

CHAPTER 9

GAS MIXTURES AND STANDARDS

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9.1 Introduction

A necessary requirement for the successful performance of many specialty gas analytical techniques is the availability of one or more gas phase calibration standards to determine absolute concentrations. There are a few absolute techniques based on wet chemical methods for quantitation however the vast majority of analyses (including “so-called” absolute techniques such as Fourier transform infrared spectroscopy (FTIR) and mass spectrometry (MS)) are absolute only in the identification of analytes. While the need for calibration standards seems like a simplistic and obvious requirement, it is an area fraught with difficulties ranging from simple availability to the specification of preparations and any additional requirements. This chapter therefore discusses important aspects of gas mixtures and standards, including cylinder packages, preparation techniques, material compatibility considerations, stability and uses of alternative approaches.

Specialty gas standards are available from most major cylinder gas suppliers and a multitude of smaller niche gas companies. Unfortunately, there are significant “equivalency” problems among suppliers. A cylinder gas standard procured from one supplier may differ significantly from that supplied by another company even with similar purchase specifications.

9.2 Definition of Gas Standards

Every gas supplier names their standards differently making it difficult to compare one with another, however, there are ways to tell them apart (at least on the face of manufacturers claims). How would the perfect standard be specified? The perfect gas standard would match the exact request of the customer and be exactly the concentration specified, i.e., the blend tolerance (or how close the actual concentration matches the specification of the customer) would be zero and the analytical uncertainty (or tolerance*) would also be zero. Depending on preparation techniques, it is possible to achieve (within the analytical uncertainty) zero blend tolerance, however, this usually entails higher cost due to greater levels of labor involved in the standard preparation. Zero analytical uncertainty is a physical impossibility. In this chapter, we define uncertainty, tolerance, and accuracy equivalently. It is also extremely useful to discuss concentration reporting conventions.

There are a number of different conventions used to report the concentration of analyte material in compressed gas standards. Some of these conventions are specific to individual industry segments or uses. The typical statement of concentration, generally taken as default in the industry at large, is concentration expressed as volume/volume also expressed as concentration by volume, volume percent, ppmv (parts per million by volume), mole/mole, and molar concentration to name a few. Concentrations expressed by volume can be, and generally are, made gravimetrically (by weight addition) or by volume addition (to pressure). However, volume additions by pressure readings must be monitored carefully for temperature increases and must allow for compressibility of materials involved in the mixtures. Thus, volume additions are normally reserved for gross or highly simplistic mixtures.

A secondary way to report concentration expresses the concentration as a weight-to-weight ratio. These are typically found in the hydrocarbon or oil and gas industries and will be reported as weight percents or ppmw (parts per million by weight). An alternative reporting value, used in the environmental monitoring industry, is percent carbon or ppmc (parts per million by carbon). This value is based on a mole/mole concentration and is reported based on the number of carbon atoms in the molecular structure of the analyte of interest. An easy illustration of the determination of ppmc would be to compare the volume/volume concentration of 5 ppmv benzene to the analog ppmc concentration. To do this, the ppmv concentration is simply multiplied by the number of carbon atoms in the molecular structure of benzene. So,

*Also known as how closely the actual concentration of the analyte matches the analyzed value reported on the certificate of analysis

5 ppmv benzene multiplied by 6 carbon atoms per benzene molecule equals 30 ppmc benzene. Regardless of the balance component (be it hydrogen, helium, nitrogen, etc.), a cylinder gas standard containing 5 ppmv benzene is equivalent to a 30 ppmc benzene standard.

Although there are many ways to express concentration, the only other typical concentration expression convention is the milligram per cubic meter (mg/m^3) or grams or micrograms per cubic meter. This is a combination of weight and volume reporting used in monitoring applications, toxicology measurements, or active bed absorption or catalysis applications. A comparison of the concentrations expressed in the normal units is shown in table 9.1 .

Table 9.1 Comparison of concentration units for a benzene/nitrogen gas standard.

Compound	ppmv	ppmc	ppmw	mg/m^3	$\mu\text{g}/\text{m}^3$
Benzene	5	30	13.93	16.177	16177

The concentration of the analyte of interest in a gas standard can be certified by one of three ways. The first of these is to prepare the standard gravimetrically (discussed in detail in Section 9.4) with the materials weighed into the cylinder on a high precision balance and the concentration calculated by added masses. Using this method, it is necessary to combine the analytical accuracy of the preparation technique with the analytical accuracy of the determined purity of the raw material used in the mixture. This method works particularly well for non-reactive analytes of interest. If there is any chance of concentration degradation in the cylinder after preparation, there is uncertainty unless the manufacturer uses flawless cylinder preparation and blending technologies, and has a documented record of stability. The second way is to analyze the cylinder by a variety of analytical techniques against another standard of known concentration. In this instance, it is necessary to determine the analytical accuracy of the analysis and combine it with the analytical accuracy of the standard since these are cumulative uncertainties. In the specific case of EPA Protocol standards preparation, the reference standard material uncertainty is defined as zero and not taken into account in the cumulative uncertainty of the final certified concentration. The third method of certification is to verify the gravimetric concentration of the prepared standard by a confirming analytical measurement against a high precision standard. If these methods agree, it is known as an interlocking analysis so named by Scott Specialty Gases (now Air Liquide America Specialty Gases).

Now, with an understanding of the significance of blend tolerance and analytical uncertainty, it is possible to compare standards from different manufacturers. We begin the discussion by considering the highest precision gas standards currently available. There are three international standards organizations that recognize each other's standards as equivalents: The U.S. National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs), the Dutch Metrology Institute (VSL) Primary Reference Standards (PRMs), and the U.K. National Physical Laboratory (NPL) Traceable Calibration Gas Standards. These standards are the highest precision available but are limited in production, materials, availability, and econ-

omy. While these are generally recognized as the supreme standards available today, they are extremely expensive, they are typically produced at a few specific concentrations, and they are sometimes hard to obtain (unavailable with long production lead times). These standards are certified at $< \pm 1\%$ uncertainty and are required for some analyses. EPA Protocol standards generation (typically priority pollutants such as nitric oxide, sulfur dioxide, carbon dioxide, carbon monoxide, and nitrogen dioxide) require certification against these SRMs or PRMs to qualify with a $< \pm 1\%$ certified uncertainty. Gas manufacturers have the option of creating a single “lot” of standards that may be analyzed by a number of samples from the lot sent to NIST to be qualified as NIST Traceable Reference Materials (NTRMs). There are additional requirements for in-house analysis as well as the NIST analyses however the quality of these standards are similar to the quality of the NIST generated SRMs. Alternatively, gas manufacturers may also generate a similar group of standards in a “lot” and perform only in-house analysis to qualify them as gas manufacturer internal standards (GMISs). These are normally used to qualify EPA protocol gas standards with a $< \pm 2\%$ certified accuracy. There are a number of other projects that may require SRM or PRM reference certification such as the qualification of Food and Drug Administration (FDA) controlled current Good Manufacturing Procedures (cGMP) drug manufacturing, however an analysis of standards cost versus requirements usually render these standards “excessive.”

The actual number of standards for which SRMs are available is fairly small and limits traceability to NIST standards by analysis to a small number of materials. VSL has proven itself to be more open to creating standards for other materials, however, this adds a significant time component to the acquisition process that may not be an affordable indulgence. There is another avenue to NIST traceability on mixtures, which is known as NIST traceable by weight. This type of traceability requires gravimetric standards preparation and calibration of the gravimetric weight scale by NIST traceable weights. The method works particularly well for non-reactive materials and allows a way to gain traceability for otherwise non-traceable materials. The negative aspect of this traceability lies in the dependence of the quality of traceability to the procedures and abilities of the manufacturer to precisely control gravimetric addition processes. In the correct instance this is effective traceability, however in the wrong instance it could mean nothing.

