

Methods for *in situ* QMS calibration for partial pressure and composition analysis



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ABSTRACT

The expectation of users of small quadrupole mass spectrometers (QMS) is that the partial pressures reported can be related to actual partial pressures present. To achieve this, a calibration of the QMS is needed followed by verification over time by analyzing a test mixture appropriate to the process. Four *in situ* calibration methods are presented: 1. For UHV base pressure and low pressure processes, an open ion source QMS is recommended with a local viscous-flow reference mixture pumped by the process vacuum system; this gives a repeatable composition of partial pressures for calibration or verification. 2. For XHV RGA an ultra-low flow rate reference gas is proposed. 3. For processes where pressure reduction by sampling system is needed, a closed ion source (CIS) QMS with a similar viscous-flow reference mixture flowing directly into the CIS is recommended for calibration. 4. For processes near atmospheric pressure, capillary sampling with a molecular leak to the CIS is recommended plus a separate sampling capillary to a reference mixture. The gas dynamics to assure known compositions is presented together with data showing QMS accuracy and stability. Repeated measurement of the reference mixture over days generates a quality assurance plot revealing changes in calibration and provides the basis data for adjustment of QMS calibration.

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1. Introduction

Small mass spectrometers (MS) have been used for years to observe the chemical species present in the residual gases in a vacuum system at base pressure and during processes [1,2]. Typically these MS devices are quadrupole mass spectrometers (QMS) with electron impact ionization and Faraday cup (FC) or electron multiplier ion detection [3,4]. Mass filtering is typically done by the quadrupole rod assembly with applied RF and DC potentials. As a result of the gas analysis function, small mass spectrometers are referred to as residual gas analyzers (RGAs). This qualitative identification of species in the vacuum plus software for He leak detection present in RGA products has made the RGA an important tool for vacuum system analysis and management.

In principle any RGA (even with non-linear response) can be calibrated by direct comparison with reference mixtures that are close to the composition of the sample being analyzed [5]. In this paper, operation of a RGA in the linear response range is required for a calibration that can extend over a wide range of compositions. Many of the RGAs on the market exhibit good stability in their day-

to-day performance that implies a calibration is possible relating partial pressures of a species in the vacuum system and an ion current measured by the RGA for an ion related to the species. Calibration methods to establish this relationship for the species and ions typically in a vacuum system are presented in this paper together with a practical *in situ* method to check the validity of the calibration over time. An additional goal is to make the calibration method traceable to national measurement standards as they relate to producing accurate partial pressures at the RGA ion source and methods to reference composition analysis to known standard mixtures.

2. Equipment and operation for analytical measurements

Measurement of partial pressure components in a high vacuum system is best done with an open ion source (OIS) RGA where the ion source, mass analyzer and ion detector of the RGA are immersed in the vacuum with a pressure of $<10^{-3}$ Pa. An open ion source has an open grid structure to assure that the ion source sees the pressure of the vacuum system [3,4]. This pressure assures a mean free path for ion motion through the mass analyzer ≥ 150 mm rod length for a typical 6 mm diameter rod (1/4") mass filter. Above this pressure, the ion beam of a standard RGA experiences scattering losses with increasing pressure as shown in the 8 eV ion energy (IE)

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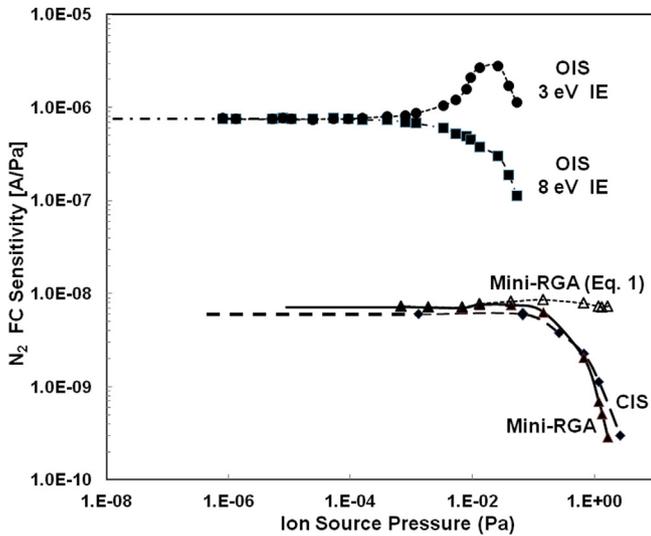


