HIGH PURITY GASES

1. Introduction

High purity industrial gases are routinely delivered in large quantities having purities exceeding 99.999% (> 5nines pure). Other commodity materials, whether in liquid or solid form, much less typically have purity exceeding 99.9%. There are many applications for gases where purity even higher than 99.999% is required. To service these applications, the technology for manufacturing and delivering high purity gases has developed into a multibillion dollar business worldwide. Japan and the United States have the majority of the market.

There is no universally accepted definition of what purity levels correspond to high purity. However, gases having total impurities specified <1 ppm on a molar or volume basis must be manufactured and handled differently from regular gases if that specification is to be maintained. A good working definition of high purity is gases having certain individual impurities held to levels <0.1 ppm.

The technology for manufacturing and delivering high purity gases has largely developed to support the manufacture of advanced semiconductor materials needed as part of the overall process of manufacturing integrated circuits. Purity requirements in some of these high performance materials have reached the point where impurity concentrations in the starting gases of 1 part in 10^{12} have been related to reduced yields and poor performance in the resulting integrated circuits. Depending on a volume, high purity gases can be delivered using either bulk systems, where a plant-wide distribution system is integrated with central gas storage facilities, or cylinders, where a short local distribution system is supplied from a single high pressure cylinder.

Gases used in the manufacture of semiconductor materials fall into three principal areas: the inert gases, used to shield the manufacturing processes and prevent impurities from entering; the source gases, used to supply the molecules and atoms that stay behind and contribute to the final product, and the reactive gases, used to modify the electronic materials without actually contributing atoms or molecules.

Nitrogen [7727-37-9], N_2; oxygen [7782-44-7], O_2; hydrogen [1333-74-0], H_2; argon [7440-37-1], Ar; and helium [7440-59-7], He, are classified as semiconductor bulk gases. The following gases are delivered in cylinders and are classified as semiconductor specialty gases: (*1*) silicon precursor gases such as silane [7803-62-5], SiH_4; dichlorosilane [4109-96-0], SiH_2Cl_2; trichlorosilane [10025-78-2], $SiHCl_3$; and tetrachlorosilane [10026-04-7], $SiCl_4$; (*2*) dopant gases such as arsine [7787-42-1], AsH_3; phosphine [7803-51-2], PH_3; diborane [19287-45-7], B_2H_6; and boron trifluoride [7637-07-2], BF_3; (*3*) etching gases such as nitrogen trifluoride [7783-54-2], NF_3; sulfur hexafluoride [2251-62-4], SF_6; boron trichloride [10294-34-5], BCl_3; hydrogen fluoride [7664-39-3], HF; chlorine [7782-50-5], Cl_2; chlorine trifluoride [7790-91-2], ClF_3; hydrogen bromide [10035-10-6], HBr; tetrafluorosilane [7783-61-1], SiF_4; and other halocarbons; and (*4*) reactant gases such as ammonia [7664-41-7], NH_3; hydrogen chloride [7647-01-0], HCl; nitrous oxide [10024-97-2], N_2O; tungsten hexafluoride [7783-82-6], WF_6; and carbon dioxide [124-38-9], CO_2.

2. Production and Purification

The separations processes used for manufacturing high purity gases are generally the same as those used for making lower purity products. Purification by distillation (qv) and adsorption (qv) are often used and, provided basic data are available, can generally be designed using standard engineering practices. Some separation processes that are not economical for the manufacture of lower purity gases do find applications in making high purity gases. Chemical conversion processes, where the impurities are converted into more easily separable forms through a selective chemical reaction, are often employed in point-of-use purifiers which typically process streams having less than five standard liters per minute flow rate.

Whereas the underlying separation or purification technology may be straightforward, the purity achieved is often far less than that which the separation processes are capable of producing. More often than not, recontamination by impurities released by the materials of construction used in the purification, storage, and delivery equipment represents the true limit to the purity that can be achieved in practice.

Generally, the purification methods used for manufacturing high purity gases can be divided according to volume throughput requirements and of course differ according to the chemical and physical properties of the gas being purified. For the manufacture of high purity gases on a large scale, the industry tends to employ a few well-known methods. When production or purification is required on a smaller scale, a greater number of separation methods and combinations of these methods are used in actual practice.

2.1. Bulk Gases. The bulk gases are usually characterized by high volume flow requirements in the manufacturing process. Historically these have consisted of nitrogen, oxygen, argon, hydrogen, and to a lesser extent, helium. Because these gases are manufactured on a large scale, small-scale supply schemes tend to be more of a distribution process for product already purified on a large scale. These small-scale distribution systems may, however, incorporate so-called onsite or point-of-use purifiers to ensure that any impurities picked up during distribution are removed.

