooling device. A hot-wire anemometer is located in a sampling duct and a constant current is run through the wire. The temperature of the wire is measured with a thermistor, and the reduction in temperature is related to the gas flowing across it	Transfer standard, calibrated against a primary standard. These are most commonly used in modern air quality monitors as they can be located in-line and converted to volumetric flow by the data acquisition software. Temperature and pressure of the gas are monitored along with the temperature change of the hot wire

Fig. 2 Examples of primary and transfer standards for flow rate/volume. Primary standards: **a** Bell prover, and **b** Bubble meter. Transfer standards: **c** Rotameters (*left*) and Orifice calibrator (*right*). Magnehelic above rotameters measures pressure drop across the orifice, and **d** Roots meter

conditions to the standardized conditions reported with the measurement standard. It is good practice to record these conditions on the device itself, as they are often specified only in the accompanying calibration certificate or operating manual. After the real-world ambient flow rate is determined, it may be necessary to adjust this to a new standardized condition for reporting purposes. The U.S. EPA [19] FRM defines PM_{10} levels for standard sample volumes at 1 atm pressure and 25 °C, while other criteria pollutant concentrations (including the $PM_{2.5}$ and Pb fractions of PM_{10}) are reported at ambient temperatures and pressures. Head and gravity devices also depend on the upstream and downstream pressures; when one of these differs from 1 atm, adjustments must be made and these do not necessarily follow the ideal gas law. For example, a rotameter reading scales as the square root of the ratio of gas densities (which depend on temperature, pressure, and molecular weight of the gas mixture), rather than as the direct ratios indicated by the ideal gas equation. A rotameter used as an in-line flow indicator should be re-calibrated against an appropriate transfer standard at the inlet to the measurement instrument.

Mass flow (F_m) needs to be converted to volumetric flow (F_v) for most air quality applications:

$$F_v = (RT/MP)F_m \qquad (2)$$

which requires knowledge of the absolute temperature (T) in the flow meter, the molecular weight of the gas (M), the gas pressure at the inlet of the flow meter (P), and the ideal gas constant (R) in units consistent with the other measurements. Note that the original calibration of the mass flow meter is probably related to standard air composition (21 % O_2 and 78 % N_2), so that adjustments are needed when measuring other gases in the preparation of gas measurement standards as described below. Other gases in air constituting <1 % (e.g., CO_2) are usually neglected as they add small additional uncertainty.

4. Gas Concentration Measurement Standards

Many gases are considered important to air quality, both for their direct effects on the environment and for their participation in atmospheric chemical reactions that create secondary gases and particles with adverse effects. Much effort has been expended in creation of gas measurement standards for CO, NO_2, and SO_2, and O_3, as these are regulated as criteria pollutants. Certain volatile organic compounds (VOCs) are O_3 and PM precursors, and some of the VOCs are classified as hazardous air pollutants (HAPs), so appropriate standards have been created. Standards for chemical end-products, such as peroxyacetyl nitrate (PAN) and nitric acid (HNO_3) are also useful for better understanding atmospheric transformation processes.

When the gases are non-reactive, small amounts can be mixed and stored in pressurized containers with the balance

