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Review of existing methods for generating dynamic reference standards of key airborne molecular contaminants

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1. Introduction

Airborne molecular contaminants (AMCs) consist of chemicals in the form of vapours or aerosols that have detrimental effects on products, processes and instruments. In particular, they may cause problems related to formation of films and particles on surfaces, lithography defects, hazing of optics, masks and wafers, counter doping and corrosion. There are several classes of AMCs including acids, bases, condensables, dopants and metals.

The major acid contaminants include hydrogen fluoride (HF), hydrogen chloride (HCl), sulphuric acid (H_2SO_4) and nitric acid (HNO_3). They primarily originate from the use of these chemicals in manufacturing and their main effects include corrosion, hazing of surfaces and electrical faults at the chip level [1]. Basic contaminants are also a major concern. Ammonia (NH_3) is the main issue as it is used in process and photoresist chemicals. Bases and acids react in air and produce small particles that can deposit on product surfaces. Molecular condensables are organic components with boiling points typically greater than 150 °C that can adsorb and irreversibly bind to product and tool surfaces [1]. These include plasticisers, antioxidants, phosphates and silicones. Boron and phosphorus are among the most wide-used molecular dopants. Their detrimental effects are associated with counter-doping of silicon which turns into more sensitive products. Airborne metals can contribute to gate oxide integrity degradation of wafers. Their sources include vehicle emissions, construction, process chemicals and tools. To ensure a minimum of contamination during manufacture, clean room facilities and state of the art monitoring instrumentation have become essential in microfabrication plants [2].

AMCs are typically present at low parts per billion to parts per trillion amount fractions, making detection very challenging [3]. Gas sensors are used to provide on-line monitoring of these components to inform the operator of their presence and ensure corrective action can be taken to minimise impact on the production process. Reference standards of these challenging components at trace amount fractions are currently unavailable and are required to provide traceability to validate these developments. This promises to hasten the uptake of a new generation of ultra-sensitive sensors to understand and control AMCs and remove barriers to efficient manufacture in ultra-clean environments.

A variety of methods has been developed for the generation of standard gas mixtures [4-7] and can be divided into static and dynamic preparations. Static methods involve the addition of a target component and a diluent (usually nitrogen or purified air) in a closed device, such as a stainless steel cylinder. The components are mixed until homogeneity is achieved and contained until use. Static methods are inexpensive however they suffer from a number of disadvantages such as potential losses due to absorption and condensation on the walls of the container, limited volumes and are susceptible to leaks. Consequently static methods are unsuitable for preparing reference standards of these challenging reactive gases especially at trace amount fractions.

Dynamic methods offer some advantages over static methods. In this approach, a reference gas of known amount fraction is continuously introduced into a diluent in a flowing system. Although more elaborate and relatively more expensive equipment is involved, as standards are generated continuously, losses due to absorption on the walls of the system are negligible after equilibrium has been achieved. They have the added benefit that large volumes of the reference standard can be produced and the amount fraction can be varied in real time to provide a wide dynamic range. This flexibility is extremely desirable for calibrating analytical instrumentation over a range of amount fractions.

This report reviews existing methods for generating dynamic reference standards for reactive components for gas sensor calibration at trace amount fractions, with a particular focus on HCl, HF, NH_3 and formaldehyde (CH_2O).

2. Dynamic reference gas standards for sensor calibration

Dynamic methods for generating gas standards are especially useful in processes involving reactive gases as the undesirable reaction products are swept away and continuously replaced by the unreacted mixtures. Dynamic methods involve the incorporation of the target gas into a flow of a matrix gas (generally nitrogen or air).

2.1 Flow control and measurement

Accurate measurements of mass flow rates are essential for accurate determination of the amount fraction generated. Fixed and adjustable flow elements can provide reliable flow rates [8]. Fixed flow elements include sonic nozzles and critical orifices. A sonic nozzle (or sonic venturi) consists of a smooth rounded inlet section converging to a minimum section area and then diverging along a pressure recovery section or exit cone [9]. As a gas accelerates through the nozzle, its velocity increases and its density decreases. At the throat, it reaches the speed of sound. The sonic nozzle is operated by pressurizing the inlet (P1) or evacuating the exit (P2), to achieve a P1/P2 pressure ratio of 1.4 to 1 or greater [9]. This ratio maintains the nozzle in a "choked" or "sonic" state. A critical flow orifice is a small circular aperture in a plate, often produced from a metal. When the pressure downstream of the orifice is less than approximately half the pressure immediately upstream, the velocity in the orifice reaches the speed of sound. In both devices, when the flow is choked it becomes independent of fluctuations in downstream pressure and is proportional solely to the upstream pressure [10-12].

Among the adjustable flow elements, mass flow controllers (MFCs) are the devices more widely used. They can be divided into thermal and coriolis MFCs regarding the principle of measurement. Classical thermal mass flow controllers have three resistance wires coiled around a stainless steel capillary. The middle wire is a heater and the wires at each side are temperature sensors. When there is no flow the temperature profile is symmetric. When there is a gas flow the temperature profile moves to the right. For low flow rates, the phase difference is proportional to the flow rate. Recent developments of thermal mass flow controllers include miniaturised thermal sensors based on complementary metal–oxide–semiconductor (CMOS) technology with a substantially improved repeatability [13]. A controllable heater element is mounted in the middle of a pressure-stable membrane and temperature sensors are mounted symmetrically upstream and downstream from this heater element in the direction of flow. Any flow over this membrane causes a transfer of heat and generates a measurable signal. Coriolis MFCs contain a vibrating tube in which a fluid flow causes changes in frequency, phase shift or amplitude. The resulting output signal is proportional to the real mass flow rate, whereas thermal mass flow meters are dependent on the physical properties of the fluid.

The main advantage of fixed over adjustable elements is that they are inexpensive and provide a highly repeatable fixed flow [12]. However, MFCs offer the advantage of being tunable and provide a range of dilutions with a single device. With both systems, relative expanded uncertainties (k=2) as low as 0.2% can be achieved [8, 12, 14]; however, MFCs are typically used with an expanded

uncertainty of 1% of maximum flow [15] to account for the stabilisation time and calibration drift. The use of Molbloc devices to accurately measure the mass flow rate in a dynamic system has been reported [16].

MFCs can be manufactured from more resistant materials for use with reactive gases. Examples include Monel (a nickel alloy primarily composed of nickel (63% minimum) and copper (28 – 34%), with some iron, manganese and other trace elements) or Hastelloy (nickel-molybdenum alloys with other trace elements).

2.2 Methods for introducing the target component

The dynamic generation of gas standards requires the continuous and uninterrupted blending of the components for a certain period of time. There are several methods for introducing the target component into the balance gas. For liquid substances with a low boiling point, diffusion and injection systems are the most widely used. For gases, systems based on permeation and dilution are most common. Other techniques include the generation of the target component by evaporation or by chemical reaction. In each case the generated component is blended with the matrix gas. For certain components electrochemical methods are employed.

2.2.1 Dilution

This is the most widely used method for mixing two or more gases. The dynamic mixtures are usually prepared by diluting a higher amount fraction reference standard of the target component in a single step with the required matrix gas. The amount fraction of the reference mixture produced is determined by measuring the flow rates of the gases before they are mixed. This method relies on having a capability to produce stable static reference standards of the target component at a higher amount fraction.

Trace amount fraction mixtures can be produced using a double dilution method. This avoids high dilution ratios and reduces the estimated uncertainty in the generated mixture. In this method, a small portion of the output from a first dilution phase is removed and diluted with more matrix gas. In both dilution steps the flow of the matrix and reference gas are required. For both experimental arrangements it is important to keep internal surfaces to a minimum and select suitable materials in order to reduce equilibrium times. Use of flow meters at the lower end of the range should be avoided in order to obtain the highest accuracy.