Fig. 1. Sensitivity vs Pressure for an OIS RGA with 6 mm- ϕ \times 115 mm ($1/4'' \times 4.5''$) rods operated at 8 eV Ion Energy, \blacksquare and the same RGA operating at 3 eV Ion Energy, \bullet . The lower curves are for a miniature RGA: \blacktriangle , for raw ion current and \triangle for ion current corrected for gas scattering by total pressure. Finally, the sensitivity vs pressure for a CIS RGA is shown with \blacklozenge data points. RGAs are linear (constant sensitivity) for pressures $< 10^{-3}$ Pa. For CIS and miniature RGA, linearity is seen for pressures < 0.1 Pa. Linearity for the miniature RGA can be extended by correction for scattering loss [8,9].

curve (1 mA emission current) in the upper half of Fig. 1. Another sensitivity curve for the same OIS RGA operated with 3 eV ion energy (1 mA emission current) shows the effect of space charge buildup when ions produced in the ion source are not efficiently extracted to the mass analyzer [6,7]. Choosing proper ion energy (typically 6 eV–10 eV depending on source design) and a low electron emission current avoids this non-linear performance of the ion source and is essential for stable RGA operation. Below 10^{-3} Pa, the sensitivity of an OIS RGA is measured to be constant and is the sensitivity used for pressures down to the partial pressure detection limit. In addition to choosing ion source operating parameters, most RGAs provide an analog scanning mode to assure that mass peaks are on location (peak measurement finds the maximum of ion transmission) using background species expected in a vacuum system. If an electron multiplier (EM) is used for detecting small ion currents, adjustment of the multiplier gain (using the EM high voltage) should be made before calibration.

A miniature RGA has been developed [8,9] with quadrupole length reduced from 125 mm for a typical round-rod RGA to a 12 mm quad length and the radius r_0 of the quadrupole assembly reduced from 2.67 mm to 0.32 mm for the hyperbolic rods of the miniature quadrupole. The result is a shorter ion path length so it performs with constant sensitivity up to 0.3 Pa (see Fig. 1) before scattering loss is evident. The use of hyperbolic poles to produce a true quadrupole field improves sensitivity by about 20% or more compared to round rods [10,11]. The linearity of the partial pressure ion current can be extended to 1 Pa by using an onboard total pressure measurement for a correction of ion scattering loss. Fig. 1 shows the linearized sensitivity of the miniature RGA using the relation

$$S_i(P) = I_i e^{aP} / P_i \quad (1)$$

where P is the total gas pressure, P_i is a component of partial pressure, I_i is the associated measured ion current and "a" is a scattering parameter determined for each instrument [8,9]. From this design, the miniature RGA can give scattering-corrected partial

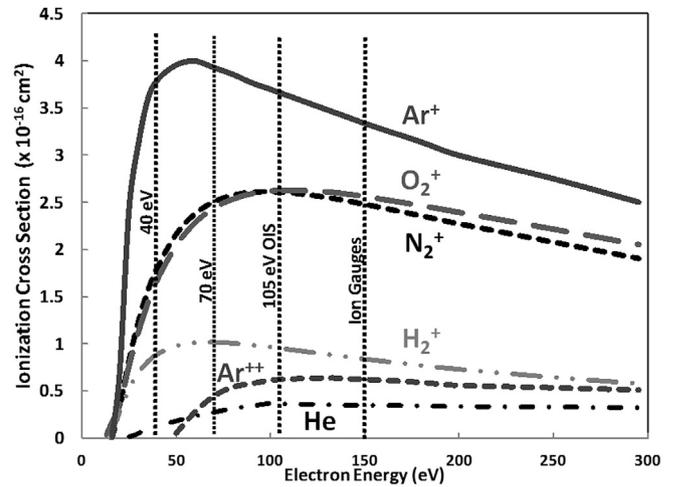


Fig. 2. Ionization cross sections as a function of electron energy. Cross sections for molecules are from Ref. [18] and for He and Ar [19].

pressure data for the user up to 1 Pa for physical vapor deposition (PVD) applications and impurity detection down to 10 ppm of the major peak (Ar) [8,10]. So OIS RGA and miniature RGA attached to a vacuum display the partial pressures with the software provided using measured ion currents and default sensitivities. Checking these sensitivities or re-calibrating them is the subject of subsequent sections.