Table 2 Methods for creating standard gas concentrations

Method (References)	Principles	Comments
Gravimetric [26, 115, 116]	The difference in weight of two identical containers, one empty and one containing the gas mixture, is translated to the gas concentration in the filled cylinder	For a two gas mixture compressed to a known pressure, the specific gravity can be solved to determine the number of moles of two gases with known molecular weights. Modern microbalances with $\sim$1 µg precision can determine concentrations with $\sim$100 ppm precision
Gas stream mixing [38, 117]	Precise flows of the pollutant and carrier gas are metered into a mixing chamber prior to pressurization into a container or presentation to a monitoring system	Precise temperature and pressure control are essential. Calibration of the flow meters must be adjusted to the molecular weight of the gas, as well as temperature and pressure for mass flow meters
Bolus injection [118]	A known volume of pure pollutant, usually measured with a syringe, is injected into a mixing chamber of known volume with internal stirring. The bolus can also be injected into a zero-air stream, this is appropriate for an integrating monitor, but not for a continuous monitor	Bolus injection is useful for synchronizing the time of several instruments on a single manifold and for determining the response functions for a detector
Exponential dilution [119–123]	A mixing chamber of known volume is filled with a pure gas (pollutant), or a known concentration in a carrier gas, then clean carrier gas is introduced. The concentration in the outflow decreases exponentially with time	A rotor or fan rapidly mixes the gas in the chamber
Evaporation [69, 124–126]	A liquid with known vapor pressure is located in a vessel with a known head space. The metered carrier gas sweeps through the saturated head space. Concentration in the head space is determined from the thermodynamic properties of the liquid	Temperature and pressure control in the head space must be precise. The sweep rate must be much less than the evaporation rate of the liquid. Temperature may be elevated above ambient to increase evaporation

being taken up by a non-reactive gas. Depending on the reactivity of the pollutant (minor) gas, the makeup gas may consist of clean air (nitrogen and oxygen mixture scrubbed of other contaminants), pure nitrogen, or a noble gas such as helium or argon. The container walls may also react with the gas [20]. Common materials considered to be minimally reactive are passivated stainless steel (polished to a mirror-like finish), stainless steel, glass, aluminum, Teflon, Tedlar (polyvinyl fluoride), and Mylar. Most commercially-prepared gases are distributed in stainless steel cylinders or passivated spheres and have lifetimes of a year or two. While glass containers may be used to create mixtures in a standards laboratory, they are impractical for field use owing to their fragility and potential danger when under high pressure. Teflon and Tedlar can be used for short-term storage, but gases will diffuse through these materials over long time periods. This permeability is advantageous for permeation tubes, as described below.

Barratt [21] and Namiesnik [22] provide good descriptions of methods for preparing standard gas mixtures, along with several other reviews [23–25]. ISO [23, 26–35] has a series of procedures for standard gas preparation. The more common methods are summarized in Table 2, and Fig. 3 shows examples of some of the apparatus used to prepare primary standards, illustrating the substantial investment needed for this work. Most stable gas standards are obtained from a specialty gas supplier with a traceability certificate, as illustrated in Fig. 4. This original certificate should be placed in a quality assurance (QA) file and a copy should accompany the cylinder wherever it is used. The information should include the nominal concentration, the balance gas, the traceability trail, the date of creation, and the maximum lifetime of the mixture. Reputable suppliers will allow the cylinders to age for a few weeks, often rotating them to assure a uniform mixture, and test them against their primary standards to assure the accuracy of the concentrations. This is why the specified and actual concentrations may differ.

Field dilution systems [36–39] are used to obtain a range of concentrations for calibration and auditing purposes. These systems incorporate activated charcoal, particle filters, and Drierite to remove water vapor and create clean air as the dilution gas [40]. While these are adequate for removing criteria pollutants and most VOCs, they may not be sufficient to remove all types of gases (e.g., halocarbons). Concentrations in the range of 20–1,000 ppb are often required for these purposes. As modern air quality monitors have become more sensitive ($\sim$1 ppb detection limits), and as these lower levels are relevant to atmospheric chemistry, there is increasing interest in accurate calibration at the lowest concentrations [41]. Adjustments for standard gas flow measurements must be made for the gas composition since its molecular weight may differ from that used to calibrate the dilution system's flow meters.

Criteria gases (e.g., CO, nitrogen oxide [NO], and SO_2), halocarbons, and a reasonable number of VOCs can retain their concentrations in pressurized containers with an appropriate carrier gas for several years. Reactive gases must be generated on-site, often using stable gas standards as reactants. Most oxides of nitrogen (NO_x) analyzers are calibrated with NO, as they convert NO_2 to NO before detection. It is still necessary to generate known amounts of NO_2, however, to evaluate the conversion efficiency. This is done with gas-phase titration [42], in which an ultraviolet (UV) lamp generates O_3 that reacts with NO to create NO_2. The UV-generated O_3 can also be used as a calibration gas when it is related to a highly maintained primary UV absorption standard [43, 44]. Many modern O_3 monitors contain a small UV O_3 generator used for daily zero/span performance tests.