At present, there are several facilities to generate dynamic reference standards by dilution at the National Physical Laboratory (NPL). One of them uses ‘Molbloc’ flow elements and is capable of generating adjustable reference standards of NO and SO_2 with an estimated relative expanded uncertainty of lower than 1% [16]. A schematic of the facility is shown in figure 1. The calibration gas mixture is produced by blending a Primary Reference Gas Mixture (PRGM) of the target gas with a diluent gas, which is either nitrogen or air. The diluent gas is passed through three filters containing silica gel, Purafil and charcoal to ensure it is nominally free from the target gas and other impurities such as water. The efficiency of the filters is checked once a year to ensure that more than 99% of residual target components in the diluent are removed. This is particularly important since the presence of target components in the diluent has a significant impact on the uncertainty at low amount fractions. The flow of the diluent can be regulated either by a 20 mg/s full-scale Viton seal thermal mass flow controller or a 100 mg/s full-scale metal seal MFC, whereas the flow of the PRGM can be controlled

by either a 0.2 mg/s full-scale Viton seal MFC or a 2 mg/s full-scale metal seal MFC. The mass flow of each gas is measured accurately with Molbloc-L laminar mass flow elements (DHI), located upstream, and matched to the full scale setting of the MFCs. In this system, a mixing chamber was not required which is often the case with dilution systems, as the turbulence caused by the components entering the stream is sufficient to promote homogeneous mixing. This facility enables the production of tunable amount fractions in the range 100-10000 nmol/mol.

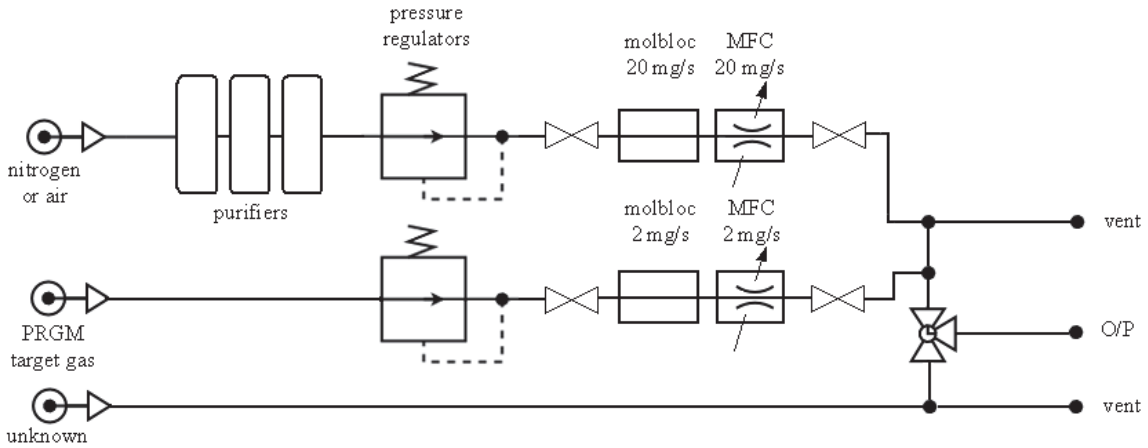

Figure 1 Schematic of the high accuracy dilution system. The output (O/P) is connected to a gas analyser. A two-way valve is used to alternate the flow of the blend and gas mixture under test to the analyser.

A more complex example of a dilution system is the NPL Preset Binary Network. It is based on a network of critical flow orifices [12] and is shown in figure 2. Six orifices are used with pre-set nominal flows corresponding to the binary sequence 1, 1, 2, 4, 8, 16 (expressed relative to the flow through the orifice downstream of valve A). The orifices are supplied with standard or diluent gas through valves labelled A to F. Each valve may also be closed. The pressures of the standard and diluent gases are controlled by two pressure regulators that are set to maintain equal output pressures of nominally 3.6 bar absolute. During the calibration procedure, the combined flows are passed through a differential pressure mass flow meter with an accuracy specified to be "0.8% of reading + 0.2% of full scale (at 1000 cm^3/min)". Since it is solely used to compare flows that are close to equal, the accuracy of the flow reading has a negligible effect on the measurement uncertainty. This is in contrast to similar systems reported previously [17,18] that depend on accurate measurements of absolute flow. The calibration procedure is required to determine the flow ratio of each orifice accurately relative to a reference orifice (the orifice downstream to valve A) under the same conditions of pressure and temperature. Flow ratios from the calibration can then be used to determine the amount fraction of the range of gas mixtures generated. The calibration procedure used is based on the principle of summing flows in a binary sequence that has been reported previously [19].

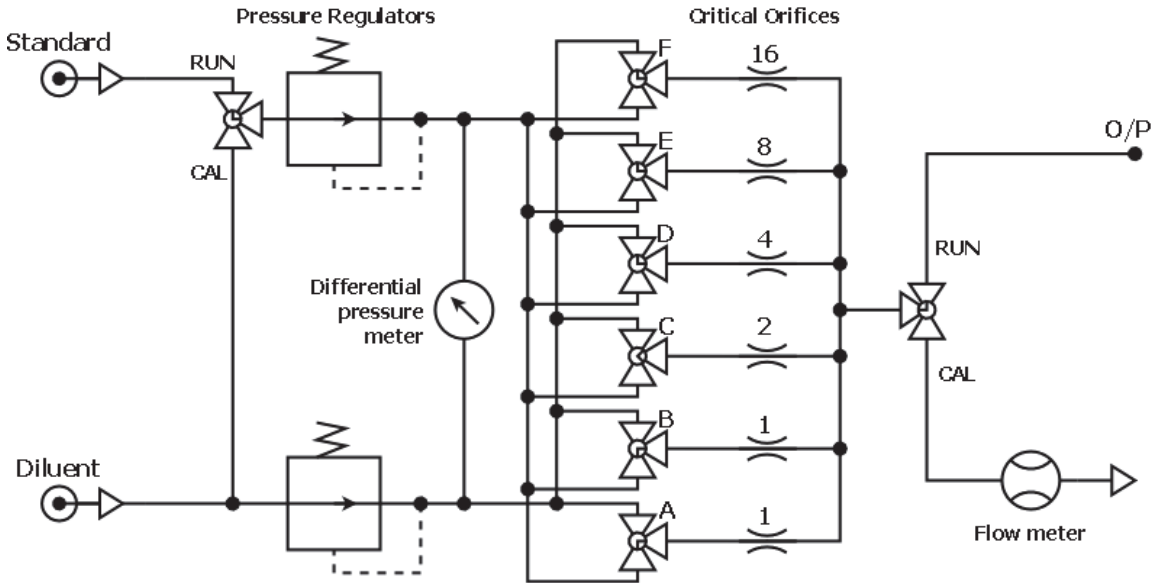

Figure 2 Schematic of the network of critical flow orifices. Valves A to F are switched to flow standard or diluent gas. An intermediate position on each valve closes the gas supply. The flow through the flow meter is vented to atmosphere. The output (O/P) is connected to a gas analyser.

2.2.2 Injection

Injection is a technique that can be used for both gases and liquids. The major components of an injection system for dynamic standards are the liquid or gas reservoir, the injection mechanism, the injection port and the vaporiser [7].

Gases and liquids can be added to moving gas streams by a wide variety of chemical dosers, injectors and pumps as well as gravity and electrolytic feeding units. Motor-driven devices have been used extensively to introduce gases, liquids, vapours and even particulate matter into moving gas streams, providing higher accuracy and precision than other reservoir emptying techniques. The component to be injected is contained in an inert reservoir, often a syringe, whose volume diminishes evenly when acted upon by the mechanical dispensing apparatus. Gas-tight syringes with a teflon-tipped barrel are particularly useful for injecting most liquids or gases as loses between the piston and the syringe body are minimised. The injection mass flow rate can be incremented using several syringes at a time. These techniques have the ability to generate high accuracy mixtures over extended time periods and typically produce amount fractions ranging from parts per million to percentage level. Gases are relatively easy to inject into a larger flowing volume of gas, but liquids present more issues. They must be injected, evaporated and properly mixed for reliable and stable mixtures. The most common injection port is a t- piece fitted with a rubber serum cap or septum where the needle is inserted. When injecting a liquid, some means must be provided to evaporate it completely and at the very tip of the needle. Evaporation can be achieved using turbulence of the diluent gas (if preparing 100 µmol/mol or less). As required amount fractions increase and solvent volatility decreases there becomes an increasing need for other methods to be employed such as increasing surface area between the liquid and the matrix gas and raising the temperature of the liquid. Small volumes of liquid should be evaporated carefully as during evaporation, the substrate material cools, thereby retarding the volatilisation of the additive liquid resulting in a pulsing concentration gradient. This can be overcome by ensuring that the temperature of the apparatus is maintained using heating tape.