Generally the bulk gases are also nonreactive with their containment systems. However, this is becoming less true because the need for large quantities of high purity HCl, trichlorosilane, and other corrosive gases has grown pushing these into the bulk gases category.

Nitrogen. Because of numerous applications in semiconductor manufacturing, high purity nitrogen is produced both at high volumes and at some of the lowest impurity levels seen for any of the high purity gases. Streams up to 10,000 nm^3/h can be produced at impurity levels of 1 part in 10^9.

Distillation. All high purity nitrogen is manufactured from air using multistage cryogenic distillation (qv). Depending on the customer's flow rate and purity requirements, the original separation from air is carried out either locally on the customer's property or at a large airseparation (qv) unit (ASU) located some distance away.

For volume throughput requirements larger than $\sim 1000\,\mathrm{nm}^3/\mathrm{h}$, self-contained and highly automated on-site generators are installed on the user's property. The gaseous nitrogen produced by the generator is then delivered throughout the user's plant using a dedicated high purity distribution system. Impurity contents on the order of 1 part in 10^9 can be achieved in the delivered product using these systems.

For smaller volume requirements,nitrogen is manufactured and liquefied in a large merchant air separation unit owned by the gas supplier. Liquid nitrogen is transported by tanker truck and stored in a large cryogenic tank on the customer's site. When needed by the customer, liquid nitrogen is withdrawn from the tank, vaporized, filtered, and delivered throughout the plant using a dedicated distribution system. Impurity levels on the order of 1 part in 10^8 can be achieved by trucking liquid nitrogen over distances exceeding 1500 km. However, product costs are determined largely by delivery distance and may be uneconomical at that range.

Chemical Conversion. In both on-site and merchant air separation plants, special provisions must be made to remove certain impurities. The main impurity of this type is carbon monoxide, CO, which is difficult to separate from nitrogen using distillation alone. The most common approach for CO removal is chemical conversion to CO_2 using an oxidation catalyst in the feed air to the air separation unit. The additional CO_2 which results, along with the CO_2 from the atmosphere, is then removed by a prepurification unit in the air separation unit.

At throughputs below 500 nm^3/h, a wide variety of inert gas purification processes based on chemical conversion can be used to produce high purity nitrogen. For the most part, these processes employ chemical reactions to convert O_2, H_2O, CO, and CO_2 impurities into nonvolatile products. Typically, the impure nitrogen is passed through a bed of reagents, which may or may not require elevated temperatures to function, where the conversion reactions occur causing the impurities to remain behind in the bed of reagents. These processes require that the bulk of the oxygen in the feed be removed by some other method. For this reason, they are mainly used to convert standard purity grades of nitrogen into high purity ones.

For nitrogen flows above 10 nm^3/h, it is important to minimize any heating or cooling of the process stream because of the energy costs. Heating for regeneration purposes does not carry this economic penalty. There are two types of chemical conversion processes in general use which meet this requirement. Both function effectively at room temperature and below and are capable of removing O_2, H_2O, CO, and CO_2 to levels below 1 part in 10^9.

The first process utilizes a bed of nickel catalyst which has been regenerated with hydrogen to reduce the nickel content to metallic form. The finely divided metal then reacts with impurities and retains them in the bed, probably as nickel oxide in the case of oxygen or as physisorbed compounds for other impurities. Periodically, the bed is regenerated at elevated temperature using hydrogen to restore the metallic content. The nickel process can be used and regenerated indefinitely.

The second process utilizes a bed of high surface-area porous zirconium–iron alloy pellets. The bed is regenerated periodically at elevated temperature to allow impurities on the surface of the pellets to diffuse into the bulk. The renewed surfaces are effective for removing impurities from the gas stream until, with use, they once again become saturated. The zirconium–iron process has the advantage of not requiring hydrogen for regeneration; however, zirconium–iron pellets must be replaced once these have fully reacted.

Combined Distillation and Chemical Conversion. On-site generators using distillation are almost always combined with chemical conversion purifiers in large bulk high purity nitrogen supply systems. Practical issues, such as ensuring a continuous supply of inert nitrogen during an interruption of electrical power or when the generator is being serviced, dictate that liquid nitrogen be stored for use when the generator is unavailable. Often backup nitrogen must be obtained from standard commercial sources that are not high purity. Also, even if high purity liquid nitrogen from the generator can be accumulated for backup purposes, commercial purity liquid nitrogen may be the only source available if the generator is out of service for more than a day or so.

The delivery of high purity nitrogen from commercial purity liquid nitrogen sources is accomplished by using high capacity chemical conversion purifiers which are active only when the backup stream is in use. Even so, the equipment cost is high and every attempt is made to tightly integrate the chemical conversion purifier with the nitrogen generator.