Fig. 3 Examples of gas preparation facilities for gas concentrations standards for: **a** a volumetric mixing chamber with clean gas dilution system (Indian Central Pollution Control Board, Delhi), and **b** a precise weighing system for quantifying gases compressed into a cylinder. The empty cylinder on the left has the same dimensions as the primary standard cylinder on the right and accounts for air displacement buoyancy effects (Indian National Physics Laboratory, New Delhi)

Fig. 4 Example of a gas cylinder certification to establish traceability to a primary standard

CYLINDER NUMBER: LL101533		CYLINDER SIZE: 80A (75 std cu ft)		CYLINDER PRESSURE: 2000 psig	
COMPONENT	CONCENTRATION (v/v) ± EPA UNCERTAINTY	REFERENCE STANDARD	ANALYZER MAKE, MODEL, S/N, DETECTION	EXPIRATION DATE	REPLICATE ANALYSIS DATA
Carbon monoxide	5090 ± 31 ppm	GMIS CYLINDER #: CC20108 @ 5110 ppmv	Carle Insts Model 8000 Serial # 8249 Methanation/FID Gas Chromatography LAST CAL DATE: 3/24/2009	4/21/2011 MEAN:	4/14/2009 4/21/2009 5100 ppm 5070 ppm 5090 ppm 5080 ppm 5090 ppm 5090 ppm 5090 ppm 5080 ppm
Nitric oxide NOx Nitrogen dioxide	50.2 ± 0.3 ppm 50.2 ppm < 0.3 ppm	GMIS CYLINDER #: CC108765 @ 50.1 ppmv	Monitor Labs Model 8440 Serial # 136 Continuous Chemiluminescence LAST CAL DATE: 4/13/2009	4/23/2011 MEAN:	4/14/2009 4/23/2009 50.3 ppm 50.2 ppm 50.2 ppm 50.6 ppm 50.1 ppm 50.2 ppm 50.2 ppm 50.3 ppm
Sulfur dioxide	51.3 ± 0.5 ppm	SMI CYLINDER #: AAL11047 @ 56.6 ppmv	Bovar/W Res Model 922M Serial # 9228379-1 Continuous UV Photometry LAST CAL DATE: 4/1/2009	4/20/2011 MEAN:	4/13/2009 4/20/2009 51.3 ppm 51.3 ppm 51.2 ppm 51.5 ppm 51.3 ppm 51.4 ppm 51.3 ppm 51.4 ppm
O2-free Nitrogen	Balance				

ppm = umole/mole   % = mole-%

The above analyses were performed in accordance with Procedure G1 of the EPA Traceability Protocol, Report Number EPA-600/R97/121, dated September 1997.
The above analyses are invalid if the cylinder pressure is less than 150 psig.

PAN must be generated on-site from liquid evaporation or a portable smog chamber [45–50].

Permeation tubes [28, 51–73] offer the widest range of gas compositions and are especially applicable to reactive gases that can be compressed to a liquid under pressure. Permeation tubes are based on Fick's law of diffusion [74] in which gases move from areas of higher to lower concentrations. The relevant gas is compressed into a container consisting of or capped by a permeable membrane. Common membrane materials are Teflon, silicone rubber, polypropylene, polyester, Tedlar, and Nylon, selected based on their durability and affinity for the gas being generated. The emission rate is determined by the mass loss over time, as determined by periodic weighings of the tube with a microbalance calibrated against traceable mass standards. In this sense, permeation tubes can be considered to be primary standards. The tubes must be maintained at a constant temperature in a continuous flow of a clean carrier gas, as the diffusion depends on both the temperature and the concentration gradient of the pollutant gas across the membrane. Many reactive pollutant standard concentrations, particularly HNO_3, ammonia (NH_3), hydrogen sulfide (H_2S), and several VOCs, can be obtained from permeation tubes that would not remain stable for long periods in a container.