2.2.3 Diffusion

Vapours have the ability to diffuse through capillary tubes or semi-permeable membranes at a constant rate provided that the temperature, concentration gradient and geometry remain unchanged. The ratio of the cross sectional area to the length of the tube should be lower than 0.3 to obtain good results [7]. Tube diameters should range from 2 to 20 mm. Diameters smaller than 2 mm make tube filling a problem and those above 20 mm lead to turbulence, which causes additional errors because of the increase in the effective diffusion path length.

Diffusion is limited to liquid components that evaporate or solids that sublime at, or close to, room temperature. Depending on the amount fraction generated, long times are often required for the mixture to reach equilibrium. Although values for the diffusion rate and diffusion coefficient can be calculated, theoretical and empirical diffusion rates can exhibit large variations so, in practice, the mass flow rate of the target component into the diluent gas is calculated from periodic weighings. A schematic of a dynamic diffusion set up is shown in figure 3. A metered gas stream is brought to the desired experimental temperature by passing it through a constant temperature bath. The preconditioned gas then passes over a diffusion tube and mixes with the vapour of interest at a constant rate. The resultant amount fraction is controlled by varying either the temperature or the flow rate of the primary or secondary diluent gas.

NPL has developed one of these systems. Research has been carried out to develop a micro-scale diffusion device based on a reservoir containing liquid of the target component. Vapour from the liquid diffuses along a capillary and mixes with a small flow of nitrogen which carries it to a gas chromatograph for analysis. This work has shown the generated amount fraction to be highly repeatable although the certified amount fraction exhibits a considerable discrepancy with the value calculated from theory. Therefore in order to realise the benefits of this dynamic method and to provide high accuracy, a suitable reference standard is required for calibration.

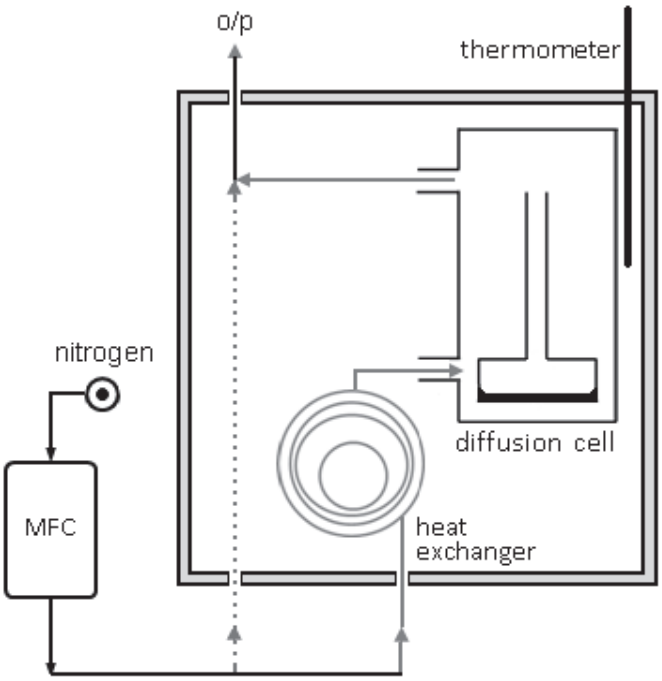

Figure 3 Schematic of a dynamic diffusion facility.

2.2.4 Permeation

Permeation is one of the most established techniques for generating reference mixtures at trace amount fractions. A permeation tube consists of the target component compressed to the point of liquefaction, sealed inside a polymeric container. The target component dissolves in and permeates through the walls of the tube at a constant rate and mixes with the passing diluent gas. This process is based on molecular diffusion as a consequence of the concentration gradient between the inner and outer surfaces of the membrane wall. Components which work best are those which have critical temperatures above 20 – 25 °C [7]. The most commonly used are NO_2 and SO_2.

There are many possibilities for tube construction. Fluorinated ethylene propylene resin (FEP Teflon) is usually chosen because of its availability and durability. Glass vials with permeable tops are also available and offer lower permeation rates than conventional tubes. Other materials have also been used such as nylon or polyethylene. In any permeation tube with a fixed geometry, all of the variables should remain essentially constant except for temperature, to which the permeation rate is exponentially dependent.

Permeation rates are usually determined gravimetrically at the experimental temperatures desired. After an initial waiting period to allow the tube to reach equilibrium, the tubes are weighed, stored in a desiccator at a known temperature and reweighed after several days. Care must be taken to make the weighings under the same conditions of humidity, as absorbed water can introduce a bias. A balance with good resolution is required to achieve high accuracy. Online weighing systems enable the permeation tube to be maintained in a constant environment and hence can reduce the uncertainty in the reference standards produced. The lifetime of these devices is an important practical consideration and depends on the volume contained within the tube and the permeation range.

Permeation tubes offer several advantages over other methods. The low degree of complexity and ability to generate reference standards in the parts per million to parts per billion range make them ideal for field instrument calibration and laboratory standards. High precision and accuracy ± 1% can be obtained if good temperature control is maintained (± 0.1 °C). Each tube must be volumetrically or gravimetrically calibrated once it is in equilibrium with its environment. Immediately after manufacture, the stresses of sealing cause the tube to exhibit differences in permeation even at the same temperature. Therefore it is desirable to wait several days after filling before weighing.

The example in figure 4 is used for trace reference standards of water vapour where nitrogen passes through a purifier system followed by an electronic pressure controller which maintains a constant input pressure to a water vapour permeation chamber [20]. The chamber contains a water permeation tube that is suspended from a microbalance through a magnetic coupling for on-line weighing. The constant input pressure eliminates changes in buoyancy and ensures that the balance records a constant mass loss from the tube. The permeation source is temperature stabilised to ± 0.05 °C to ensure a stable permeation rate and negligible balance drift. The flow from the permeation vessel (Q_A) is split by an array of critical flow orifices. The flow from each critical flow orifice passes to a three-way valve that can be set to direct the flow to either a vent or “output”. It is then diluted with a flow of dry nitrogen (Q_B) also delivered from the output of the pressure controller through one or two critical orifices with nominal flows of 1.5 l/min.

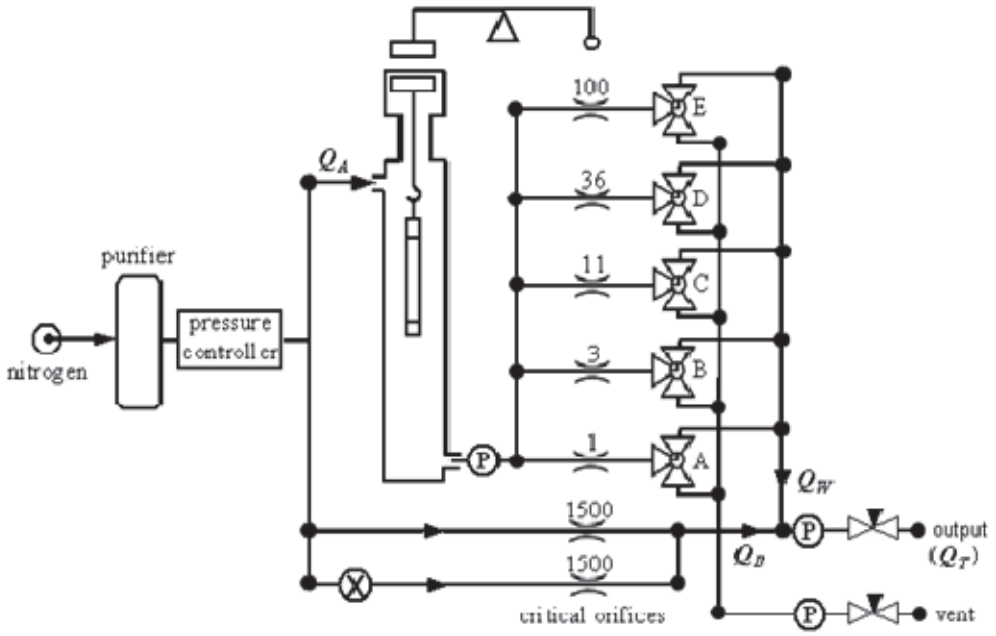

Figure 4 Schematic of a dynamic facility for generating reference standards of water vapour at trace amount fractions using permeation. The nominal flow through the critical flow orifices is shown in cm^3/min.