Oxygen. High purity oxygen for use in semiconductor device manufacture is produced in relatively small quantities compared to nitrogen. There are two different purification processes in general use for manufacturing the gas: distillation and chemical conversion plus adsorption.

For applications in semiconductor device manufacture, it is important to remove the chemically nonreactive noble gas impurities such as krypton, xenon, and particularly radon. Through spontaneous decay, radioactive isotopes of these gases in the purified oxygen can cause a wide range of radioactive daughter products to be incorporated into the electronic device materials. Further decay of the radioactive daughter elements provides a continuous source of ionizing radiation inside the device that can lead to a type of defect known as soft errors, particularly in large dynamic memories.

Distillation. As for nitrogen, all high purity oxygen is derived from air through the air separation (qv) process using cryogenic; distillation (qv). Generally, air separation units that manufacture commercial purity oxygen also remove nitrogen and other light impurities to levels low enough for high purity applications. Argon is still present at concentrations above 1 part in 10^5, but is not considered an impurity for most applications of high purity oxygen. Heavy impurities, typically hydrocarbons and noble gases, are usually not removed from commercial purity oxygen. To make high purity grades, an additional distillation column is added to the process. Some on-site nitrogen generators are also able to generate a small stream of high purity oxygen.

Chemical Conversion and Adsorption. Where additional distillation is not practical, hydrocarbons and heavy noble gases can also be removed by combining chemical conversion with adsorption. Commercial purity oxygen is passed through a high temperature bed of oxidation catalyst; usually combinations of platinum and rhodium on a high surface area alumina support. Hydrocarbon impurities are oxidized to CO_2 and H_2O. Temperatures in excess of 700°C are needed in the catalyst bed to ensure complete oxidization of methane. Because the process flow rates are typically small, these temperatures can be maintained without excessive energy costs. The CO_2 and H_2O products from catalytic oxidation of hydrocarbon impurities are removed using a temperature swing adsorption (TSA) process. The adsorbent is typically one of the molecular sieves (qv), such as 13×. If designed appropriately, the adsorption process can also be used to remove the heavy noble gases. Usually, however, only radon removal is necessary. Because radon has a 3.8-d half-life, it is only necessary to slow its transit through the adsorber bed for sufficient time for natural decay to reduce the concentration to an acceptable level.

Argon. High purity argon has many applications as an inert gas during the manufacture of semiconductor devices. High consumption rates are typical during processes which deposit high purity silicon epitaxial films onto polished wafers. Lower volume applications range from silicon crystal pulling to sputter deposition of metal films. In all these applications, nitrogen is a reactive impurity which, in addition to O_2, H_2O, CO_2, CO, and all hydrocarbons, must be removed from the argon to low levels.

Distillation. Conventional purity argon is separated from air using a combination of distillation and chemical conversion. High purity argon is made the same way. However, more stages of distillation are designed into the low pressure and pure argon columns in the air separation plant. The improvement in the efficiency of the low pressure column typically reduces the nitrogen impurity to below 1 ppm. Because argon is found at a concentration of only 1 vol% in air, it is not practical to supply argon from on-site generators.

Chemical Conversion. Except for control of nitrogen impurity levels, the same chemical conversion methods used for nitrogen purification at low flow rates can also be used for argon purification. Although used less commonly for argon purification than for nitrogen purification, these chemical conversion methods are applied in point-of-use purifiers located close to where the gas is consumed.

There are also chemical conversion purifiers which remove nitrogen in addition to other more reactive impurities. These purifiers require elevated temperatures to function and consequently are restricted to small process flow rates of typically a few liters per minute.

Hydrogen and Helium. Whereas hydrogen and helium are very different chemically, these gases have low boiling points and are normally liquefied during manufacture. Because the boiling points are so low, even very small amounts of trace impurities tend to freeze and form solid deposits. To prevent formation of these deposits, which can eventually plug process lines, trace impurities must be removed prior to liquefaction. Similar methods are used to purify hydrogen and helium prior to liquefaction.

Hydrogen. High purity hydrogen is usually delivered and stored as a cryogenic liquid and vaporized when needed. This vaporized liquid seldom needs any further processing to meet high purity specifications. However, in situations where liquid hydrogen cannot be used, high pressure hydrogen gas can also be delivered and further purified on-site to meet high purity specifications.