Returning to the discussion of standards for generalized use, most gas manufacturers name their standards according to the accuracy defined in their list of blend and analytical tolerances. Figure 9.1 is a representative listing of standard names. Other manufacturers will have similar names, but careful attention must be paid to quotations regarding blend and analytical tolerances as well as traceability (if applicable).

Gas and Liquid Mixtures Typical Specifications

Our seven product classes redefine mixture versatility. Each has unique specifications to meet different needs as summarized below. Refer to the following pages for additional information about each product class.

Typical Specifications	Dual-Analyzed Standards		Dual-Certified Standards	
	EPA Protocol		GRAVIMETRIC	
	BMTA Class = Calibration to meet Government Regulations	Compliance Class = Calibration Standards and Process Control	Reference Class = Master Calibration and Process Control	Working Class = Master Class = Calibration and Process Control
Typical Applications				
Concentration Range				
Blend Tolerance ±%	5	5	5	10
Process Accuracy ±%	2	2	2	5
Blend Tolerance ±%	5	5	5	10
Process Accuracy ±%	2	2	2	5
Blend Tolerance ±%	5	5	5	10
Process Accuracy ±%	2	2	2	5
Blend Tolerance ±%	5	5	5	10
Process Accuracy ±%	2	2	2	5
Blend Tolerance ±%	5	5	5	10
Process Accuracy ±%	2	2	2	5
Blend Tolerance ±%	5	5	5	10
Process Accuracy ±%	2	2	2	5
Blend Tolerance ±%	5	5	5	10
Process Accuracy ±%	2	2	2	5
Blend Tolerance ±%	5	5	5	10
Process Accuracy ±%	2	2	2	5
Reproducibility ±% for Concentration Range of 100 ppm - 1%	2	2	2	7
Analytical Traceability	NIST, VSL or Other Recognized Reference Standard	NIST, VSL or Other Recognized Reference Standard	NIST, VSL or Other Recognized Reference Standard	At-Liquid or Other Reference Standards
Process Traceability	NIST, VSL or Other Recognized Reference Standard	NIST or VSL Weights	NIST or VSL Weights	At-Liquid or Other Reference Standards
Component Verification	Laboratory Analysis of All Minor Components	Laboratory Analysis of All Minor Components	Laboratory Analysis of All Minor Components	Weight, Pressure or Standards
Critical Impurities Analysis	Not Applicable	Not Applicable	Available	Not Applicable
Minor Components Available (Balance)	Inert and/or Reactive	Inert and/or Reactive	Inert and/or Reactive	Inert and/or Reactive
Liquid Gas Phase	Not Applicable	Not Applicable	Inert and/or Reactive	Inert and/or Reactive
Standard Industry Methods	EPA GI or State Protocol Used	EPA GI or EPA G2 Protocol Used	Not Applicable	ISO Methods Available
Reference Standard Accuracy	Directly traceable to NIST or other standards	NTRMs or EPA G1/G2 Used	Meets or Exceeds Analytical Accuracy Specifications	Achieves Analytical Accuracy Specifications
Certificate of Accuracy	Protocol Concentration, Traceability and EPA Expiration Date Reported	Protocol Concentration, Traceability and EPA Expiration Date Reported	Analyzed Concentration, Traceability and Shelf Life Reported, Requested and Blended Concentrations Shown	Certified Concentration, Traceability and Shelf Life Reported; Requested Concentration Available
Physical Property Notifications	Mixture Property Warnings Available	Mixture Property Warnings Available	Actual Mixture Properties Available and Vapor Pressure Restriction	Mixture Property Warnings Provided
Raw Material Quality Control	Verified for Specification Compliance	Verified for Specification Compliance	Complete Purity Analysis	Verified for Specification Compliance
Product Shelf Life	Meets Regulatory Specifications	Meets Regulatory Specifications	ACULIFE™ and Other Proprietary Processes Guarantee Stability and Shelf Life	ACULIFE™ and Other Proprietary Processes Guarantee Stability and Shelf Life
				Customer-Specified Accuracy
				Customer Design Available
				Actual Mixture Properties Available
				Complete Purity Analysis
				Component Dependent

* Special circumstances apply to certain low level reactive components (i.e. nitric oxide - please consult your At-Liquid representative).

Figure 9.1 Representative listing of standard names [7].

While there are many ways to specify standards, it is important to understand the variability and flexibility in requirements. The intricacies of gas standards selection may be reduced to a reasonable number of required pieces of information – materials in the standard, precision requirements of the standard desired, convention used in reporting the concentration, and the traceability desired, if any.

9.3 Cylinders and Valves – Sizes, Types, and Material Compositions

It is not within the scope of this chapter to present all possible types and combinations of cylinders and valves along with the compatibilities (incompatibilities), however, it is extremely useful to list cylinder sizes and designations cross correlating the major gas companies’ nomenclature. Tables 9.2, 9.3, 9.4, 9.5, and Figures 9.2 and 9.3 present a thorough description of various cylinder sizes and compositions.

Table 9.2 Designation by company for various sizes of standard high pressure aluminum cylinders [7].

Air Liquide	Custom Gas					Praxair
	Scott	Solutions	Matheson	Linde	Airgas	
47AL	KAL	265AL				AT
30AL	AL	150AL	1R/1I	A31	150A	AS
16AL	BL	88AL	2R/2I	A16	80A	AQ
7AL	CL	33AL	3R/3I	A07	33A	AG
3AL	DL	15AL				A3
1AL		AL170	6R/6I			

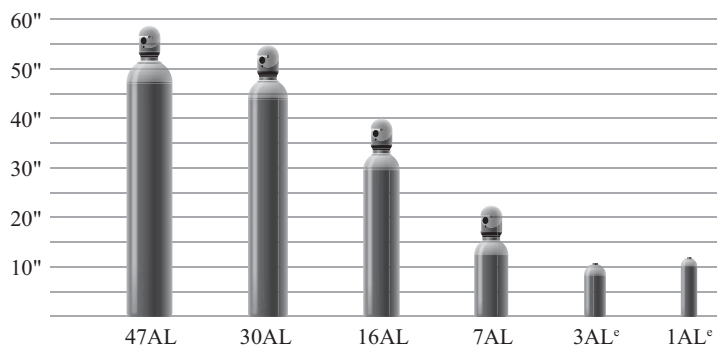


Figure 9.2 Standard high pressure aluminum cylinder height and size comparison [7].

Cylinder requirements for different materials become somewhat more complicated when a treatment (cylinder passivation technique) changes the materials compatibilities rather drastically. Aluminum cylinders with correct passivation are the preferred

Table 9.3 Standard high pressure aluminum cylinder specifications [7].

Size	DOT Spec	Svc Press	Approximate Capacity ^c		Out Dmtr	Height ^a	Tare Wt ^b	Internal Water Volume ^d	
			cu ft	L				cu in	L
47AL	3AL	2216	244	6909	9.8	51.9	90	2831	46.4
30AL	3AL	2015	141	3993	8	47.9	48	1800	29.5
16AL	3AL	2216	83	2350	7.25	33	30	958	15.7
7AL	3AL	2216	31	878	6.9	15.6	15	360	5.9
3AL ^e	3AL	2015	8	227	4.4	10.5	3.5	103	1.7
1AL ^e	3AL	2216	5	142	3.2	11.7	2.3	61	1

^a Without valve^b With valve, nominal^c For N₂ at 70°F 1 atm^d Nominal^e Resale cylinder only**Table 9.4** Designation by company for various sizes of standard high pressure steel cylinders [7].