Applications where, the process pressure exceeds the ion source operating pressure require a pressure reduction by gas sampling. A closed ion source (CIS) is recommended to increase the dynamic range of composition measurement. Sampling methods that preserve the integrity of composition are described previously [12]. In Fig. 1, the CIS linearity extends to 0.1 Pa for good operation; sampling system designs for CIS operation need to target this pressure as an upper bound. The advantage of a CIS is that the ion source pressure with sample present is much higher than the analyzer pressure. The sample gas flows through the CIS with a 1 L/s exit conductance to the analyzer which typically experiences a pumping speed of 25 L/s. Thus the pressure ratio $P_{CIS}/P_{Analyzer}$ is about 25 [12]. This makes the effect of background species in the analyzer vacuum system reduced by a factor of 25 relative to the ion source sample pressure. This low background level allows impurity concentrations of 1 ppm or less to be measured by difference in ion current for a species with sample present vs no sample.

Stable RGA operating conditions of electron energy and emission current together with ion energy, mass scale accuracy and EM gain need to be established before any calibration efforts. This normally means using the manufacturer's recommended operating settings that apply to your measurement needs or other settings determined by the user for their application. A general guideline for setup is to fix an electron energy and emission current. Fig. 2 shows the ionization cross section ($\times 10^{-16}$ cm 2) as a function of energy for common gases. There are published species sensitivity values for ion gauges [13] that are often used as a relative sensitivity reference for RGAs. But RGAs typically operate at lower electron energy to find maximum partial pressure sensitivity (e.g. 105 eV or 70 eV) or at 40 eV to minimize species fragmentation which simplifies interference corrections (see Fig. 2). The 40 eV also avoids $^{36}\text{Ar}^{2+}$ production that can mask the measurement of low levels of H_2O at mass 18. An OIS RGA normally operates at 70 eV (or 105 eV) with 1–2 mA of electron emission current per the specifications for the particular RGA. For CIS RGA compositional analysis, the low electron energy (40 eV) and a low emission current in the range 0.1–0.4 mA is recommended for linear operation. Choosing ion energy

in the 6–10 eV range is also needed to extract ions from the source effectively for mass analysis and to avoid space charge accumulation in the ion source [6,7].

In modern RGAs, the mass scale is controlled by a firmware algorithm that measures a value of ion current for each mass that is the “maximum” ion current for that mass. The mass scale is temperature sensitive; as quadrupole rods warm to the operating temperature, small changes in the r_o of the rod assembly will shift the mass scale. Many RGAs recommend a 30 min warmup to achieve mass scale accuracy and general operation. Initial calibration of the mass scale is done by the vendor. A check of this calibration can be done with analog scans of common residual gas species, e.g. $M/e = 2\text{-H}_2^+$, $18\text{-H}_2\text{O}^+$, $28\text{-CO}^+/\text{N}_2^+$, 44-CO_2^+ that are normally present in the background residual gas at any vacuum level.

Most OIS RGAs have electron multipliers (EM) to measure ion currents from low partial pressures in UHV and definitely for XHV. The electron multiplier is subject to gain loss with use due to damage from the dose of e^- charge that flows through the EM structure. This gain loss requires that the gain be measured and adjusted periodically to give a constant gain for calibrated partial pressure measurements. The gain is restored by increasing the voltage across the EM structure. Since the EM multiplies baseline noise as well as ion signals, the signal-to-noise improvement using an EM is only about a factor of a hundred for RGAs. This does extend detection limits to lower pressures by a factor of ~ 100 . It also says that the high voltage across the EM can be kept low for gain of 100–500. Lower applied voltage across the EM extends the lifetime of the EM element. A good gas to use for EM gain measurement and adjustment is natural abundance Ar: The minor isotopes at mass 36 (0.334%) or 38 (0.063%) of Ar can be used as repeatable small ion currents to measure ion current with EM On and ratio this current to the current when EM is Off. The EM gain can be defined as

$$\text{Gain} = I_{\text{Ar-36}}(\text{EM On})/I_{\text{Ar-36}}(\text{EM Off}). \quad (2)$$

This gain value can be used with sensitivities determined by Faraday Cup (FC) current measurements, S_i to give sensitivity with EM on, $S_i(\text{EM})$

$$S_i(\text{EM}) = S_i \cdot \text{Gain}. \quad (3)$$

Thus the partial pressure associated with an ion current measured with EM on is given as

$$P_i = I_i(\text{EM})/S_i(\text{EM}) \quad (4)$$

which lowers the detectable partial pressure by a factor $1/\text{Gain}$ compared with FC measurements.

If rather than duplicate a gain, the desire is to repeat a sensitivity, $S_i(\text{EM})$, the EM high voltage can be adjusted to re-establishing a particular ion current for the Ar-36 or Ar-38 or other repeatable but small ion current from an *in situ* calibration gas. This allows adjustment of gain (or sensitivity) without a large ion dose to the EM that can damage or reduce EM lifetime.