On-site purification of gaseous hydrogen is accomplished using combinations of chemical conversion, cryogenic adsorption, and palladium membrane processes depending on the purity and throughput requirements (see MEMBRANE TECHNOLOGY). For small hydrogen streams, stand-alone hydrogen purifiers based on selective permeation through palladium membranes are available. These units take advantage of the high permeability of hydrogen through palladium metal. Generally, the membranes are heated to get higher processing capacity per unit area. However, provisions must then be made to remove hydrogen from the membrane prior to cool-down to prevent formation of small cracks which then allow impurities to leak through the membrane. Small to large hydrogen streams can be purified by adsorption carried out at cryogenic temperatures, usually near the boiling point of liquid nitrogen. Activated charcoal and silica gel are both effective adsorbents for purification. However, if any significant quantity of oxygen must be removed, activated charcoal should not be used because of the potential for an explosive chemical reaction with the adsorbed oxygen during regeneration. Regeneration of the adsorbent is accomplished through a process of heating and reverse purging. Large hydrogen streams can be purified using a room-temperature palladium catalyst bed to convert oxygen impurity into water followed by cryogenic adsorption. Because the oxygen impurity has been removed, the higher adsorption capacity of activated charcoal can then be utilized without danger of explosion.

Helium. High purity helium is usually not required in large quantities and is therefore not commonly delivered as a cryogenic liquid. Instead, high pressure cylinders are filled from a liquid helium source by the gas supplier and then transported to the customer. When high purity helium is required, the high pressure gaseous helium is processed through an on-site purifier.

Because helium is not chemically reactive, the same chemical conversion processes used for purification of nitrogen and argon are also applied to helium purification. Additionally, cryogenic adsorption processes are used to remove the nonreactive impurities. As for hydrogen, the same precautions must be taken against possible adsorbent explosions when dealing with significant amounts of oxygen impurity.

Helium is separated from helium-bearing natural gases usually, but not always, in the process of removing nitrogen to improve the fuel value of the natural gas. Thus, in a sense, the principal part of commercial helium is as a by-product. Natural gas components include methane and heavier hydrocarbons, helium, nitrogen, water vapor, carbon dioxide, sometimes hydrogen sulfide, small amounts of argon, and traces of neon and hydrogen.Water, carbon dioxide, and sulfides are first removed by scrubbing with monoethanolamine and diethylene glycol, followed by drying with alumina. Then the natural gas is concentrated in helium as the higher boiling hydrocarbons are liquefied and collected. Crude helium, concentrated to about 70% and containing other permanent gases, undergoes a cryogenic purification where the majority of nitrogen and argon are liquefied. Activated charcoal operating at liquid nitrogen temperatures or below is used to adsorb all remaining nonhelium gases. Helium that exceeds 99.9999% in purity results.

2.2. Specialty Gases. The specialty gases are generally more reactive than the bulk gases and usually have low volume flow requirements in their applications. Historically, these have been delivered almost exclusively in standard compressed gas cylinders. However, as the need for increased quantities has arisen, bulk specialty gas supply systems utilizing larger ton-sized containers and tube trailers are being developed.

Purification of specialty gases can be divided into two areas: purification done by the gas supplier on a bulk scale prior to filling the cylinder or other delivery container, and purification carried out by the consumer on a point-of-use scale generally just prior to use.

Bulk Purification. Many specialty gases originate as by-products or low purity intermediate chemicals produced during the course of manufacturing something else. For example, most of the high purity silane produced in the United States originates as an intermediate in the manufacture of metallurgical silicon.

In some cases the chemical manufacturer purifies a portion of this intermediate stream to make a high purity product. In other cases, the chemical manufacturer sells a low purity product to a gas company and the gas company purifies it to make a high purity product. In both bases, purification is done on a continuous basis, rather than cylinder by cylinder. The purification processes tend to utilize standard methods.

Distillation. Processes which utilize either simple liquid vapor flash processes or multistage distillation tend to be used often for purification of bulk specialty gases. The fact that the separation process is well understood goes a long way toward reducing overall risk when the gases are difficult to handle. Distillation has been applied to the manufacture of flammable gases, for example ultrapure silane, as well as many corrosive gases.

Adsorption and Chemical Conversion. In some cases, removal of moisture or oxygen added by small amounts of air contamination is all that is necessary to make a gas suitable for high purity applications. For example, high purity HCl is available in tube trailer quantities but may require removal of moisture inadvertently added during transport before it is distributed to process equipment within a semiconductor plant. With a limited objective, it is usually most effective to use an adsorption process. As long as the total mass of impurity which must be removed is low enough, the process may be designed either with or without the capability for repeated regeneration.

Chemical conversion processes can also be used for moisture and oxygen removal. These tend to be the same ones developed for the smaller point-of-use purifiers. Consequently there is little economy of scale and they are seldom able to be regenerated.

Point-of-Use Purification. For the user of cylinder quantities of reactive specialty gases, there are only a limited number of ways to remove impurities and obtain high purity. Specialized point-of-use purifiers have been developed that purify small streams of many important reactive gases. Whereas these point-of-use purifiers cannot remove all important impurities, they are usually effective for removing the contamination added by the users' gas distribution system, mostly air and moisture.