Air Liquide	Custom Gas					
	Scott	Solutions	Matheson	Linde	Airgas	Praxair
49	K	300ST(K)	1L	049(T)	300	T/UT
44	A	200ST(A)	1A	044(K)	200	K/UK
44H		3K	1H			3K
44hh		6K	1U	485	3HP	6K
16	B	80ST	2	016(Q)	80	Q/UQ
7	C	30ST	3	007(G)	35	G/UG
3	D	15ST	4	3		F
LB	LB	LB	LB	LBR(LB)	LB	LB/RB
LBX		LB-CGA	7X		LX	EB

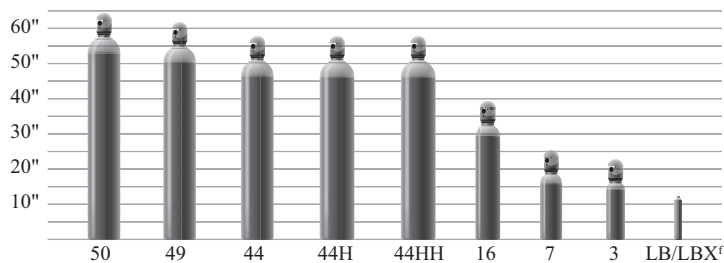
standard for the majority of low level standards including reactive materials. Alternatively, nickel coated steel cylinders are equally acceptable for low level reactive standards that are inherently corrosive or otherwise reactive (either bonding to the cylinder surface or decomposing in a catalytic manner on the surface). Uncoated steel cylinders tend to accumulate rust layers (and even, in some instances, measureable levels of powdered rust in the bottom of the cylinder). Not only is rust (iron oxide) a reactive surface, the nature of iron oxidation creates a highly porous layer that continually flakes away to allow more rust formation to occur, and compromise low

Table 9.5 Standard high pressure steel cylinder specifications [7].

Size	DOT Spec	Svc Press psig	Approximate Capacity ^d		Out Dmtr in	Height ^a in	Tare Wt ^b lb	Internal Water Volume ^e	
			cu ft	L				cu in	L
50	9809-1 ^c	2900	335	9373	9	58.2	130	3051	50
49	3AA	2400	277	7844	9.25	55	143	2990	49
44	3AA	2265	232	6570	9	51	133	2685	44
44H	3AA	3500	338	9571	10	51	189	2607	44
44HH	3AA	6000	433	12261	10	51	303	2383	43
16	3AA	2015	76	2152	7	32.5	63	976	16
7	3AA	2015	33	934.6	6.25	18.5	28	427	7
3	3AA	2015	14	396.5	4.25	16.75	11	183	3
LB/LBX ^f	3E	1800	2	53.8	2	12	3.5	27	0.4

^a Without valve^b With valve, nominal^c UN/ISO specification^d For N₂ at 70 ° F 1 atm^e Nominal^f Non-returnable cylinder. Price of cylinder included in price of gas.

Note: LBX is an LB cylinder with a CGA valve other than 170 or 180.

**Figure 9.3** Standard high pressure steel cylinder height and size comparison [7].

level reactive gas standards that react proportionally to the actual surface area in the cylinder. We will address these issues in greater depth in Section 9.7.

The selection of the correct cylinder valve is also important. The Compressed Gas Association (CGA) is a membership organization for gas producers that provides a number of services to the gas manufacturing community including recommending cylinder valve connections as well as providing safety forums and information. In the CGA – V7 publication the guidelines are provided that control the majority of cylinder gas connection selections for the industry in the U.S. While this organization holds no enforcement authority, their “suggested” usages are taken less as suggestions and more as requirements and/or restrictions.

Valve selections (gas connection not withstanding) are typically based on both material compatibilities and purity specifications. Valves are usually constructed in two primary designs: Packed stem and diaphragm pack-less. For lower purity materials, the packed valve is normally chosen due to cost (lowest cost per unit available in cylinder valves). These packed valves have a stem that closes directly against the flow orifice. The stem is packed with a Teflon[®] type grease material for lower reactivity and is sealed by a compression nut that can be tightened if the valve shows signs of leaking. These valves are recognized as an industrial valve and the use on high purity and specialty gases and standards is extremely limited. Diaphragm pack-less valves use a two part stem separated by multiple stainless steel spring diaphragms. The gas-wetted surfaces of these valves are normally stainless steel or a mixture of stainless steel and brass parts. This design is particularly easy to clean and takes passivation processes well thereby becoming the industry standard for specialty gas standards. Some highly corrosive materials or materials that tend to deposit residual materials between the orifice and the diaphragms may cause the diaphragms to stick shut and render the valve inoperable. If this scenario occurs (and it can with a reasonable regularity for materials like hydrogen chloride and other halogen acids), the remediation and hazardous materials disposal fees become excessive. There is a variation on this design that includes a tied-diaphragm that minimizes this occurrence. In this design, the diaphragm is actually connected to the valve stem and the hand wheel actually pulls the valve open.

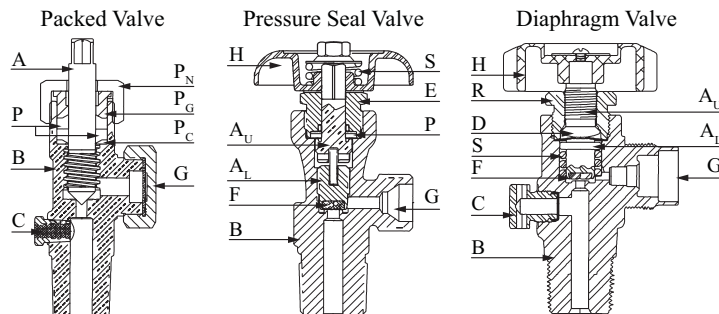


Figure 9.4 Valve diagrams for packed, pack-less or pressure seal, and diaphragm valves. A) Stem; A_U) Upper Stem; A_L) Lower Stem; P) Packing; P_N) Packing Nut; P_G) Packing Gland; P_C) Packing Collar; B) Valve Body; C) Pressure Relief Device; G) Outlet (with cap); H) Handwheel; S) Spring; E) Bonnet; F) Valve Seat; R) Retainer; D) Diaphragm.

Another major consideration with the valve selection for a particular application is the material of construction. Cylinder valves are manufactured from brass, stainless steel, and an alloy of aluminum, silicon, and bronze (known as ASB composition). The valves constructed of brass are also available as chrome plated brass. Again, it's beyond the scope of this discussion to give a detailed analysis of materials compatibility for different gas products and mixtures. That discussion is best held with a knowledgeable representative of your favorite gas standards supplier.

9.4 Preparation Techniques for Gas Standards

As mentioned in Section 9.2, cylinder gas standards may be prepared in a number of different ways and in a number of different cylinder configurations. The typical preparation methods used in the industry today include gravimetric addition, volumetric addition, dynamic blending, and liquid injection. Each of these methods has benefits and specific blend specifications usually dictate the use of one over another. It makes sense to address each one independently and then discuss relative accuracy.