3. Calibration methods for partial pressure and composition

3.1. Basic calibration

Sensitivity measurements can be done using pure gases (e.g. Ar, N_2 , H_2 , He) introduced with a flow control system to produce partial pressures of the added gas at a pressure measured by an ion gauge measuring the same pressure as the RGA. The sensitivity measured by pure gas addition is the change in ion current associated with the gas species added divided by the change in ion gauge pressure from the gas addition:

$$S_i = (I_i - I_i(0))/(P - P(0)) \quad (5)$$

where $I_i(0)$ and $P(0)$ denote background values before gas addition. Measurements over a range of pressures produces data for sensitivity vs ion gauge pressure plot like that in Fig. 1. This is a method used for determining the initial sensitivity value for each gas species of interest for the RGA before installing on the vacuum system. This is a traditional calibration approach like that reported by Malyshev and Middleman [14] and others [15–17]. This generates a set of sensitivities that can be used to measure the partial pressure of a species present in the vacuum system due to all sources: Gas introduction, wall outgassing and pump backstreaming. The collective partial pressure from these sources is related to the measured (FC) ion current by the sensitivity from the calibration:

$$P_i = I_i/S_i \quad (6)$$

or if the electron multiplier is turned on, the partial pressure is given by Eq. (4).

Reporting accurate P_i to the user is the goal of residual gas measurement done by an OIS RGA for UHV and XHV vacuum systems.

Many processes that use a vacuum system involve the addition of gas to a pressure greater than that of the operating pressure of the RGA. For these applications the RGA may have a direct connection to the vacuum system for measuring base vacuum and doing leak detection. But when operating at process pressure, a pressure reduction system is needed to provide a sample of the gas to the RGA. The local partial pressures of the sample measured by the RGA can be used to determine the composition of the gas in the process. The composition molar fraction at the RGA is defined to be

$$X_i = P_i / \sum_{\text{All } i} P_i \quad (7)$$

where the sum over all species “i” assumes the user knows the species present and of importance. Since the sample is added to the background gases in the RGA, it is necessary to subtract the background of the CIS RGA (ion currents present when no sample is introduced) and to subtract interference fragmentation ions at the species of interest from some higher mass species present. The result is the net partial pressure in the ion source that represents the sample that flows into the ion source. This net partial pressure of sample is

$$P_i(\text{Sample}) = \left[I_i - I_i(0) - \sum_{\text{All } k \neq i} A_{ik} \cdot (I_k - I_k(0)) \right] / S_i \quad (8)$$

Components A_{ik} are determined from data for pure gas that exhibits the fragmentation interference (e.g. 44-CO_2^+ giving 28-CO^+ , 16-O^+ and 12-C^+):

$$A_{ik} = [I_i(M_i) - I_i(M_i, 0)] / [I_k(M_k) - I_k(M_k, 0)] \quad (9)$$

where $I_i(M_i, 0)$ and $I_k(M_k, 0)$ are background ion currents in the ion source with no sample present. Using the $P_i(\text{Sample})$ from Eq. (8) in the definition for molar fraction composition in Eq. (7), the composition of the gas in the ion source is calculated. By design of the sampling system, the composition measured in the ion source represents the composition in the process.

3.2. Calculated sensitivities

Direct measurement of the pure gas sensitivity for each chemical species expected is a laborious and expensive task. For minor

Table 1

Species sensitivities relative to N₂ for a CIS RGA operated at 40 eV and 200 μA electron emission. Calculated relative sensitivities are based on ionization cross sections at 40 eV times a efficiency factor $\epsilon(M) = [28/M]^{0.25}$. Measured relative sensitivities are the ones used by the CIS RGA in Fig. 8 producing the composition data in Fig. 9.

Key mass-species	σ (40 eV) ($\times 10^{-16}$ cm ²)	$\epsilon(M) = [28/M]^{0.25}$	Calculated S_{Rel} (40 eV)	Measured S_{Rel} (40 eV)	Ratio $S_i(\text{Calc})/S_i(\text{Meas})$
2-H ₂	0.892	1.93	0.95	0.91	1.04
4-He	0.152	1.63	0.14	0.13	1.05
15-CH ₄	2.3808	1.17	1.54	1.24	1.24
17-NH ₃	2.481	1.13	1.55	1.55	—
18-H ₂ O	1.716	1.12	1.06	1.25	0.85
28-N ₂	1.812	1.00	1.00	1.00	1.00
29-CH ₂ O	3.215	0.99	1.76	1.89	0.93
32-O ₂	1.687	0.97	0.90	0.78	1.15
34-H ₂ S	3.852	0.95	2.03	1.98	—
40-Ar	2.410	0.91	1.22	1.49	0.81
44-CO ₂	2.475	0.89	1.22	1.66	0.73