One important class of point-of-use processes utilizes a porous polymer containing reactive metals. Variations in the metal and polymer chemistry are made to optimize the process for different gas applications. This is an active area of development and purifiers are available for most of the principal specialty gases.

3. Delivery and Control

Once a gas has been purified, it must be brought to its intended point of use without being degraded by the addition of excessive contamination. This transport or delivery process can be technically challenging. Often, contamination is unintentionally added even before the gas has left the purifier during its original manufacturing process. This is especially true for the corrosive specialty gases, where minimizing contamination by iron and other metallic species arising from the purification system is a primary concern.

Technologies to prevent recontamination during the delivery process have been an intense area of development. Work in the 1970s focused mainly on preventing contamination of high purity inert gases such as N_2 and Ar by atmospheric leaks and the release of atmospheric impurities which had been adsorbed on the inner surfaces of delivery systems during assembly. More recently, work has focused on preventing contamination of corrosive gases, such as HCl and HBr, with contaminants that contribute metallic impurities such as Fe and Ti to the electronic materials.

Delivery methods for high purity gases can be divided both according to chemical reactivity with respect to the containment system and, to a less significant degree, according to volume throughout requirements. Many highly flammable gases such as H_2 and SiH_4 are still inert with respect to the containment systems. Even though special provisions must be made because of flammability, the technology used to deliver flammable gases is similar to that employed for inert gases.

3.1. Bulk Gases.

Attaining high purity gases where they are used requires a suitable gas distribution system. To achieve a high purity distribution system, there must be an absence of dead zones, external leakage, outgassing, and particulate contamination. Dead zones are obvious sources of carry-over contamination and must be designed out of the system. External leakage can arise from the diffusion of air through small holes, which takes place despite a reverse pressure gradient. Leakage can also occur because of permeation, especially through organic polymers used for gasketed seals.*Outgassing* is a general term applied to the release of any gaseous contaminants from the materials of construction. It can result from impurities adsorbed on surfaces and dissolved within the bulk material of both system components and particulate contamination.

Over the years, substantial technology has been developed for minimizing the recontamination of high purity gases by the distribution system. The use of high cleanliness components having low outgassing surfaces is extremely important. Low permeability materials, typically 316L stainless steel, must be employed throughout the system. Minimum dead volume designs and leak-tight fabrication techniques are essential. High efficiency filtration (qv), using low permeability materials to reduce outgassing from adsorbed/dissolved contaminants, is employed frequently. A typical bulk gas tanker features electropolished 316L stainless steel inner vessels and piping, as well as proprietary tank fill lines, bellows or diaphragm-sealed valves, and cryogenic filters in the product delivery line. Such a vessel and piping system minimizes welds, oxidized joints, and rough surfaces that might trap or generate particulate contamination.

3.2. Specialty Gases.

The purity of specialty gases depends on the systems and procedures adopted by the distributors for bulk gas supply and cylinder preparation, filling, and delivery. The distributors need to follow strict cylinder selection, preparation, and filling procedures to ensure the quality of the products. Most of the precautions taken into consideration in the bulk gases delivery system are also applied for specialty gases to eliminate recontamination.

4. Analysis and Certification

Ensuring that the purification and delivery processes are working properly is essential to successful applications of high purity gases. Gas analysis technology is especially critical during startup of high purity processes. Once a process is demonstrated to be operating property, it can generally be maintained by following rigorous operational protocols and using statistical process control techniques to identify deviations from these protocols.

4.1. Particulates.

Particulate impurity and particulate control are significant issues in virtually all applications of high purity gases. In the semiconductor industry, gas specifications requiring <350 particles/m^3 (10 particles/ft^3) greater than 0.1 μm in diameter are typical. Separation of particulate impurities is an important part of the process for manufacturing high purity gases and the most common approach is through filtration (qv) technology. As a separation process, filtration is understood well enough that off-the-shelf filters can remove particles down to the limits of detection available in analytical instruments.

4.2. Description of Analytical Methods.

Procedures for analyzing both gas and particulate impurities in high purity bulk gas products such as nitrogen, argon, oxygen, helium, and hydrogen are available. Typical gaseous impurities include oxygen, moisture,carbon monoxide, carbon dioxide, total hydrocarbons (THC), argon, and nitrogen analyzed to the low ppb level. Particle impurities are analyzed to the 0.1-μm level.

Recommended Equipment. A list of analyzers (stand-alone or in a mobile cart) and level of detection for specific gas and particle analysis follows:

Instrument	Detection level	Detection mechanism
atmospheric pressure ionization mass spectrometer (apims)	<1 ppb	
moisture analyzer	<5 ppb	dew point or microbalance
oxygen analyzer	<1 ppb	electrolytic
H_2, CO, CO_2, THC analyzer	<10 ppb	gc-RGA gc-FID with methanizer
Ar, N_2 analyzer	<50 ppb	gc-DID, gc-HID
particle counter	≥0.1 μm	LPC

The operation manual accompanying each analyzer should be consulted for the recommended startup, installation, and calibration procedures.