9.4.1 Gravimetric Standards Preparation

Gravimetric blending is defined as weighing controlled amounts of pure gases or gas blends into a cylinder to create a standard of known concentrations. The term gravimetric is loosely taken from the world of chemical analysis where it can be defined as quantitative determination of an analyte based on the mass. In chemical analysis, there exist a set of methods whereby materials in a liquid solution are precipitated (either through chemical means including solvent environment changes (polarity, pH, etc.) or through derivatization) and then weighed to determine the fraction of analyte originally present in the solution. It's not quite that simple but the idea translates. In the case of gas standards, we know the initial weights of materials added to a cylinder, and we can therefore define the resulting concentrations.

The first step in manufacturing a gravimetric gas standard is the determination of the various component gram additions. As discussed earlier, the typical industry designation of concentration is a volume per volume quantity. The unit of material used is a mole. As an example, a typical large high pressure aluminum cylinder (designated in the industry as a 1R, 1L, AL, 150AL, etc) contains 165 mol of nitrogen at 2015 psia. The molar calculation is another unit taken from chemistry and is defined as the number of grams required to equal Avogadro's number of units (either molecules or atoms depending on the gas – molecules for nitrogen and atoms for monatomics such as helium or argon). One mole of material is defined as 6.023×10^{23} molecules. The direct calculation of the number of moles (n) is given by:

$$n = \frac{m}{M} \quad (9.1)$$

where m is the mass in grams and M is the molecular weight.

For the purpose of this example we will calculate the gram additions of carbon dioxide and nitrogen required to make a standard at the concentration of 1% carbon dioxide in nitrogen in a typical aluminum cylinder at full pressure. There are reasons to limit the final pressure for some mixtures which will be discussed in Section 9.5.

In this case we first calculate the required number of moles of carbon dioxide and then the required number of moles of nitrogen. Define total number of moles as 165 for this example. The calculation to determine the number of moles of minor component, or carbon dioxide in our example, is:

$$n_m = C \times n_t \quad (9.2)$$

$$n_b = (1C) \times n_t \quad (9.3)$$

where n_m is the number of moles of minor component, C is concentration of minor component expressed as a decimal, n_b is the number of moles of balance gas, and n_t is the total number of moles. The number of moles of carbon dioxide required to make a standard at the concentration of 1% carbon dioxide in nitrogen in a typical aluminum cylinder at full pressure is 1.65.

When Equation 9.1 is re-arranged to $m = nM$, the required number of moles along with the molecular weight of carbon dioxide can be inserted to find the mass of carbon dioxide required in grams. In our example, 72.62 g of carbon dioxide are required. The same calculations can be performed for the major component (or balance gas) which is nitrogen.

To manufacture this standard gravimetrically, we would first add 72.6 g of high purity carbon dioxide and then subsequently add 4575.4 g of nitrogen. Following manufacture, the cylinder is removed from the manifold, inspected for leaks, and transferred to a cylinder roller where the cylinder is rolled for a minimum of 30 minutes to ensure homogeneity of the final product. Standards manufactured gravimetrically can be striated and require agitation (in this case in the form of the cylinder roller) to fully mix the gases together. Without this step, a sample analyzed from the newly manufactured cylinder would show a lower than expected concentration of carbon dioxide with the concentration rising as a disproportionately larger quantity of nitrogen is removed initially. After the gases have mixed, in general, they will not separate. However, as will be discussed in Section 9.5, this is not always the case.

In order to manufacture lower concentration standards at commensurately high precision, this standard (or rather gaseous premixture) may be used as a component in the subsequent gravimetric addition. We continue this example by using this premixture (or blending standard) to create a lower concentration standard through dilution. This procedure can be performed repeatedly (known as successive serial dilutions) to create extremely low concentration standards. In this example, a standard at 100 ppmv will be created. First, we calculate a mass composition of carbon dioxide in the pre-mixture as a mass ratio expressed as grams of minor component to total grams of standard (in the industry this is known as a gram per gram value).*

$$\frac{C_m}{T} = V \quad (9.4)$$

where C_m is the mass in grams of minor component, T is total mass in grams in the blend, and V is gram per gram value.

In our example, the total mass of carbon dioxide in the blend is 0.0156 g per gram of mixture. Knowing the target quantity of material needed to make a full pressure standard in an AL150 cylinder (165 mol), we use Equation 9.1 to calculate the addition of pure carbon dioxide and pure nitrogen. The mass of carbon dioxide required is 0.726 g and the mass of nitrogen required is 4621.2 g. Since the amount

*Exercise care with carrying the correct number of significant figures in this calculation. It is easy to believe in greater precision because of the number of digits displayed by calculators.

of carbon dioxide is so small that it cannot be reliably measured we use Equation 9.4 to calculate a statistically precise gram-addition amount of material. In our example, that amount is 46.5 g of standard.

To determine the actual amount of major component required to complete the dilution mixture, we must account for the amount of major component (nitrogen) in the pre-mixture. To do so, we must subtract the amount of minor component required from the gram-addition amount of material, then subtract that amount from the total amount of major component required. In our example, we find 4573.3 additional grams of nitrogen.

To complete the dilution of the standard through gravimetric addition to 100 ppmv, we add 46.5 g of standard (carbon dioxide in our example) followed by the addition of the balance gas (in this example nitrogen) using the additional amount calculated above (4573.3 g) resulting in a final pressure of 2015 psia, and followed again by the standard operations of leak check and cylinder roll for homogeneity.

This procedure can be repeated again and again to reach lower and lower concentrations with very reliable precision. A discussion of additive error will be included at the end of this section. In this section, a detailed discussion of gravimetric blending procedures has been given for three very important reasons. First, this method provides the backbone of high precision standards manufactured in the specialty gas industry today. Second, many of the methods and terminology introduced in this section translate through all blending procedures. Third, gravimetric blending is easily misunderstood, misinterpreted, shortcut or corrupted leading to substantial errors in mixtures.

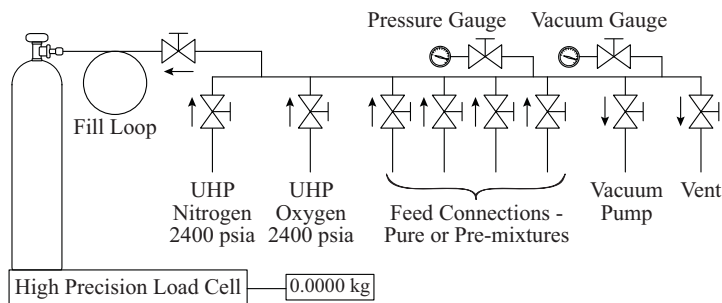


Figure 9.5 Typical gravimetric blending station.

A typical gravimetric blending station is illustrated in Figure 9.5. A gas cylinder to be used for standards preparation is situated on a high precision floor balance and attached to a gas manifold by flexible connection. The components of a manifold usually include a vacuum pump, pressure gauges, and multiple connections to gas cylinders or high pressure facility feed manifolds.

9.4.2 Gas Standards Prepared by Liquid Injection

A variation on the method presented in Section 9.4.1 involves the injection of a precisely measured amount of a liquid minor component directly into an evacuated gas cylinder followed by the addition of the balance gas according to Equations 9.1, 9.2, and 9.3. As the liquid is introduced into the vacuum it immediately volatilizes in preparation of the standard. The discussion in Section 9.5 becomes much more relevant for materials that exist as liquids at or near room temperature due to their lower vapor pressures.