2.2.5 Evaporation

Evaporation techniques involve the matrix gas flowing in close proximity to a liquid or volatile solid. This is achieved either by dispersing it through the liquid or by passing it over the liquid or solid of interest. The gas stream can be saturated or partially saturated with the target component and diluted if required. Since the vapour pressure is directly dependent on the temperature, different amount fractions can be produced by adjusting the temperature of the vessel containing the target component. This is an excellent technique for adding a single volatile liquid or solid to a gas stream and is routinely used, often with a subsequent dilution step, to prepare dynamic standards of mercury vapour [21]. However, evaporation methods have limited use for producing reference standards as an independent standard is required to certify the mixture produced. Provided the pressure and temperature of the reservoir containing the target component are kept constant, this technique is capable of producing stable and repeatable amount fractions. As the solvent evaporates, the liquid cools causing a rapid decrease in the vapour output. A circulating constant temperature bath will help ensure a more uniform evaporation and reduce the time required to reach equilibrium. Also, the change in the depth of the column of liquid above the dispersion tube as the liquid evaporates can affect the evaporation rate. This effect can be minimised by using a reservoir to replenish the liquid supply [7] or by using systems with large width/height ratios.

2.2.6 Electrochemical

Many gases can be synthesised on a laboratory scale using electrolytic or coulometric methods. Electrolysis of any solution takes place when current flows between two electrodes arranged in a solution. As the potential difference is raised a significant current increase is observed at a certain

point (the decomposition potential) and the amount of gas evolved is a theoretically linear function of the applied potential. Electrodes are usually constructed from an inert metal such as Pt. The gas generated can be subsequently diluted with carrier gas and a mixture of known amount fraction is produced.

Selection of an appropriate electrolyte involves consideration of four requirements [22]. Firstly it is essential to ensure that no side reactions occur at the electrode of interest. Providing a pure and plentiful supply of electrolyte will prevent this. There must be more electrolyte at the electrode than can be used; otherwise deviations from the expected gas evolution rates may occur. Secondly gases produced at the other electrode must be diverted from the carrier gas stream. Thirdly the time to attain equilibrium amount fraction should minimised. This can be accomplished by optimising the geometry of the electrodes used. The solution level should only contact about 1 mm of the exposed electrode wire. This configuration favours the almost immediate saturation of the surrounding solution so that the diluent gas thus receives all of the evolved gas. Finally the amount fraction produced should be as constant as possible. The smallest current provided should not be lower than 10 μA since constant gas evolution then becomes difficult. High currents cause excess heating and should be avoided.

The electrolytic method of adding trace contaminants has the advantage of producing very low amount fractions at the flick of a switch. The small volumes generated make this ideal for reference standards at trace amount fractions, but they cannot access percentage amount fractions due to not producing sufficient volumes.

An example of this technique is used at Physikalisch-Technische Bundesanstalt (PTB) for generating reference standards of trace water vapour [23]. Volume fractions of water vapour are produced by means of a Coulometric Trace Humidity Generator (CTHG) which operates on the principle of Faraday's law of electrolysis. The system generates a zero gas stream of nitrogen containing a negligible amount of oxygen and water vapour using a two-stage purifier. This is passed into an electrolysis cell where a defined quantity of hydrogen and oxygen is generated. The gas from the electrolysis cell is then dried using a cold trap. The generated hydrogen and oxygen is then recombined back into water using a Pt/Pd-catalyst. The generated water is then added to the zero gas stream to produce the reference standard.

2.2.7 Chemical

Controlled addition of a target component to a moving gas stream can be accomplished using chemical reaction techniques. Such reactions are of the type usually encountered in organic and inorganic chemistry and include combination, catalytic and thermal decomposition, rearrangement and photochemical dissociation in both gas and liquid phases. The reaction system usually involves a gas/liquid or gas/solid interface. This technique is particularly useful if the material of interest is unstable, reactive, commercially unavailable, or prohibitively expensive.

Although the number of reactions available is practically limitless, two factors should be considered before selecting an appropriate reaction. Firstly, the products should be formed within a reasonable period of time after mixing and secondly the reaction should proceed stoichiometrically to completion. The rate of most reactions can be found in the literature from experimentally determined rate constants. The degree of quantitative completion is also an experimental quantity given by the equilibrium constant. If the reaction system does not proceed to completion, or if doubt exists as to the character of the effluent gases and vapours, then time consuming analysis is required to assay the true nature of the reference gas mixture.

This follows the same issues as diffusion in that if operated under the controlled conditions it can offer highly repeatable mixtures, however the accuracy from theoretical calculation may be compromised. Hence reference standards are required for calibration. There are however further disadvantages with this technique. The reactant feed mechanisms required are often more complex that the usual dynamic system as often two or more reactants in the gas phase are required or some carefully regulated reaction vessel when liquids are used. The rate of reaction is a exponential function of the temperature which further complicates the determination of the generated amount fraction. Many reactions produce unwanted by products. These along with unreacted starting material must be removed by filtration, absorption or adsorption.

2.3 Feasibility of available methods

Due to the reactive nature of HCl, HF, NH_3 and CH_2O, preparation of both static and dynamic standards is very challenging. In the following sections an overview of feasible methods used to generate reference standards of these compounds is given. The state of the art in reference standards for these components lies at part per million amount fractions. A step change is required to achieve reference standards at amount fractions required to underpin measurements of AMCs.

2.3.1 Hydrogen chloride

Under normal conditions HCl is a colourless gas. It is highly corrosive, toxic and extremely water-soluble. In moist conditions, HCl gas reacts with water in the air to produce aqueous HCl droplets.

Systems that use HCl must be kept dry to avoid corrosion to metal surfaces. Purging the system with dry inert gas before and after use is good practice. Also, it is recommended that when the system is not in use it should be maintained under a positive pressure of dry inert gas.

Carbon steel, stainless steel, nickel, Monel and Hastelloy B are commonly used with dry HCl. Aluminum, brass and copper should be avoided. In the presence of moisture, nickel, Monel, Hastelloy B, platinum or gold provide good resistance. Polytetrafluoroethylene (PTFE) or Polychlorotrifluoroethene (PCTFE) offer good resistance when elastomers are required. Piping used to supply HCl into any liquid system must include backflow prevention. PTFE-lined hoses should not be used for HCl, especially liquid, to avoid static charge-induced failure [24].

Pure HCl is available from gas suppliers with different purity grades. Purity higher than 99.9995% is commercially available. Standard mixtures of HCl in nitrogen can be prepared gravimetrically. NPL's Current Calibration and Measurement Capabilities (CMCs) include the preparation of HCl mixtures in nitrogen in gas cylinders ranging from 10 µmol/mol (4% relative uncertainty, $k = 2$) to 1000 µmol/mol (3% relative uncertainty, $k = 2$). The reference materials are prepared gravimetrically by transferring pure HCl quantitatively to the cylinder in which the reference gas will be contained. The amount of parent material added to the cylinder is determined by weighing after each addition. All apparatus in contact with HCl is made from Monel.

The procedure used at NPL for preparing HCl static reference standards involves the use of a transfer loop (which consists of 1/4″ or 1/8″ diameter tubing with Swagelok fittings on each end). The transfer loop is connected to position A on valve 1, figure 5, and a vacuum system, figure 6, to position C so that the transfer loop can be evacuated until the pressure is 1×10^{-5} mbar. The evacuated transfer loop is sealed by adjusting valve 1 to position 2 (figure 5). Subsequently, the evacuation system is

disconnected from valve 1 at C and reconnected at B. A cylinder of pure HCl is connected to C on valve 1. The transfer loop is then open to the pure HCl cylinder. Once the target mass of HCl has been transferred into the loop, the valve on the HCl cylinder is closed. The transfer loop is weighed with valve 1 connected by comparing to a tare of equal mass. An evacuated cylinder is then connected to position C on valve 1 using the minimised dead-volume valve. The cylinder connection is evacuated until the pressure is 1 x 10^{-5} mbar. Then, the empty cylinder is open to the transfer loop and the pure HCl contained in the loop can be transferred to the evacuated cylinder. After a period of 3 minutes, the cylinder and the evacuation system are disconnected from valve 1, and the cylinder with the mass of pure HCl is weighed. The transfer loop with valve 1 attached are also weighed. The transferred mass of HCl can be obtained from the two weighings of the transfer loop (with and without HCl).