Gaseous Impurities. Instrument calibration (excluding the apims) typically consists of two steps: zeroing and spanning. Zeroing is accomplished by allowing the analyzer to sample a gas, the contaminant level of which is below the lower detection limit of the analyzer. This is called a zero gas. A typical method for generating zero gas is to take the actual sample gas and run it through a gas purifier.

In some analyzers, background readings associated with noise or minute internal levels of impurities can be removed electronically. Other analyzers may not allow electronic zeroing. Background levels must still be checked using the zero gas. For gas chromatographs (gc), it is important to determine that there are no background peaks that can interfere with the integration of true impurity peaks. If large background levels are evident, the system must be checked for leaks and/or more purging time must be allowed.

Spanning, accomplished using a sample gas containing a known volume concentration of impurity, is performed at levels that are the same order of magnitude as the required detection. The actual span concentration is selected so that the majority of expected measurements fall at or within its value.

As was the case for the zeroing procedure, some analyzers may need to be electronically spanned. The analyzer is allowed to sample the span gas until a stable reading is obtained and then this span concentration is entered. This particular method represents a single-point calibration. Some analyzers require that more than one span concentration be sampled so that a calibration curve can be generated, known as a multipoint calibration. For gas chromatographs the peak area counts associated with known concentrations are used to generate the calibration curve. For low ppb detection, accurate span gases can only be produced using a high purity blending system. This procedure involves taking a cylinder containing between 1 and 5 ppm volume concentration of impurity and diluting to ppb concentrations with zero gas. For best results, the cylinder matrix gas and zero gas must be of the same species as the gas to be analyzed. It is good practice to recheck the analyzer's zero after spanning is completed.

Single-point calibrations and zero determinations are performed whenever instruments are shut down and/or relocated to a different sampling location. Should the recalibration vary by more than 10% of the value obtained during the initial calibration, the analyzer is recalibrated until stable calibration data are obtained.

The calibration procedures for an atmospheric pressure ionization mass spectrometer (apims) involves the generation of separate calibration curves for each of the monitored impurities. Because of the instrument's high level of detection sensitivity (ppb to<ppb), a dedicated, high purity blending system must be utilized to minimize background and produce accurate low ppb calibration gases. To carry out calibration, apims response is measured for a zero gas and at least five blended impurity concentrations. These concentrations are evenly distributed in the range of 0–50 ppb. The ion-current response recorded at each concentration for the individual impurity is normalized against the total ion-current response. The data are expressed as a percentage in terms of relative ion intensities, $R_a = 100\, I_a/I_T$, where R_a is the relative ion intensity of impurity *a;* I_a, the ion-current response of impurity *a;* and I_T, the total ion-current response. The relative intensity response data is regressed against blended impurity concentration data to produce the linear model, $R_a = k_a(C_{am} + C_0)$, where C_{am} is the blended impurity concentration of impurity *a;* C_0, the background impurity level; and k_a, the multiplication constant. Possible sources of background response include instrument noise, sample system outgassing, or interference from other impurity response signals. Proper setup, purging, and operation of the instrument should reduce background levels well below 1 ppb.

Rearranging the above expression yields impurity concentration as a function of relative intensity, $C_a = R_a/k_a$, where C_a represents both sample concentration and any background effects. The stability of the calibration must be confirmed at least every two weeks by analysis of a known mixed impurity standard.

Particulate Impurities. Particle counters require factory calibration every two years. In addition, the background signal associated with both the instrument and its sampling system (tubing, sampler, sample valves, regulators, and fittings) must be quantified so that it may be subtracted from sample measurements. To accomplish this, an absolute filter (<0.01 μm rating) is employed. The absolute filter removes all particles entering the sampling system, so any particle registered by the counter can be directly attributed to the sampling system or instrument noise.

To measure background, the absolute filter is placed at the beginning of the sampling system and purged for a minimum of one hour at a rate of 100 standard liters per minute (SLPM). After the purge, the sampling system is plumbed up to the particle counter and a minimum of 0.14 standard cubic meters (5 SCF) of gas is analyzed in 0.003 or 0.0003 standard cubic meter (0.1 or 0.01 SCF) increments. The average of these runs is accepted as the system background. It is recommended that the background be checked again at the completion of certification measurements for a particular system. The background varies depending on the matrix being analyzed, therefore when switching matrices, the background must again be quantified.