After performing the standard preparation using liquid injection of the minor component, all remaining procedures are identical to the gravimetric blending procedures presented in Section 9.4.1. Again, to dilute these standards to lower concentrations, the standard prepared by liquid injection may be used for successive (or serial) dilutions.

The liquid injection technique may be used to prepare multi-component standards in a similar manner. In many instances, it is preferable to prepare a multiple component liquid pre-mixture prepared with the correct ratio of materials followed by the injection of an aliquot of the liquid pre-mixture to the cylinder as a single component. Multi-component mixtures such as EPA Methods TO-14 and TO-15 gas calibration standards as well as an infinite variation with as many as 100 or more minor components may be prepared with a high degree of accuracy. The number of components is limited only by the imagination, creativity, and budget of the requesting analyst – limited, of course, by the requirement of non-interaction between components. Many of these mixtures contain components that are subject to loss during the injection and/or degradation in the cylinder. Therefore, it is always preferable to provide a final certification of the mixture by laboratory analysis. The typical certification of the standard is performed by gas chromatography/mass spectrometric (GC/MS) detection due to the high specificity and precision inherent in that technique.

9.4.3 Gas Standards Prepared by Volumetric Addition

An alternative to weight addition of the gas components is the formulation of gas standards by volumetric addition. This technique involves the dilution of either a pure material or gas pre-mixture by pressure addition. For example, to obtain a 100:1 dilution of a 1% carbon dioxide in nitrogen standard to a final concentration of 100 ppmv (as was discussed in the gravimetric addition example in Section 9.4.1) 20 psia of the 1% gas pre-mixture is added followed by the addition of pure nitrogen to a final pressure of 2000 psia. There are several inherent weaknesses in the technique that must be understood to effectively utilize the procedure. First, to control and measure the addition of 20 psia of the pre-mixture, it is necessary to use a highly accurate and precise pressure gauge. Second, as gas is added to the receiving cylinder (i.e., the target gas standard), the compression of the gas to high pressure leads to heat evolution (the cylinder gets hot). Using the ideal gas law below, we can see a one to one correlation between temperature and pressure.

$$PV = nRT \quad (9.5)$$

where P is the pressure, V is the volume, n is the number of moles, R is the ideal gas constant, and T is the temperature. The increased temperature of the gas in the cylinder will lead to an erroneous determination of pressure (higher temperature results in a higher pressure). It is necessary to prepare the mixture very slowly, thereby allowing the heat to dissipate as it is generated, or allow the temperature of the cylinder to cool to room temperature and then adjust the mixture slightly to compensate for the artificially high pressure. Another option for mixtures prepared regularly (such as synthetic air blends performed on large multi-position manifolds) is to characterize the heating effect with sufficient accuracy to account for the effect as it occurs in mixture preparation.

The benefits of this technique are ease of use (for low precision blends) and lower cost of equipment. The disadvantages of using this blending method include loss of accuracy and, usually loss of any NIST traceability in the blend preparation, and the loss of time required to prepare the mixture with any reasonable accuracy or precision at all. In this instance, the only true traceability of the mixture would be by analytical comparison in the laboratory with recognized gas standards (NIST or VSL).

9.4.4 Gas Standards Prepared by Dynamic Addition

An important preparation technique used for the preparation of gas standards is known as dynamic blending. This method was designed to prepare a larger quantity of standards simultaneously with identical results for each cylinder. In this method, the gaseous materials (pure or pre-mixtures) are diluted with the balance gas at a low pressure, analyzed in situ, and referenced to a known standard (locally prepared or NIST certified) and then compressed to high pressure to fill the final products. This method could be considered a large scale version of volumetric blending. The benefit of this process is the simultaneous fill of multiple cylinders with identical components and concentrations. Methods similar to this are normally used to manufacture batch lots of mixtures that ultimately become NIST or VSL primary standards.

9.4.5 Notes on Additive Uncertainty

The specific uncertainty in the certification depends on a number of factors. For gravimetric mixtures these can be expressed in an equation form as follows:

For the preparation of initial mixture from pure materials by gravimetric addition:

$$(U_T)^2 = (U_B)^2 + \Sigma(U_M)^2 \quad (9.6)$$

where U_T is total uncertainty expressed in grams, U_B is uncertainty of the balance measurement expressed in grams, and U_M is material purity uncertainty expressed in grams.

For example, can a gravimetric blend of $\pm 1\%$ uncertainty be made using the following parameters: Ethylene purity of $> 99\%$ (indicates a relative uncertainty of $\pm 1\%$) with a weight addition of 150 g and gravimetric balance accuracy of ± 0.5 g absolute?

$$U_T = ((1.5)^2 + (0.5)^2)^{1/2} = (2.25 + 0.25)^{1/2} = (2.50)^{1/2} = 1.58 \quad (9.7)$$

Therefore, the absolute or total uncertainty (U_T) divided by the addition then multiplied by 100 will give the percent uncertainty, which when rounded down, equals 1% in our example:

$$\frac{1.58}{1.50} \cdot 100 = 1.05 \quad (9.8)$$

So the answer is yes, with an uncertainty of $\pm 1\%$, a gravimetric mixture can be manufactured using these parameters.

For the next mixture in a serial dilution preparation of a standard requiring multiple dilutions the total uncertainty of the first mix then becomes a component of the equation for the second mixture. This progression continues and it can be seen that the ultimate uncertainty of the final product becomes greater as well. So, for mixture 2:

$$(U_{Tn})^2 = (U_B)^2 + \Sigma[(U_{D1})^2 \dots (U_{D(n-1)})^2] \quad (9.9)$$

where U_{Tn} = total uncertainty of the n^{th} serial gravimetric dilution expressed in grams, U_B = uncertainty of the balance measurement expressed in grams, and $\Sigma[(U_{D1})^2 \dots (U_{D(n-1)})^2]$ is the sum of uncertainties for all previous dilutions in grams.

These equations may be manipulated to show that for a standard floor balance used in gravimetric blending, the lowest amount of material allowable to achieve a $\pm 1\%$ or better uncertainty in the blend would be 40.0 g. So-called mass comparators have a higher precision, readability, and repeatability; however more extreme measures must be taken to isolate these weighing devices from vibrations, air movement, and changes in humidity and temperature.

For the analytical certification of standards, the cumulative uncertainty would look more like:

$$(U_T)^2 = (U_S)^2 + (U_C)^2 + (U_P)^2 \quad (9.10)$$

where U_T = the total uncertainty expressed as a percentage, U_S = the standard uncertainty expressed as a percentage, U_C = the calibration residual uncertainty expressed as a percentage, and U_P = the measurement precision (or coefficient of the variability) expressed as a percentage.

Based on this information, we may characterize standard gas certification uncertainties. For a certification to be appropriate for a $\pm 1\%$ certification, the following must be true: U_S is $< 1\%$ and U_C is $< 0.8\%$ and U_P is $< 0.4\%$ yielding the following calculation.

$$(U_T) = (1.0^2 + 0.8^2 + 0.4^2)^{1/2} = 1.34 \quad (9.11)$$

which rounds to 1% uncertainty. For a certification to be appropriate for a $\pm 2\%$ certification, the following must be true: U_S is $< 1.5\%$ and U_C is $< 1\%$ and U_P is $< 0.8\%$ yielding the following calculation.

$$(U_T) = (1.5^2 + 1.0^2 + 0.8^2)^{1/2} = 1.97 \quad (9.12)$$

which rounds to 2% uncertainty. In addition, for a certification to be appropriate for a $\pm 5\%$ certification, the following must be true: U_S is $< 3.0\%$ and U_C is $< 3.0\%$ and U_P is $< 3.04\%$ yielding the following calculation.

$$(U_T) = (3.0^2 + 3.0^2 + 3.0^2)^{1/2} = 4.7 \quad (9.13)$$

which rounds to 5% uncertainty. In this manner a true determination (sometimes based on informed estimates) of the standard uncertainty may be made.