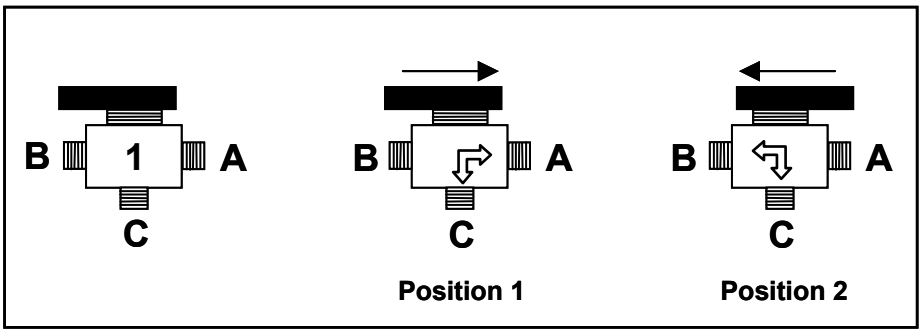

Figure 5 Schematic of 2-way valve 1 with 3 connections (A, B and C). The direction of flow is indicated for positions 1 and 2. The arrows above the middle and right schematic match the arrow marked on the valve.

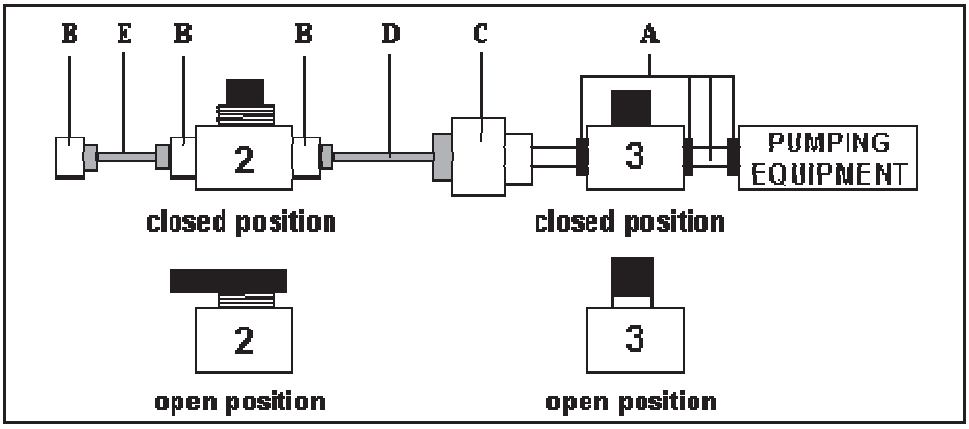

Figure 6 Schematic of the evacuation system with valves 2 and 3 (which are initially closed). The valve open positions are shown below. This is achieved for valve 2 by turning through 90° to the closed position and for valve 3 by twisting the gate valve 1 turn anti-clockwise. (A: vacuum hosing and seals, B: 1/8" nut, C: 1/4" nut, D: 1/4" to 1/8" reducing port connection, E: 1/8" port connector).

As a last step, a cylinder of high purity nitrogen is connected to the cylinder containing the added HCl. The cylinder to be filled is placed on a balance. Purging of the connecting tubing with nitrogen is performed before filling the cylinder. The valve on the nitrogen cylinder is opened followed by the

one of the cylinder to be filled. When the target mass of nitrogen has been added, the valve on the filled cylinder is closed followed by the nitrogen cylinder. The filled cylinder is then reweighed and the amount fraction of HCl is obtained from the mass of HCl and the mass of nitrogen added to the cylinder.

Dynamic standards of HCl obtained by dilution of a higher amount fraction mixture can be prepared provided that stable static standards are available.

Permeation tubes of HCl are currently available from commercial sources. Gas standards with a few tenths of nmol/mol can be produced with this method. To achieve high accuracy, the permeation tube should be connected to a high resolution magnetic suspension balance to provide an on-line measurement of the permeation rate. In order to achieve adjustable and trace amount fractions, the permeation system would need to be coupled to a novel dilution device with minimum internal surface area to prevent reaction of the HCl.

Evaporation of vapour from the pure material is not possible as it exists in the gaseous phase at room temperature. However, HCl is soluble in water and therefore an aqueous solution could be used for the evaporation technique. This would have several disadvantages; first, some water could be also added to the diluent flow with associated corrosion issues; and, second, the evaporation of the target component would depend on its concentration in solution and therefore the generated amount fraction would be variable as the experiment proceeds. This system has been reported before [25] for amount fractions at the μmol/mol level.

In order to generate reference standards of HCl by a chemical reaction, hydrogen can be passed over nickel (II) chloride heated at 600 ^{0}C in nitrogen, as shown:

$$H_2 + NiCl_2 \longrightarrow 2HCl + Ni \quad (1)$$

It can also be produced from the addition of hydrogen and chlorine under ultra violet light:

$$H_2 + Cl_2 \longrightarrow 2HCl \quad (2)$$

Or from the reaction of chlorine with hydrazine sulphate:

$$2Cl_2 + N_2H_4.H_2SO_4 \longrightarrow 4HCl + H_2SO_4 + N_2 \quad (4)$$

These reactions, however, involve large experimental efforts due to the reactive nature of HCl. Injection presents the same issues and diffusion and electrolytic methods are not viable.

2.3.2 Hydrogen fluoride

HF is one of the most reactive components to handle in the gas phase. Static systems have been used but must be made from inert polymeric materials, such as polyethylene, polypropylene or Teflon. HF reacts with glass and most metallic materials [26].

Dynamic methods are generally employed for generating HF gaseous standards due to its reactivity. Injection of aqueous hydrofluoric acid directly into a gas stream using a polyethylene syringe with a PTFE tip to achieve amount fractions in the 50 to 100 μmol/mol has been reported [26]. Heating the air slightly may be required to help stabilize the resultant amount fraction. However, if dry standards are required this option is not adequate. Injection of the gaseous component is also feasible; however,

is somewhat complicated because of its highly reactive nature at high amount fractions, leading to large inaccuracies in the mixtures prepared.

Nebulizers containing dilute solutions have also been used, surrounded by a constant-temperature bath [26]. As mentioned before, the main drawbacks are that some water is also added to the diluent flow and the generated amount fraction varies with time due to the decrease in HF concentration in the solution.

HF can be produced from the addition of hydrogen and cobalt (III) fluoride in nitrogen at 300 °C as shown:

$$H_2 + 2CoF_3 \longrightarrow 2HF + 2CoF_2 \quad (4)$$

It is also produced by adding sodium fluoride to either water or sulphuric acid:

$$NaF + H_2O \longrightarrow 2HF + NaOH \quad (5)$$

$$2NaF + H_2SO_4 \longrightarrow 2HF + Na_2SO_4 \quad (6)$$

Dynamic dilution has also been used [27]. Amount fractions ranged from 1 to 60 μmol/mol and were used to calibrate instruments used in occupational hygiene. Gas mixtures prepared by dilution were measured by potentiometry and the results were compared to theoretical values from the mass balance of the system. Monel and stainless steel were used in this system and losses from the expected theoretical values were observed (~15%).

As stated for HCl, permeation is also a promising candidate for the generation of dynamic reference standards of HF at trace levels. Permeation tubes of this component are readily available.

2.3.3 Formaldehyde

CH_2O is a colourless pungent smelling gas that can be present in significant amount fractions both indoors and outdoors. It is a chemical widely used by industry to manufacture building materials and numerous household products. It is also a by-product of combustion and certain other natural processes. As the need for measurement of CH_2O at lower amount fractions increases due to device fabrication size getting smaller and more intricate, the preparation of gaseous reference standards at lower amount fractions becomes more critical.