Sampling and Analysis Guidelines. As a general safety consideration, all gases should be vented to an external area and whenever possible, inert gases should be used as the test gas for piping systems.

Sample Line Connection Procedure. The following procedure is used for connecting sample lines to sampling ports. For best results, a one-eighth in. (0.318 cm) diameter 316SS electropolished tubing having one-fourth in. (0.635 cm) end fittings is recommended for sampling gas for both gaseous and particulate impurity analyses. The one-eighth in. diameter tubing allows a larger degree of flexibility than does the one-fourth in. tubing. Butt weld glands that adapt one-fourth in. end fittings to one-eighth in. tubing are available (Swagelok). The actual orbital welding can be performed by fabricators.

The following are mandatory: (*1*) a new pair of clean, dry, plastic, disposable gloves must be worn during this procedure to prevent the potential contamination of the gas system by oils, dirt, and moisture present on the hands; (*2*) prior to making a connection, all required materials must be gathered and close at hand, including all tools, gloves, gaskets, adapter fittings, sample line, etc; (*3*) all sampling components must be precleaned prior to assembly, and these components must be kept clean at all times with ends capped and stored in cleanroom plastic bags; (*4*) appropriate precautions must be taken if making a connection to a hydrogen system, which includes grounding all components prior to and after making the connection and confirming that there is no ignition source or oxidizer near by (area must be isolated with red “Hazard Area” tapes); (*5*) sample connections are made to valved ports only; (*6*) for bulk gases other than hydrogen, the valve is opened slightly to ensure that a flow comes out the port once its cap is cracked open (for hydrogen, it is recommended that the connection be made with the valve closed and the next step omitted); (*7*) standing to the side of the port (ie, not in front of the line of flow), the analyst should crack open the fitting slightly and ensure that gas is flowing out of the fitting, use the valve to adjust the flow leaking past the fitting to a substantial but manageable level, and if there is no flow with the valve opened, the fitting must be resealed immediately and the cause determined; (*8*) the cap and old gasket are removed and the sample line with new gasket connected; and (*9*) prior to connection to the analyzer distribution manifold, the sample line must be purged. The purge flow rate should be as high as possible, given all safety and gas consumption constraints. Sample line purging should be performed for at least 30 minutes. If the connection is made to a hydrogen system, this purging step is eliminated and the sample tubing immediately isolated until such time as it can be connected to the analyzers.

Sample Analysis. The following procedure is used for sample analysis: (*1*) after sample connections are made and the sample tubing purged for 30 minutes, the tubing is connected to the sampling manifold which serves to distribute sample gas to each of the analyzers, and should analyzers have specific pressure and/or flow requirements, a means of regulating these parameters should be incorporated into the manifold (suggested design: high purity regulator attached to a multivalve manifold having flow meters on each flow-critical leg); (*2*) the sampling system and analyzers are then purged for at least two hours (if this is the first use of the system, or if it has been shut down for a significant time, longer purge times will likely be required to reach representative level). It is crucial that the analytical system be continuously purged or effectively isolated when moving to a new point to avoid contamination and a mobile analytical cart with a purified, on-board purge is ideal for maintaining high purity conditions; (*3*) when analyzing multiple locations, it is recommended that separate sample lines be set up purging in advance to reduce analysis cycle time, but this should only be done when all safety considerations and gas consumption factors are taken into account; (*4*) repeated analyses are then performed for approximately one hour to determine the stability of the analyzers and if the required specifications have been met; (*5*) it is recommended that five consecutive analyses showing the impurities within specification be completed (average concentrations are recorded on a standard certification form given the following information: customer facility, sampling location, analyst, time and date, impurity specification, measured impurity concentration for each completed analysis, measured impurity concentration mean, and analyzers employed); (*6*) if any impurity fails to meet specification, the analyst should check for leaks, check the calibration, and/or increase purge flow (slowly) if safe to do so. Another option is to cycle-purge the system by repeatedly closing the vent valve to pressurize and then opening the valve wide to rapidly depressurize. The analyzers must be isolated during this process and care should be taken not to allow the system pressure to fall so low (eg, <69 kPa (<10 psig)) that air can gain access and contaminate the system; (*7*) after the above six steps have been taken, sampling conditions are returned to normal and the system retested; (*8*) gas chromatographic analyses are based on a direct comparison of the area or peak heights of the individual impurity against its respective standard calibration curve, however, if the concentration of impurity found in the sample is less than the lowest standard evaluated, then an extrapolated linear regression value may be determined; (*9*) the particle count for a measured gas is the difference between the count taken during the analysis of the sample and that measured for the sampling system background according to standard statistical procedures; and (*10*) particle measurements are generally accomplished more effectively when performed separately from vapor impurities because a higher level of purging is usually required for particle analysis and a complex sampling system can generate additional particles under these conditions.