9.5 Pressure Restrictions and Compressibility Considerations

The actual physical contents of a cylinder of gas depends on pressure and temperature as we discussed in Section 9.4.3 in relation to Equation 9.5 known as the ideal gas law. The ideal gas law is an approximation for gases that behave in a certain manner (ideal interaction). Most real gases even obey this law near ambient conditions. In Section 9.5.1 we discuss the restrictions placed on the pressure of a gas phase standard and in Section 9.5.2 we introduce the compressibility factor which predicts how real gases behave under high pressure.

9.5.1 Vapor Pressure Restrictions for Gas Phase Mixtures

An important consideration in the manufacture of gas standards using liquid or solid components is the adjustment of the final pressure of the mixture to take into account the vapor pressure of the component material at a given temperature (usually taken to be 0 °C by North American gas mixture manufacturers). If the final pressure of the mixture exceeds the allowable vapor pressure of the component, the minor component in the mixture will condense out of the gas mixture onto the walls of the cylinder. There are differing opinions about whether the material can be returned to the gas phase and recreate the accuracy and dependability of the original formulation. Some practitioners in the gas business believe that heating the cylinder (carefully in a controlled manner) followed by rolling, can re-vaporize the minor component. *. The author has enough doubts regarding this practice to not utilize it nor recommend it to customers and partners.

For simple two component mixtures, the calculation of the vapor restriction is a fairly simple process. The following equation allows a simple and quick evaluation of the allowable final pressure of the mixture based only on the concentration required for the minor component and the vapor pressure of that minor component at some given temperature. Most manufacturers choose to restrict gas standards to withstand temperatures down to 0°C. As an example, we will calculate the final pressure restriction for a 100 ppm ethanol in nitrogen mixture. The equation for the determination

*Note that aluminum high pressure gas cylinders should never be heated due to the potential for temper destruction in the metal which could ultimately cause catastrophic cylinder failure such as cylinder rupture and/or explosion

of the pressure restriction is:

$$P_f = \frac{P_m}{C} \quad (9.14)$$

where P_f is final pressure, P_m is vapor pressure of minor component at 0 °C, and C is concentration expressed as a decimal.

For example, if 100 ppm expressed as a decimal is 0.0001, and the vapor pressure of ethanol at 0 °C is 0.229 psia, then the final pressure will be 2290 psia. In this instance, the standard can be manufactured to full pressure in any high pressure aluminum cylinder with a maximum pressure rating of 2216 psia or less. If the parameters of the blend requirement are changed to 1000 ppm, the final pressure becomes 229 psia.

As shown by the calculation, the scaling occurs in a linear manner and standard requirements can be adjusted accordingly depending on use requirements. Higher concentrations may be chosen as an alternative to higher mix pressures (corresponding to a lower gas content in the cylinder) or a higher pressure may be chosen for the mixture, resulting in a lower concentration to maximize the amount of standard gas in the mixture. These requirements are dependent on the intended use of the standard.

9.5.2 The Compressibility Factor

The physical amount of gas that can be put into a cylinder at high pressure can be expressed as (or rather derived from) a variation of the ideal gas law (Eq. 9.5):

$$PV = ZnRT \quad (9.15)$$

where P is pressure, V is volume, Z is compressibility factor, n is number of moles, R is ideal gas constant, and T is temperature. For gases that deviate significantly from the ideal behavior at high pressures, such as xenon, the compressibility factor, Z , is significantly < 1 . In this instance, there is significantly more gas in the cylinder at high pressure than would be predicted by the simplistic version of the ideal gas law (Eq. 9.5). Gases that have a compressibility factor closer to one will have real contents in the cylinder much closer to that predicted by the simplistic ideal gas law expression. An example of this is the amount of gas contained in a normal high pressure aluminum cylinder such as the AL150 cylinder filled to 2015 psia. The cylinder filled to this pressure will contain 162 mol of helium. The same cylinder filled to the same pressure contains 463 mol of xenon. In this example, the compressibility factor of xenon for this fill is 0.362 while the compressibility factor of helium in this fill is 1.035.

While this concept is important in understanding, the amount of standard contained in a cylinder, its primary importance lies in the preparation of the mixture itself. The gas manufacturer must understand and use this knowledge in determining actual weights of material to add to the cylinder.

9.6 Multi-Component Standards – General Considerations

Most of the discussions regarding gas standard preparation in previous sections have used simplistic examples of two component mixtures consisting of a primary component and a balance gas. These same concepts can be extended to gas standards containing almost as many components as one can imagine. While conceptually and theoretically possible and reasonable there are a few caveats surrounding multi component standards preparations that must be addressed prior to manufacturing the mixture. These are additive vapor pressure effects and material compatibility within the gas standard. Even with these additional concerns, gas manufacturers are regularly producing reliable low level gas standards per the EPA guidelines TO-14, TO-15, and ozone precursors requiring exact blending of 39, 57, 69, or more components in a single gas mixture. The prudent purchase of standards of this complexity requires a knowledgeable grasp of requirements as well as knowledge of the true capabilities of a potential gas standard vendor.

9.6.1 Additive Vapor Pressure Restriction Effects

The simplest explanation of additive vapor pressure effects is to list the steps in determining the ultimate restriction on a gas standard pressure:

Step 1: List components and concentrations by vapor pressure in ascending order.

Step 2: Using Eq. 9.14, calculate the mixture restriction for the first component.

Step 3: Add the concentrations of first and second component and use Eq. 9.14 to calculate the restriction using the sum of concentrations and the vapor pressure for the second component.

Step 4: Repeat Step 3 through all components (creating the additive concentration for all materials with lower vapor pressures).

Step 5: Choose the lowest pressure allowable under all previous calculations and set that as the maximum pressure for the mixture.

Step 6: Calculate additions per Section 9.4.1 and manufacture the standard.

Step 7: Test and certify concentrations.

This is a critical calculation that must be performed to determine allowable final pressures of multicomponent mixtures. Without this consideration there is always a danger of minor component condensation and a subsequent degradation of standard concentrations and dependability.

9.6.2 Material Compatibility Considerations

Another important consideration in the manufacture of multicomponent standards is the internal compatibility of the minor components. This is a separate issue

from cylinder and valve compatibilities and passivation discussed in Section 9.3 and should not be confused with degradation reactions requiring cylinder treatment or passivation. Every multi-component mixture should be reviewed carefully by an individual trained in materials properties prior to manufacture. This can be a chemist, materials engineer, or experienced gas manufacturer. Typically reactions occurring in a cylinder will lead to the formation of materials that are unwanted or the disappearance of desired components. Reactions of this type include, but are not limited to, acid-base reactions, oxidation-reduction reactions, and combustion. In most cases the degradation reactions are benign, leading only to the unreliability of the standard, however, in extreme cases and higher concentrations, these reactions could potentially generate enough heat and/or pressure to rupture the cylinder causing any number of safety concerns. Reputable gas manufacturers will recognize these dangers and recommend safe alternatives.

9.6.3 Additional Considerations

There are a number of methods used to manufacture multi component standards and most are specific to the actual gas standard mixture or to the manufacturer themselves. It is beyond the scope of this section to explain all of these methods. Suffice it to say there are any number of ways to produce these standards precisely and just as many (or more) ways to make them badly. Again, the educated end-user asking the gas supplier the correct questions will help mitigate problems.