Materials compatible with CH_2O include glass, stainless steel and PTFE. Static reference standards of CH_2O in nitrogen have recently been prepared at 10 μmol/mol by diffusion of trioxane and thermal decomposition to CH_2O at NPL [28]. This method has enabled, for the first time, the amount fraction of CH_2O of these mixtures to be determined gravimetrically. The mixtures also demonstrated reasonable stability with two examples exhibiting decay rates of 1.5 and 0.07 nmol/mol.

A schematic of the equipment used for the preparation of static standards is shown in figure 7. A granule of phosphorous pentoxide is placed into a transfer loop (1/8”). A pellet of 1,3,5-trioxane is formed and added to the transfer loop. The transfer loop and a vacuum pump are connected to a two-way valve (positions B and C in figure 7(a), respectively). Valve 2 is adjusted to position 2 and valve 1 is then opened to evacuate the transfer loop and remove any air present on the surface of the trioxane. When a pressure of 4 $x10^{-3}$ mbar is achieved, valve 1 is closed and valve 2 is adjusted to position 1. The transfer loop and valve 2 are disconnected from the vacuum line and weighed. A thermal converter is then connected to position C on valve 2 as shown in figure 7(b). The converter is

set to the optimum conversion temperature of 230 °C. The output of the converter is connected to a minimised dead volume valve on an evacuated cylinder. The vacuum line is connected to position A and valve 1 is opened to evacuate the line between valve 2 and the cylinder (valve 2 is still in position 1). Valve 1 is then closed and valve 2 is set to position 2 to open the line between the transfer loop and the evacuated cylinder. The cylinder valve is then opened to enable the transfer of trioxane via the converter to the cylinder.

In order to prepare a mixture containing 10 mmol/mol CH_2O in a matrix of N_2, the system is left for approximately 8 h in order to transfer 13.4 mg of trioxane. This is calculated from the vapour pressure of trioxane at 20 °C. When the transfer is complete, valve 2 is adjusted to a half way position between 1 and 2. A wait time of two minutes is employed to allow the transfer of trioxane / CH_2O from the capillary to the cylinder. After this time the cylinder valve is closed. The transfer loop and valve 2 are then weighed after being disconnected from the converter and the cylinder. The cylinder is then weighed. To prevent repolymerisation of CH_2O, the cylinder is filled in two stages; initially, with 10 bar of N_2 and then with 90 bar of N_2. After each addition of N_2 the cylinder is rolled for 20 min. After the second filling of N_2 the cylinder is re-weighed.

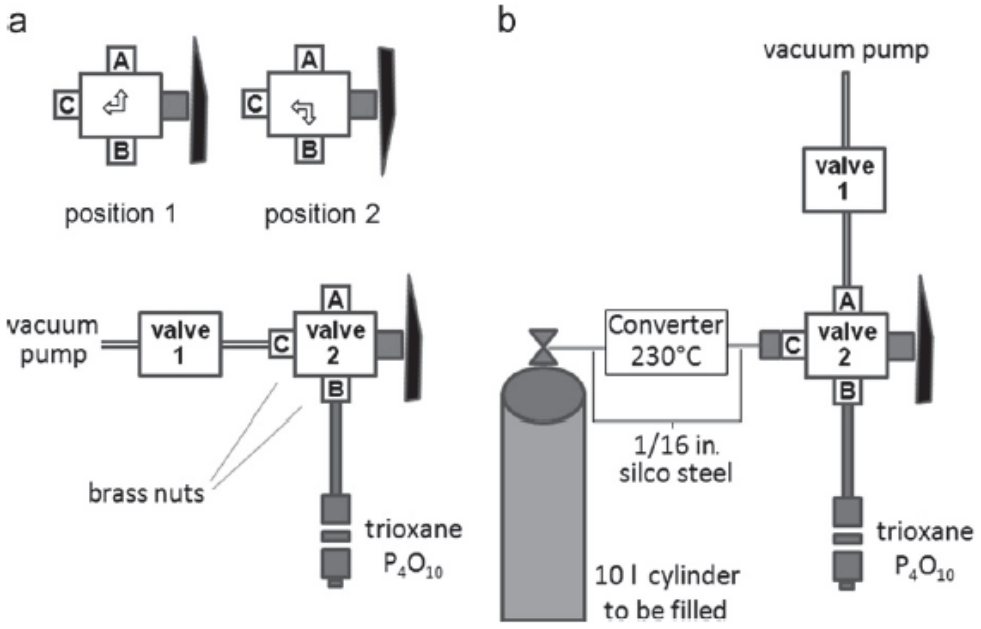

Figure 7 Schematic of the static preparation of CH_2O reference standards. (a) Transfer loop filling and evacuation, and (b) conversion to CH_2O and transfer to cylinder.

Several methods have been reported for generating dynamic gaseous mixtures of CH_2O. These include the gas-phase reaction of ethene and ozone [29] and the catalytic conversion of methanol [30] or methane [31, 32]. An alternative approach involves the depolymerisation of para-formaldehyde, a polymeric structure with 8 to 100 CH_2O units per molecule, and diffusion of the CH_2O released. The depolymerisation temperature is 60 °C. This is the dynamic system available at The Van Swinden Laboratory (VSL). Other mixtures of polymers can also be used such as alpha-polyoxymethylene (POM) [33-36]. However, the difficulty presented by these methods is the generation of a gas flow that is solely in the monomeric form and is free from the release of any bound water. For example, the

sublimation of POM typically gives rise to as much as 10% trioxane (a cyclic trimer of CH_2O) and water, the latter is chemically bonded into the POM at the level of approximately 4%.

Permeation tubes of para-formaldehyde and POM are commercially available. Dynamic systems using this approach can generate adjustable levels of CH_2O in nitrogen. The facility at the Bureau Internationale des Poids et Measures (BIPM) can generate CH_2O levels between 1 and 10 μmol/mol, by using continuous measurements of the mass loss from a permeation tube containing para-formaldehyde coupled with a dilution system. The relative uncertainty of the permeation rate can be as low as 0.05 % if there is a precise control of the temperature and pressure inside the permeation chamber, as well as accurate calibration of the balance, well characterized and well calibrated flow control and flow measurement devices [37]. Quantification of the water content that permeates together with CH_2O is essential for achieving accurate standards. This procedure has recently been described [38].

Another method which was developed to produce percentage level amount fractions of CH_2O in air is the vapour phase depolymerisation of trioxane [39]. The method involved bubbling air through molten trioxane and passing the vapour through a catalyst. Conversion yields as high as 89% were reported. Higher yields were expected, but not obtained, due to some re-polymerisation of the CH_2O [40]. Since its initial development, this method has been modified and, eventually, a conversion efficiency close to 100% was reported [41, 42]. This approach has the benefit that high purity trioxane is readily available for use as the source material. Its formula is better defined than other mixtures of polymers of CH_2O such as POM and the amount fraction of water chemically bonded into the solid is considerably less. A system based on the sublimation and diffusion of trioxane and subsequent thermal conversion to CH_2O has been set up at NPL. The system has been used to generate reference standards at 10 μmol/mol with a relative expanded uncertainty of better than 3%. It has been validated by comparison to gravimetric reference standards also prepared from trioxane. This facility provides a very good starting point with the opportunity for development to achieve the trace amount fractions required for underpinning measurements of CH_2O in manufacturing environments.