5. Applications of High Purity Gases

The applications of high purity gases are primary in the semiconductor industries. From 1991 to 1995, the North American semiconductor bulk gas sales increased from U.S. \$214 to \$252 million (annual growth rate of 4.2%) and specialty gas sales increased from U.S. \$78 million to \$169 million (annual growth rate of 21.4%).

In addition to the microelectronics industry, other applications for high purity oxygen include fiber optics manufacturing, production of pharmaceuticals, and usage as calibration media in research and development laboratories, and in the pollution control field.Applications for high purity hydrogen include oxidation processing and epitaxial growth for both silicon and gallium arsenide.

Argon has become an important commodity owing to its ability to remain inert even under extreme conditions of temperature and pressure. High purity argon is likely to be used in the high technology fields of electronics, fiber optics, research and development, powder metal spraying, and hot isostatic pressing.

Other applications of high purity specialty gases include hydrogen bromide for etching single-crystal silicon, polysilicon, and aluminum; nitrogen trifluoride as a fluorine source for *in situ* cleaning processes for chemical deposition equipment, semiconductor etching and deposition, and high energy chemical lasers; and sulfur hexafluoride as a key etching material in certain semiconductor manufacturing processes because it has a selectively high etch rate of silicon compared to silicon dioxide or silicon nitride.

The primary driving force for high purity gases has been the increasing purity demands from high technology industries such as ceramics, optical fibers, and silicon wafer fabrication. In 1985, the typical impurity requirement in high purity nitrogen for wafer fabrication was on the order of 500 to 100 ppb on a molar or volume basis. The impurity requirement changed to the range of 10 to 1 ppb in 1990 and to 1 to 0.1 ppb in 1995. Future demands for even higher purity gases are expected.

In addition to purification to remove contaminants, accurate analyses of extreme purity gases and selection of storage and delivery equipment to minimize recontamination, all the while keeping costs down, pose serious challenges for the manufacturers of high purity gases. One analytical breakthrough in the 1990s was the development of atmospheric pressure ionization mass spectrometers that monitor <ppb levels of impurities continuously. Further improvement of analytical techniques is a focus of industrial research and development facilities.

BIBLIOGRAPHY

"High Purity Gases," in *ECT* 4th ed., Suppl. Vol., pp. 184–197 by W. H. Whitlock, E. F. Ezell, and S.-C. Hwang, The BOC Group, Inc.

GENERAL REFERENCES

1. R. DiNapoli and A. M. Sass, in J. J. McKetta, ed., *Encyclopedia of Chemical Processing and Design*, Vol. **31**, Marcel Dekker, Inc., New York, 1990, p. 236.
2. W. H. Whitlock, "The Ultra-High Purity Challenge", in *Separation of Gases, Proceeding of the Fifth BOC Priestley Conference*, Birmingham, U.K., Sept. 19–21, 1989, Royal Society of Chemistry, 1990.
3. M. Finnergan, *CryoGas Int.*, 13 (Apr. 1996).
4. H. A. Grieco, *CryoGas Int.*, 20 (Apr. 1996).
5. J. D. Borkman, W. R. Couch, and M. L. Malczewski, *Microcontamination*, 23 (Mar. 1992).
6. S. D. Cheung, G. L. Mooney, and D. L. Jenson, *Micro*, 59 (Oct. 1995).
7. N. M. Chodhury and L. J. Mostowy, *Micro*, 33 (Sept. 1995).
8. J. M. Davidson and T. P. Rhane, *Microcontamination*, 34 (Mar. 1987).
9. E. F. Ezell, A. Athalye, and M. Chigrinskiy, *Microcontamination*, 93 (July/Aug. 1996).
10. J. Hart and A. Paterson, *Microcontamination*, 63 (July 1994).
11. G. Kasper, H. Y. Wen, and H. C. Wang, *Microcontamination*, 18 (Jan. 1989).
12. K. Siefering, H. Berger, and W. Whitlock, *Microcontamination*, 31 (Sept. 1992).
13. *Ibid.*, p. 23 (Nov. 1992).
14. K. Siefering, W. Whitlock, and A. Athalye, *Microcontamination*, 41 (Mar. 1994).
15. R. M. Thorogood, A. Schwarz, W. T. McDermott, and C. D. Holcomb, *Microcontamination*, 28 (Aug. 1986).
16. P. Burggraaf, *Semicon. Int.*, 70 (Mar. 1990).
17. R. Iscoff, *Semicon. Int.*, 52 (Mar. 1991).
18. *Ibid.*, p. 42 (Apr. 1992).

WALTER H. WHITLOCK
EDWARD F. EZELL
SHUEN-CHENG HWANG
The BOC Group, Inc.