Ref. [13]: Molecular σ (40 eV); Ref. [14]: σ (He); Ref. [15]: σ (Ar).
Measured Sens in italics inferred from Calculated S_{Rel} .

components it is simpler to calculate a set of sensitivities from literature references. Table 1 is an attempt at that task by modeling the production of ion current:

$$I_i = i_e \sigma_i \epsilon_i (P_i/kT) \quad (10)$$

where i_e is the electron emission current, (P_i/kT) is the number density for ion source species, I_i , σ_i is the cross section for single ion formation at the incident electron energy, and ϵ_i is an ion extraction–transmission–detection efficiency factor for each species for a particular RGA. Given the definition of sensitivity in Eq. (5), a model for sensitivity is

$$S_i = i_e \sigma_i \epsilon_i kT. \quad (11)$$

For normal RGA operation, the electron energy and emission current are fixed; temperature T is constant and so the sensitivity depends on the cross section for ionization σ_i and efficiency for ion transmission/detection, ϵ_i . Table 1 models what the sensitivities for common species should be relative to nitrogen. The relative sensitivities are proportional to cross sections for 40 eV electrons in the example times an efficiency factor that is a function of mass. An efficiency function $\epsilon_i(M) = [28/M]^{0.25}$ for the CIS RGA analytical system described later in this paper minimizes the error between the model and measured sensitivities. The cross sections are from calculation models in the NIST web book for small molecules at 40 eV [18] and cross sections for He and Ar are found in the literature [19]. Results are shown in Table 1. The cross sections σ_i , and values of $\epsilon_i(M)$ are given in the next columns followed by the calculated relative sensitivities from the model. The actual relative sensitivities from gas measurements are listed in the next column where the calculated relative sensitivity (in italics) is used for species where real gas measurements were not done. The final column gives the ratio of model calculated sensitivity to measured sensitivity $S(\text{Calc})/S(\text{Meas})$ as an indication of goodness of fit. The model fit has a standard deviation of ~25%. This implies that to achieve accuracy of ~5% of component, a real gas calibration is necessary and is recommended. A minimal real gas calibration is H₂, N₂ and Ar or CO₂. These measured sensitivities covering the mass range of common vacuum system impurities gives a reference for determining a transmission/detection factor $\epsilon_i(M) = [28/M]^z$ where z for a particular RGA is determined by fitting the cross section for each gas times a value $[28/M]^z$ compared to the corresponding measured sensitivities relative to the N₂ sensitivity.

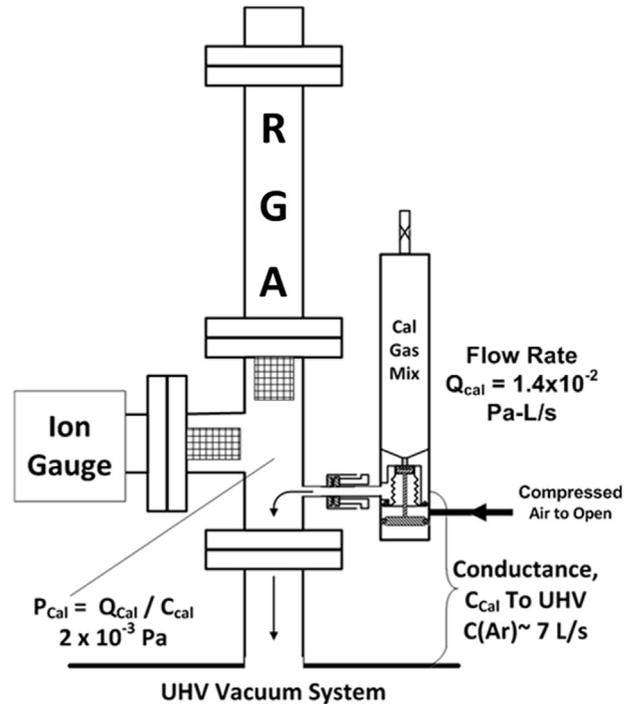


Fig. 3. An OIS RGA, ion gauge and calibration reference source connected to a UHV vacuum port to establish a known pressure at the RGA and ion gauge when flow is turned on.