A schematic diagram of the diffusion system used to dynamically generate CH_2O from trioxane is shown in figure 8. Approximately 5g of trioxane was pressed into small rods and placed in a borosilicate glass cell. Diffusion was governed by a glass capillary 79 mm long and with 4.9 mm inside diameter. The cell was designed to generate trioxane at a rate of approximately 700 mg/h. The cell was placed in an oven at 35 °C together with a thermal converter operated at 230 °C and a heat exchanger. The heat exchanger was 2.5 m of 1/16 in. silco steel tubing and served to equilibrate the incoming nitrogen to the temperature of the oven before reaching the diffusion cell. A flow of approximately 0.75 l/min of nitrogen was passed into the system using a MFC and was measured using a high accuracy Dry-Cal Flow Calibrator (ML-800, Bios International Corporation) under controlled conditions. Prior to entering the oven, the flow was split into two paths (shown with solid grey and black lines in figure 8). The solid grey path way flows at approximately 0.02 l/min through the heat exchanger and then through the diffusion cell. Trioxane in the vapour phase is removed from the cell by the balance gas flow and is converted to CH_2O by the thermal converter. The solid black path way flows at approximately 0.7 l/min and dilutes the output from the converter. A mixture of approximately 10 mmol/mol CH_2O in nitrogen is generated and analysed by a cavity ring-down spectrometer.

The mass loss of trioxane from the diffusion cell was measured periodically over an 8 month period. Initially the diffusion rate was 727 mg/h and decreased to a value of 710 mg/h. The reduction in diffusion rate of approximately 2% over 8 months can be attributed to the release of water initially

adsorbed on the trioxane. As the water is removed the rate of mass loss from the diffusion source will reduce. A second experiment was performed in which 1 g of trioxane was melted into an identical diffusion cell. The mean diffusion rate determined from this experiment was 733 mg/h compared to 723 mg/h from the first experiment. This confirms that the diffusion process is not influenced by the surface area of the trioxane and is therefore operating as expected.

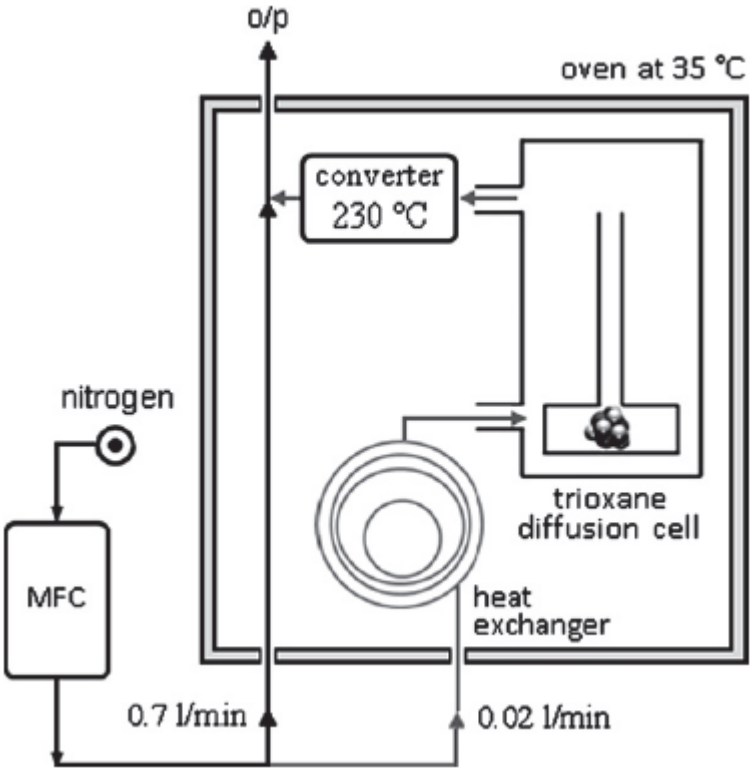

Figure 8 Schematic of the dynamic facility for generating reference standards of CH_2O at NPL.

2.3.4 Ammonia

Accurate gas standards and measurements of ammonia (NH_3) in air are particularly challenging. The polar NH_3 molecule adheres to many materials commonly used to produce gas standards, leading to inaccuracies and long response times of analytical instruments. Minimal tubing length is particularly important and dynamic systems are essential to generate accurate reference standards at trace amount fractions.

The state of the art concerning the quality of PRGMs of NH_3 is summarised in the report of the international Committee of Weights and Measures Consultative Committee of Amount of Substance (CIPM CCQM) key comparison K46 carried out in 2007. There was observed a non-concordance in the certified amount fractions between the world leading NMIs. These discrepancies have not yet been resolved. Figure 9 shows the degrees of equivalence for each participating laboratory. The degree of equivalence is defined as the difference between the result submitted for each participant and the key comparison reference value (~30 μmol/mol). It can be seen that only two of the participating laboratories agree with the reference value within their measurement uncertainty and the deviations from the reference value are in both directions.

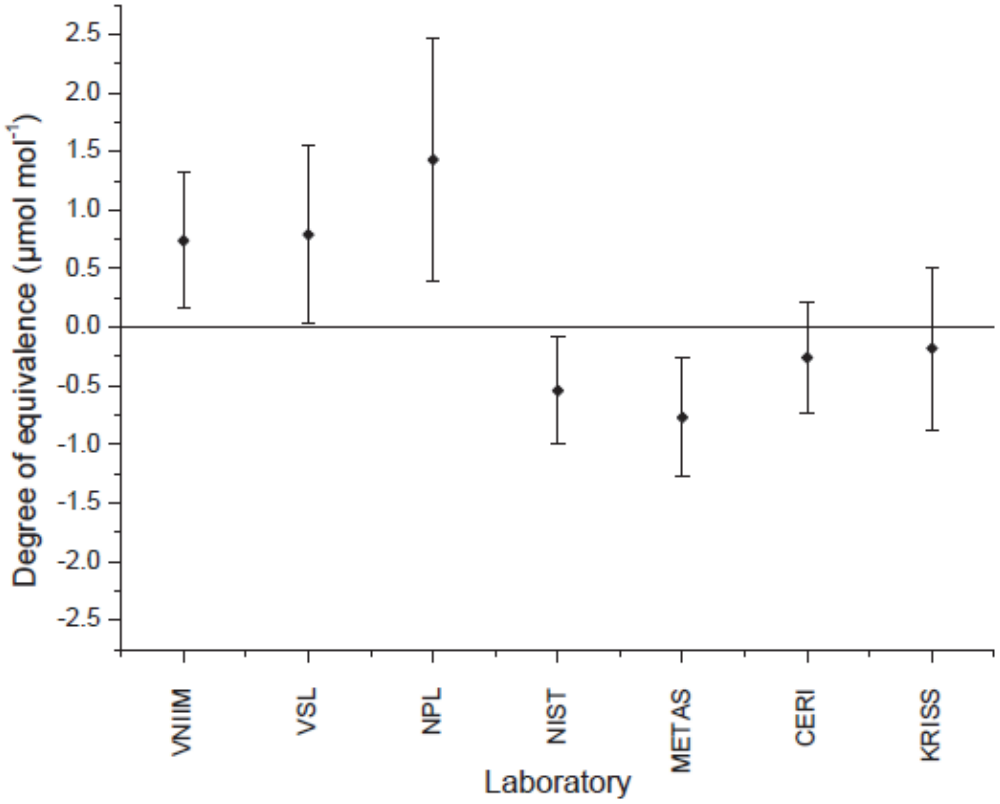

Figure 9 Results of participants and the key comparison reference value (~30 µmol/mol).

There are several studies on the adsorption of NH_3 in different materials. It has been observed that the surface coverage tends to zero with low amount fractions of NH_3 (0.5 µmol/mol) for Pyrex, quartz and polymer materials; whereas for stainless steel a significant adsorption persists even at low amount fractions [43]. The adsorption on electropolished stainless steel was observed to be larger than on non-treated stainless steel [43]. Whitehead *et al.* [44] compared the adsorption of 100 nmol/mol NH_3 on five metre long tubes made of stainless steel, silco steel coated tubes, polytetrafluoroethylene (PTFE) and polyethylene (PE). They found that the polymer tubes performed better than Silcosteel coated and plain stainless steel although the coating improved the performance of the stainless steel. Shah *et al.* [45] studied five different tubing materials (PTFE, perfluoroalkoxy (PFA), fluorinated ethylene propylene (FEP), high density polyethylene (HDPE) and polyvinylchloride (PVC)) at 1 and 10 nmol/mol. The authors did not find statistically significant differences between them and concluded that the cheapest one – PVC - might be the best. In another study [46], adsorption in low density polyethylene (LDPE) was found to be significantly higher than on PFA. A recent study concluded that among treated and non-treated stainless steel and polymer tubes, the latter were all less adsorptive than any of the stainless steel surfaces. Polyvinylidene fluoride (PVDF) was found to be less adsorptive than the other studied polymers (PTFE, PFA, FEP and LDPE) [47].