When deciding on a gas standard, a realistic assessment of the lower limit of detection and quantitations for the method under study should be taken into account. If a specific method or instrument suggests the detection range as 0.1–100 ppm, don't order a gas standard at 0.1 ppm unless the method is established and optimized and ready to quantify the extreme lower end of the detection range. A newly installed instrument will not likely be able to detect or quantify the extreme lower limit of the published specification without considerable optimization.

A final concern to the end-user is the cost of purchasing complex gas standards. Standards used for air monitoring (a normal product such as TO-14 or TO-15) will typically cost approximately \$50–\$150 per component. Complex mixtures with 78 components might cost anywhere from \$3900–\$11,700 for the standard. Complex mixtures with more exotic components can cost even more. It is advisable to carefully assess the number of components required in the gas standards as well as approaching the ordering process with a realistic assessment of the limit of quantification (LOQ) for the technique requiring the gas standard.

9.7 Cylinder Standard Stability Consideration

An important characteristic of any gas standard is the stability of that standard. One specification not discussed earlier in Section 9.2 is “shelf life” or “expiration period”. While most quality systems require a published expiration date, many gas standards

can remain stable for a much longer period of time than documented. This is one of the reasons many gas manufacturers offer recertification services, albeit reluctantly.

The single most important factor in the continuing stability of a gas standard is the absence of contaminants in the standard at the time of blending as well as the absence of reacting contaminants in the pure materials used to make the mixture. The most common contaminants present in all cylinders to some degree are moisture, atmospheric oxygen, and rust. There are varying levels of cylinder preparation used to remove these contaminants and prepare a cylinder for a specific service – some of these were mentioned in passing in Section 9.3. Many low purity bulk gases such as nitrogen, oxygen, argon, helium, air, etc., are packaged in cylinders that have virtually no preparation. They may be subjected to a forced air drying cycle prior to valve installation or they may have been subjected to purging or a rough vacuum. Higher purity bulk gases and simple gas standards require the additional steps of a heated evacuation in a cylinder treatment oven. These devices are well controlled heated vacuum systems in which readiness is characterized by the achievement of a specific vacuum reading. Gas standards at percentage levels or non-reactive materials such as hydrocarbons are suitable to be filled in either steel or aluminum cylinders prepared in this manner.

A higher level of cylinder preparation is required for corrosive gas standard manufacture. At concentrations $< 1\%$ it is advisable to use a steel cylinder which has been internally coated with nickel (normally an electroless nickel coating process). The nickel coating is usually applied to a newer clean cylinder with minimal or no rust, or to a cylinder which has been bead or sand blasted to clean surface rust. This final cleanliness verification is performed by visual inspection. While rust is not necessarily a reactive material, the exponential increase in surface area created by rust/flake cycles is a huge contribution to degradation. As the surface area increases, the potentially reactive metallurgical components are exposed thereby increasing chances and rates of standard degradation. In processes where particle count is important, rust is a particularly onerous contaminant.

For standards where the highest level of purity and non-reactivity is required, there are a number of proprietary methods of cylinder passivation and preparation. Most of the true intellectual properties of gas manufacturers reside in this part of the process. Therefore, it falls loosely into the category of “magic”. Realistically, this involves the baseline heated evacuation cycle mentioned earlier followed by a passivation process that could be as simple as exposing the cylinder to the reactive material, that will ultimately be the minor component of the final mix, at some higher level than the final blend (often called the “pickling process”). The belief is that if all the active sites in a cylinder have been bound previously to the material in the mixture, there will be no further degradation of the standard when it is manufactured in the following step. If the degradation process is a simple adsorption process this would potentially passivate the cylinder. The danger is that when the cylinder standard pressure drops below a certain level, the material will begin to migrate out of the cylinder walls causing the measured concentration of the standard to inexplicably increase over time.

Several more advanced treatments exist that are proprietary and essentially based on silanization processes. The processes succeed, to a greater or lesser extent depending on the exact treatment used and the control of the process, in creating a “glass-like” coating on the inside of the cylinder thereby decreasing reactivity. Most of these processes have been around for more than 30 years and constitute “public secrets”. The majority of these methods were modified versions of treatment technologies used in the manufacture of gas chromatography columns (mostly capillary gas column manufacture). The development of more advanced cylinder passivation technologies representing the first true advances in cylinder passivation, derived from actual cylinder/molecule interaction models based on chemical interaction and standards observation/measurements, are in progress in some laboratories. These developments are driven by the requirements of the end-user and regulatory agencies for lower concentrations of more reactive minor components.

While the cylinder passivation is of inestimable importance, the purity of the raw materials in the mixture also contributes to the accuracy and stability of the packaged gas standard. A perfect example of this type of degradation is the manufacture of low level nitric oxide standards. Nitric oxide degrades by the following process:



This equation shows that a single molecule of oxygen reacts with two molecules of nitric oxide to form two molecules of nitrogen dioxide (actually a dynamic equilibrium exists where the arrow goes both ways and the balance of the equation depends on temperature and pressure conditions). In this example, it only requires 0.5 ppm of oxygen in the nitrogen balance gas to completely degrade a 1 ppm nitric oxide standard, even when the best cylinder passivation technology is used. However, in that case, the end-user would read the standard as 1 ppm nitrogen dioxide with little if any nitric oxide present. That would make this a “bad” gas standard. Analogous scenarios exist for other gases.

It is beyond the scope of this chapter to discuss cylinder passivation and standards degradation in more depth. A knowledgeable and experienced manufacturer of gas standards should be able to guide the user through this maze to effectively order the correct gas standard that best fits their needs. In some instances it becomes necessary to question the certified concentrations and/or stability of a particular gas standard. Most gas manufacturers are pleased to have technical support services assisting users through the learning process involved.

9.8 Liquefied Compressed Gas Standards – Preparation Differences and Uses

An alternative formulation of standards used in specific industries (primarily the petrochemical industries) involves the use of liquefied gas standards for certain calibration requirements. These can be produced in normal cylinders with the use of so-called “dip tubes” or “educator tubes” with a pressurized head gas used to force liquid out of the cylinder or they may be manufactured into piston cylinders.

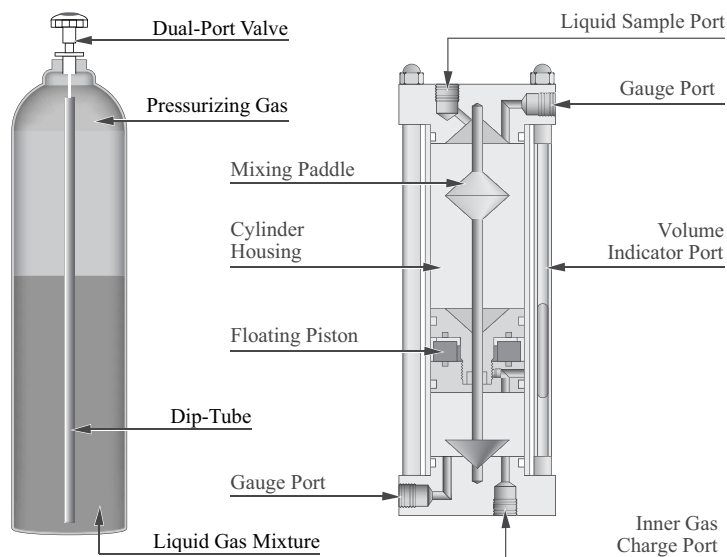


Figure 9.6 Dip-tube and piston cylinder diagrams.