4. In situ calibration systems and methods

4.1. Calibration systems for UHV: system pressure $< 10^{-3}$ Pa

For RGA based analytical measurements, it is valuable to have a reference gas mixture accessible by the RGA *in situ* as a means to check the calibration of the RGA without removing the RGA sensor [20]. The use of a mixture as the reference gas provides multiple species with known partial pressures (composition) that can be used to monitor mass scale (peak location) and sensitivity calibration drift. An *in situ* reference gas mixture has multiple advantages: Eliminates a vacuum break, avoids the question of changes to the sensor by exposure to air and saves the time of remounting and pumpdown. In many applications, this down time is unacceptable. Thus the following sections describe *in situ* calibration methods for four different vacuum systems and process applications. Common to all of the systems are designs that deliver a predictable composition to the ion source of the respective RGAs.

A UHV vacuum monitoring installation is shown in Fig. 3 with the OIS RGA as an appendage to the vacuum system. The addition of a total pressure gauge is optional but in this position, it is at the same pressure as the RGA. A simple *in situ* INFICON calibration reference source [21] is added between the ion gauge and RGA in Fig. 3 and the connection to the UHV vacuum system. The resulting pressure at the ion gauge and RGA ion source is the sum of the partial pressures established when gas species from the calibration reference source in viscous flow enter the source region and exit by molecular flow pumping through the conductance to the UHV vacuum system. The partial flow rate q_i of each species into the ion source region is given by

$$q_i = Q_0 X_i(\text{Ref}) \quad (12)$$

where Q_0 is the total gas flow rate of the reference source and $X_i(\text{Ref})$ is the molar fraction of the species in the calibration

Table 2

Two examples of Tank Mixtures with viscous flow into and molecular flow out of the ionization region. The composition of the gas species in the RGA ion source is calculated by application of Eqs. (15) and (16).

Component	Ar/5% impurities		Ar/PPM impurities	
	Tank mix	X _i -ion source	Tank mix	X _i -ion source
Ar	95.00	95.34	99.6730	99.6312
H ₂	1.00	0.22	0.0200	0.0045
He	1.00	0.32	0.1000	0.0316
N ₂	1.00	0.84	0.0050	0.0042
CO ₂	0.00	0.00	0.0020	0.0021
Kr	1.00	1.45	0.1000	0.1449
Xe	1.00	1.82	0.1000	0.1816

reference mixture. At steady state operation, the flow rate out of the ion source region for each species is equal to the flow rate in. The ion source operates at low pressure so the flow rate out is molecular flow. This establishes a partial pressure P_i for each species:

$$P_i = Q_o X_i(\text{Ref})/C(M_i) \quad (13)$$

where $C(M_i)$ is the molecular flow conductance for species i with mass M_i (amu). For a conductance-limited flow structure, the mass dependence of the conductance compared with N_2 is

$$C(M_i) = C_{N_2} [28/M_i]^{1/2} \quad (14)$$

Substituting Eq. (14) into Eq. (13) gives a practical expression for added partial pressure, P_i in the ion source region:

$$P_i = Q_o X_i(\text{Ref}) [M_i/28]^{1/2} / C_{N_2} \quad (15)$$

Equation (15) predicts a mass-dependent alteration of the reference mixture where light species have a higher exit pumping speed and thus are depleted from their composition in the reference mixture. The new composition (molar fraction) in the RGA ion source region is calculated from the partial pressures in Eq. (15):

$$X_i(\text{RGA}) = P_i / \sum_{\text{All } k} P_k \quad (16)$$

Table 2 summarizes these calculations for real mixtures with 95% Ar and 1% each of H₂, He, N₂, Kr and Xe and a similar mixture with ppm levels of impurities. These mixtures have mass markers from mass 2 through 136 amu for calibration of QMS mass scale. The 95% + 1% impurity components have a known composition with abundances useful for determining the conductance, C_{N_2} used in Eq. (15) and for calibration of selected sensitivities, S_i .

The calibrated ion gauge in Fig. 3 can be used for a practical determination of the conductance used in Eq. (15). The molecular flow present in the ion gauge and RGA pumping assures that each gas species flows independently through the conductance to the UHV pumping system. The total pressure present at the IG/RGA, P , is related to the pressure indicated by the ion gauge, P_{IG} as the sum of partial pressures represented by the molar fraction at the RGA times the species-corrected ion gauge reading P_{IG}/R_i :

$$P = P_{IG} \sum_i X_i(\text{RGA})/R_i \quad (17)$$

In Eq. (17), the components $X_i(\text{RGA})$ are the values calculated from Eqs. (15) and (16) for the particular Tank Mixture (e.g. see Table 2) and R_i is the ion gauge relative sensitivity factor for each species “ i ” present in the mixture. The relative sensitivities are values provided by the manufacturer typically referenced to N_2 [13]. Given that molecular flow through the exit conductance is independent for each species, the best candidate for calculating a