Both permeation and dilution of NH_3 have been used to generate standards for analyser calibration [48, 49]. With the former, a short quartz inlet is internally coated with a fluorinated silane coating and heated to 40 °C to limit condensation of water and the interaction of NH_3 with inlet surfaces. A critical orifice was used to control the flow and drop the pressure in the sampling line, which further minimizes NH_3 adsorption effects. With the latter, the authors use both permeation and dilution to achieve a wider range of generated amount fractions. All internal surfaces are made from passivated

Pyrex tubing, which is cleaned and rinsed out with a solution of NaOH after fabrication. The authors estimate the permeation rate by periodical weighing the tube. It is also verified by conversion of NH_3 on hot platinum foil followed by chemiluminescent NO detection.

Despite the fact that this method is frequently used to calibrate NH_3 analysers, the uncertainty of the amount fractions generated by dilution is very large and often unknown. Successful dilution from a high amount fraction standard is subject to the availability of stable and accurate static standards; and further work is needed to develop these.

NH_3 is industrially obtained with the Haber-Bosch process by reaction of hydrogen and nitrogen using a suitable catalyser; however this reaction needs high pressure (from 60 to 180 bar) and high temperature (400 - 450 °C) which makes it unsuitable for laboratory purposes.

Other reactions have also been described to produce NH_3 that could be applied on a lab scale:

$$Ca(OH)_2 + 2NH_4Cl \longrightarrow 2NH_3 + CaCl_2 + 2H_2O$$

$$Mg_3N_2 + 6H_2O \longrightarrow 2NH_3 + 3Mg(OH)_2$$

Nevertheless, the chemical technique usually requires more complex mechanisms than the permeation or dilution systems.

NH_3 can be synthesised at room temperature from electrochemical methods [50]. In 1985, for the first time, it was reported the electrochemical synthesis of NH_3 at room temperature through protolysis of cis-$[W(N_2)_2(PMe_2Ph)_4]$ [51].

NH_3 has also been synthesised from nitrogen and water. Kordali *et al.* [52] reported the heterogeneous electrocatalytic synthesis of NH_3 from nitrogen and water at ruthenium cathodes, using a Solid Polymer Electrolyte Cell (SPE), at atmospheric pressure and low temperature (< 100 °C). Murakami *et al.* [53], proposed a novel NH_3 synthesis method from water vapour and nitrogen gas under atmospheric pressure at lower temperature than the Haber-Bosch process (~300 °C). In this process, water vapour reacts with nitride ions (N^{3-}) to form NH_3 and oxide ions in molten salts, however the efficiency is 23%. By conducting electrolysis, nitride ions are supplied into the melt at the cathode and oxide ions are removed from the melt at the anode. The overall reaction in this process is shown below:

$$6H_2O + 2N_2 \longrightarrow 4NH_3 + 3O_2$$

NH_3 was also successfully synthesised from hydrogen and nitrogen under atmospheric pressure using $CoFe_2O_4$ as catalyst together with silver at the cathode, Ag-Pd at the anode and carbonate-$LiAlO_2$ composite as electrolyte [54]. The temperature of the reaction was around 450 °C:

$$3H_2 + N_2 \longrightarrow 2NH_3$$

There are a number of studies in the literature of electrochemical reduction of nitrate containing solutions to NH_3. It has been demonstrated that on freshly deposited copper the reduction of silver nitrate to NH_3 is quantitative for pHs from 0-3 [55].

As for HCl and HF, NH_3 is soluble in water, thus evaporation from an aqueous solution may also be feasible. However, as before, the presence of water would compromise the stability of the reference standard.

3. Recomendations

The dynamic generation of gas standards of reactive gases is especially challenging due to the reactive nature of these components and the low amount fractions required. Although they could currently be generated at nmol/mol levels, the uncertainties in the amount fractions would be unacceptably large due to losses of the target molecule in the system (i.e. reaction and/or adsorption mechanisms) and the lack of traceable, accurate and stable reference standards to compare against. Besides, when such low amount fractions are required, the target gas content in the balance gas becomes an important source of uncertainty. In general, sources of uncertainty that can be neglected when producing high amount fraction standards become significant when the concentration decreases.

To overcome these issues, minimisation of tubing length and careful selection of construction materials are key to reduce the uncertainties of the system. Equilibrium times of several hours may be needed to achieve stable amount fractions. In all cases the capability of producing static gas standards at 10 µmol/mol must be previously developed for validation of dynamic systems. Quantification of the target component in the balance gas is also essential but can be very challenging due to the detection limits of current analytical techniques. Purification of zero gases down to ultra-low levels may be necessary but the detection of these impurities could still be an issue. Development of ultra-linear analytical systems that can be extrapolated downwards with confidence may help overcome these problems.

One of the most important variables of these systems is the accurate and precise control and measurement of the flow. Fixed and adjustable flow elements can provide reliable flow rates. The main advantage of fixed over adjustable elements is that they provide a highly repeatable flow. Adjustable elements have the advantage of being tunable and provide a range of dilutions with a single device.

There are several possibilities for producing reference standards of HCl. Dynamic dilution is one of them, but further work needs to be done regarding the accuracy and stability of static standards of higher amount fractions. Permeation tubes of HCl are commercially available and this is another strong candidate. To achieve high accuracy, the permeation tube should be connected to a high resolution magnetic suspension balance to provide an on-line measurement of the permeation rate. In order to achieve adjustable and trace amount fractions, the permeation system would need to be coupled to a novel dilution device with minimum internal surface area to prevent reaction of the HCl. It can be generated from several chemical reactions, however due to its reactive nature, the experimental efforts involved are large. Injection presents the same issues. Hence dilution and permeation techniques are recommended for HCl.

HF has similar chemical properties to HCl. Development of static reference standards requires much work due to safety considerations. Hence dynamic reference standards by dilution from a stable static mixture are not achievable in the short term. Like HCl, permeation is a viable solution and would require a system as previously described. There are several options for generating HF by chemical methods however they involve considerable efforts to overcome the safety requirements as a result of the toxicity of the substance. Moreover the reactions produce a number of unwanted by products which would need to be removed from the reference gas stream. Using an injection technique would result in a similar difficulty. Hence permeation presents the best option for generating dynamic HF reference mixtures.

Dynamic standards of CH_2O can be obtained by chemical reaction, diffusion or permeation, with the last two methods being most widely used. As it is a highly reactive component, CH_2O precursors are used to produce the gas standards. Trioxane, para-formaldehyde and alpha-polyoxymethylene are often used but the last two have been found to be present in the CH_2O standards together with some bound water. Sublimation and diffusion of trioxane and subsequent thermal conversion to CH_2O has been shown to produce CH_2O standards with a relative expanded uncertainty of better than 3% for 10 µmol/mol. This is an excellent starting point to achieve CH_2O standards at lower amount fractions.

Static standards of NH_3 with the required accuracy and stability to be used in dynamic dilution systems are still not available. Further research regarding cylinder materials and coatings and studies on the stability are required. Once these issues have been overcome, dynamic dilution is a potential successful method to produce NH_3 gas standards. Permeation is also a promising candidate technique. Tubes are commercially available and this method has already been used previously. Chemical and electrochemical methods can also be applied for the production of NH_3; however, they require more complex mechanisms than the previous systems.

Overall, for generating dynamic standards of HCl and NH_3 at trace amount levels, permeation and dilution are recommended as the most viable candidates. The success of both of them is subjected to the availability of accurate and stable static standards of HCl and NH_3 in N_2 at higher amount fractions (~10 µmol/mol) either as a source of the target gas or as a way of validation of the system. The experience gained with HCl will help to develop a future strategy for generating reference standards of HF as this is significantly more challenging than HCl. CH_2O static and dynamic standards at 10 µmol/mol from diffusion of trioxane and subsequent thermal conversion to CH_2O have been produced with relative expanded uncertainties of better than 3%. Further research on this technique to achieve lower amount fractions is recommended in this case.

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