5. Using Standards to Evaluate the Measurement Process

An air quality measurement consists of four attributes [75], each of which requires measurement standards for its quantification: (1) the value of the measurement (C_m), which is most commonly reported and used for determining compliance with AAQS; (2) the precision (σ_m), which is the standard deviation of repeated measurements of a known concentration (C_i), where i refers to one of the many responses to a performance standard; (3) the accuracy (A), which is the relative difference between C_m in response to sampling of an audit standard (C_t); and (4) validity, the extent to which specified measurement procedures were followed, including maintenance or recalibration when A and C_i exceed pre-set tolerances. A and σ_m are calculated as:

$$A(\%) = \frac{100(C_m - C_t)}{C_t} \tag{3}$$

and

$$\sigma_m = \sqrt{\frac{\left[\sum_i (C_i - AvgC_i)^2\right]}{(n - 1)}} \tag{4}$$

$i = 1$ to I (total number of performance tests)

Validity is expressed in terms of pre-defined data flags that indicate the deviations from the standard operating procedures (SOPs). These flags do not necessarily invalidate the C_m, but they assist the interpretation of the information when used for data analysis and modeling.

Table 3 summarizes calibration, performance test, and audit activities and the standards used for each one. These tests provide the input data for applying Eqs. 3 and 4 and for assessing the validity of air quality measurements.

Table 3 Primary and transfer standards with calibration, performance test, and audit frequencies for flow rates and gas concentrations at an air quality monitoring site, modified from Watson et al. [127]

Observable (method)	Percent tolerance	Primary standard	Calibration standard	Calibration frequency	Performance test standard	Performance test frequency	Performance audit standard	Performance audit frequency
Flow rates								
TSP mass (high-volume sampler)	±5 %	Bell Prover (>1,000 L/min)	Calibrated orifice/Rootsmeter	Quarterly	Calibrated orifice	Monthly	Calibrated orifice	Yearly
PM$_{2.5}$ mass (2 single-channel FRM[a] samplers)	±5 %	NIST[b]-certified bubble meter (1–25 L/min)	Mass flow meter/bubble meter	Quarterly	Calibrated bubble meter (Gillibrator)	Monthly	Mass flow meter	Yearly
Gas concentrations								
NO/NO$_x$ (chemiluminescence)	±10 %	NIST-traceable NO mixture	Certified NO mixture and dynamic dilution	Quarterly or when out of specification	Span with certified NO and zero with scrubbed air	Daily	Certified NO mixture with dynamic dilution	Yearly
O$_3$ (UV absorption)	±10 %	ARB[c] primary UV photometer	Dasibi 1003H UV photometer	Quarterly or when out of specification	Span with internal O$_3$ generator and zero with scrubbed air	Daily	Dasibi 1008 with temperature and pressure adjustments	Yearly
CO (infrared absorption)	±10 %	NIST-traceable CO mixture	Certified CO mixture and dynamic dilution	Quarterly or when out of specification	Span with certified CO and zero with scrubbed air	Daily	Certified CO mixture with dynamic dilution	Yearly
Non-methane hycrocarbon (NMHC) (flame ionization)	±10 %	NIST-traceable VOC mixture	Certified VOC and dynamic gas dilution	Quarterly or when out of specification	Span with certified VOC and zero with scrubbed air	Daily	Certified VOCmixture with dynamic dilution	Yearly

[a] U.S. EPA Federal Reference Method
[b] National Institute of Science and Technology, Gaithersburg, MD, USA
[c] California Air Resources Board, Sacramento, CA, USA

6. Summary

Accurate and precise measurement standards for flow rate/volume and gas concentrations are essential components of any air quality monitoring program. Several methods are available for generating these standards and tracing them to fundamental primary standards. These methods are not necessarily equivalent, and compensation must be made for differences between the gas mixtures and the operating environments. The molecular weight, pressure, and temperature are important variables for both flow rates and gas concentrations.

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