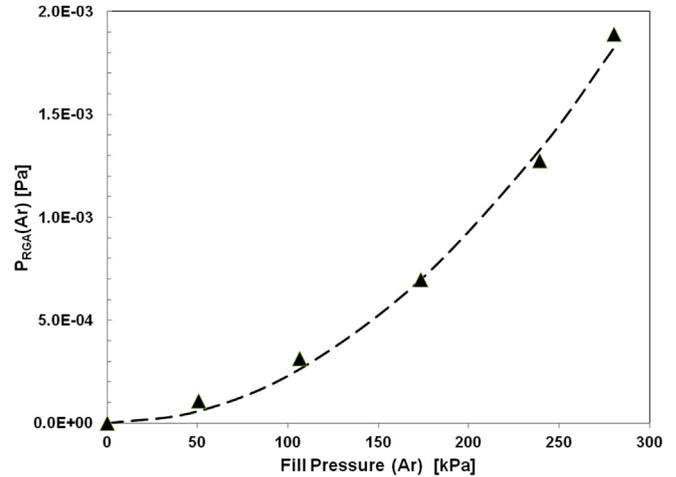


Fig. 4. OIS RGA partial pressure for Ar, \blacktriangle , as a function of fill pressure of the Calibration Reference Source. The dashed line is fit of data to a viscous flow model, $P_{\text{RGA}}(\text{Ar}) = A P_{\text{fill}}$.

value of conductance is the major component of the mixture. Using the mixtures in Table 2, the Ar species dominates; thus a value for Ar conductance can be calculated by solving Eq. (13) for C_{Ar} and using the Ar pressure component of the sum in Eq. (17):

$$C_{\text{Ar}} = X_{\text{Ar}}(\text{Ref}) Q_o R_{\text{Ar}} / [(X_{\text{Ar}}(\text{RGA}) P_{\text{IG}})] \quad (18)$$

Note in Table 2 that the major component at the RGA is nearly the same as value in the Ref mixture; this is not true for minor components where $X_i(\text{Ref})/X_i(\text{RGA})$ is not unity. Using the molecular flow model in Eq. (14), a value for C_{N_2} can be calculated from the C_{Ar} measured result:

$$C_{N_2} = C_{\text{Ar}} [40/28]^{1/2}. \quad (19)$$

The 95% Ar plus 5% impurities mixture shown in Table 2 has components large enough to produce stable ion currents that are much greater than the corresponding background species.

Using Eq. (15) and the values of C_{N_2} , Q_o , $X_i(\text{Ref})$, and the associated ion current, I_i and background ion current $I_i(0)$ from the RGA, sensitivity values can be calculated for each species in the mixture:

$$S_i = (I_i - I_i(0))/P_i. \quad (20)$$

This is similar to the definition in Eq. (5) but the added pressure P_i is calculated from Eq. (15). Typically background ion currents $I_i(0)$ are $\ll I_i$ when the reference gas is added. A new measurement of RGA sensitivity can be made each time the calibration reference source flow is turned on; the primary variation in sensitivity comes from the ion transmission and detection of the RGA. Thus monitoring sensitivities over time provides data to show stability and accuracy of the RGA. Monitoring trends in sensitivity from low mass to high mass over time can reveal changes in ion transmission vs mass due to various causes. Yet the sensitivity measured on that day is appropriate for measuring partial pressures in the vacuum system which is the goal of this *in situ* calibration.

4.2. Flow standard design

There are currently at least two manufacturers that make low-flow standards ($\sim 1.4 \times 10^{-2}$ Pa-L/s) for RGA calibration: Vacuum Technology Incorporated (VTI) Positive Shut-Off (PSO) [22] and the INFICON Calibration Reference Source [21]. The VTI PSO uses a gas supply in a small volume and a crimped capillary leak as the flow control element with a soft-seat valve tip seal on the end of the