The simplest version of a liquid standard uses a standard gas cylinder either low pressure or high pressure dictated by the mixture and the proposed usage. The components may be added before the valve is inserted into the cylinder if the materials have sufficiently low vapor pressures. Additional components may be subsequently added after the valve has been inserted and the head space removed. Depending on the specific components in the mixture the pressure of the head gas can be adjusted to keep the majority of the components in the liquid phase. Note the use of the word “majority”. There still exists a measurable vapor pressure even under significant head pressure. Therefore, even with extreme care and master blending techniques there can still exist an additional uncertainty in the standards because of the physical properties of the materials themselves.

A more accurate method for the preparation of liquid standards is through the use of piston cylinder technology. In this case, liquids (primarily liquefied compressed gases) are added to the piston cylinder under pressure and in the liquid state. This is achieved because a piston cylinder has a floating piston that separates the pressurizing head gas from the standard material. During and after addition to the piston cylinder, the pressure behind the piston is adjusted to maintain all components in the standard in the liquid state. In many of these cylinders, there also exists a floating mixer that allows a final homogeneity to be accomplished prior to use. Carefully prepared standards in these cylinders are extremely accurate and reproducible from first use to last use. Both styles of liquid mixture preparations are equally valid however the use of the piston cylinder technology guarantees the consistency of samples from first to last (including the continual delivery of liquid sample).

9.9 Cylinder Standard Alternatives

Cylinder gas standards are normally an excellent calibration choice, however, some applications are better served with dynamic calibration generators. These devices generate highly characterized standard concentrations by passing a diluent gas stream across a semi-permeable membrane. The diffusion of the target compound across the membrane occurs in a reproducible manner dependent primarily on temperature and membrane surface area [20]. The flow of diluent gas across the membrane can be changed to vary the final concentration of the generated standard. The generator tubes are certified as producing some specific quantity of material per unit time (i.e., nanograms per minute at a specified temperature). These devices are known as permeation tube devices and are recognized by NIST as reliable standards generators (on a case by case basis). The primary manufacturer of permeation tube calibration generators is Kin-Tek Laboratories and VICI Metronics. Figure 9.7 illustrates the device.

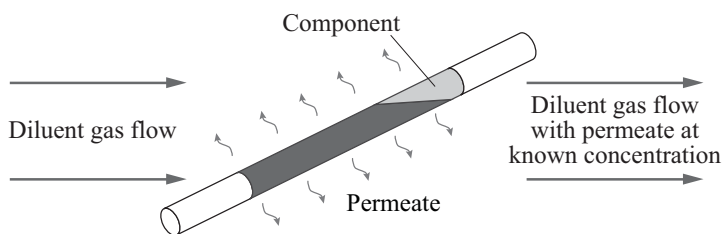


Figure 9.7 Permeation tube principle.

Devices of this design are quite effective for generating gas standards with a small number of components (usually in the range of 1–4 different materials) and within given concentration ranges however the requirement of many components in a gas standard can make the hardware quite cumbersome. They are also not particularly effective with higher concentrations.

9.10 Dilution Devices and Calibration Uses

Another useful strategy of the gas standard user is the gas diluter. Dilution devices combine a gas standard (or multiple gas standards) with a dilution gas (also known as the diluent), to allow the accurate and reproducible generation of multiple gas standards from a single cylinder. In this way a full calibration curve of multiple points may be created with one gas cylinder and tested or verified with one or more check standards.

The first design uses the pressure drop across glass capillary tubes of varying lengths to create varying flows that are combined with the diluent gas (Figure 9.8). The caveat associated with this design is that the physical characteristics of the gas standard and diluent gases must not be too different and the pressures of the diluent

gas and the gas standard delivered to the diluter must be set carefully and controlled per the manufacturers specifications. This type of diluter can only be used to dilute a single standard gas into a number of preset dilutions (usually 0–100% in 10% change increments).

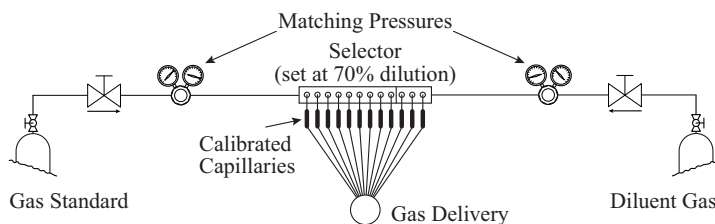


Figure 9.8 Diagram of a capillary dilution device.

The second design is similar except the pressure drops occur through fixed orifices instead of capillary tubes (Figure 9.9). The concept is the same and functionally the system performs in the same manner.

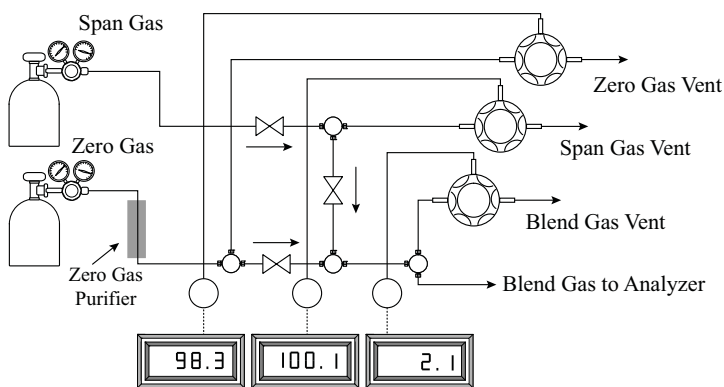


Figure 9.9 Diagram of a pressure drop dilution device.

The third design relies on the use of mass flow controllers to accurately control flows mixing with the diluent gas (Figure 9.10). These systems can be as simple as single component dilutions or can combine a number of different standards or pure gases to create any number of gas standards. Again, the more gases added together to form a single standard, the more cumbersome the system. The benefit of using a system of this design is the ability to “dial in” a concentration with no pre-set dilutions. The mass flow controllers can also compensate for materials with significantly differing physical properties and they can be used to create high concentrations calibration standards as easily as low concentrations.

The caveat associated with using a system of this design is the regular requirement of calibration. Mass flow controllers are notorious for losing calibration or “drifting” over long periods of time. While it has not been the experience of these authors,

it is strongly recommended that the complete dilution device be returned to the manufacturer every year for calibration and certification of accuracy. This maintains the peace of mind of the user as well as providing an important supporting document for quality programs such as ISO 9002 systems.

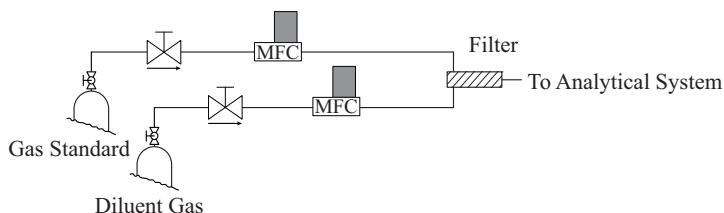


Figure 9.10 Mass flow configured dilution device.

Gas diluters are available from a number of different vendors, but they are based on only two designs. Neither design is more reliable or accurate than the other for any given application however the mass flow design requires regular calibrations. In either case, the diluter allows the gas standard user a way to reduce a large number of cylinder gas standards to a few critical standards without losing calibration accuracy or capabilities while significantly reducing cylinder rental fees and storage space requirements.

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