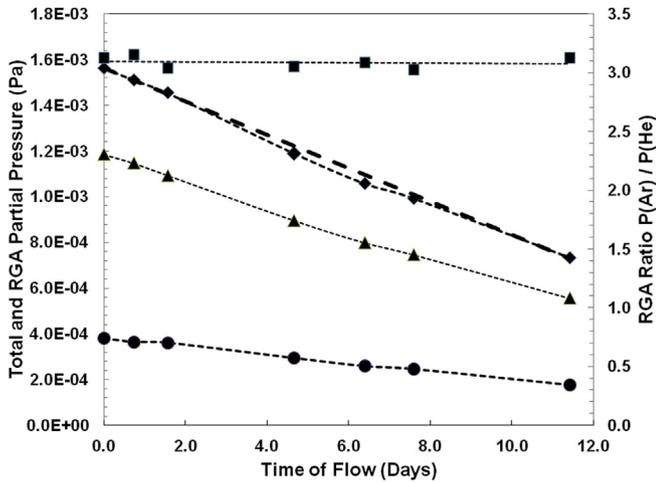


Fig. 5. RGA data from a Calibration Reference Source for an 11 day depletion experiment. Partial pressure for P(Ar) ▲, and P(He) ● both show depletion; yet the ratio P(Ar)/P(He) ■, is constant at 3.08 ± 0.05 . The sum of P(Ar) + P(He) as P(Depletion) ◆, fits a model for depletion (heavy dashed line) given in Eq. (19).

capillary to accomplish shutoff. During closure, the gas pressure between seal and leak fills the small volume to reservoir pressure; when opened the expansion gives a pressure burst ~ 5 times normal flow pressure at the RGA but it does not turn off filament emission. A similar shutoff occurs with the INFICON device where the flow element is a stainless steel frit.

Fig. 4 shows the relationship of flow rate $Q(P_{\text{fill}})$ and associated pressure produced at the RGA as a function of reservoir fill pressure, P_{fill} for the INFICON device. The dashed line shows a P_{fill} dependence predicted by the equations for viscous flow and the data points indicate actual RGA pressures for various fill pressures in kPa. A typical fill pressure is 280 kPa.

Viscous flow of a gas mixture from the flow standard produces partial flow, q_i , for a component given by Eq. (12). The total flow rate Q_0 of the INFICON calibration reference mixture is established by direct comparison to a NIST traceable VTI-calibrated flow device [22] using an interpolated RGA signal for Ar. The flow rate determination of the VTI calibrated flow device is made by measuring the accumulated gas flowing into an evacuated certified volume with a calibrated pressure transducer over a time period. The volume, pressure and time values are calibrated with traceability to the US based National Institute for Standards and Technology (NIST). For practicality during manufacturing, each INFICON calibration reference source is compared with the VTI flow standard and a value for flow is established and labeled along with gas mixture composition.

A key element in the INFICON Calibration Reference Source or the VTI flow standard is a viscous flow element which assures that a gas mixture flows with average viscosity with no separation of molecular species. This assumption of no alteration of the mixture has been checked at INFICON (by the author while employed there) where a mixture of Ar = 49.7%, He = 50.3% was allowed to flow for 11 days with periodic analysis of the ratio of Ar/He by a RGA. The results of this test are shown in Fig. 5 where the RGA measures a composition of 74.8% Ar and 24.2% He which is predicted by Eqs. (15) and (16) with ratio Ar/He of 3.08 ± 0.05 measured. Note in Fig. 5 that the partial pressure measured by the RGA and total pressure in the RGA decreases over time as the reservoir pressure is depleted yet the ratio Ar/He remains constant. A model for the pressure depletion in the RGA vs time is

$$P_{\text{RGA}}(t) = P_{\text{RGA-0}}[1 + Q_0 t / P_{\text{res}} V_{\text{res}}] \quad (21)$$

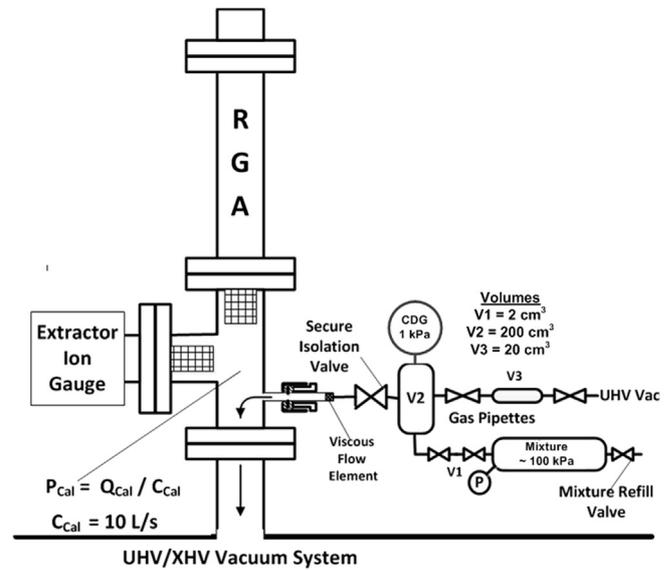


Fig. 6. A proposed XHV *in situ* calibration system. An OIS RGA and extractor XHV total pressure gauge is on a port of a UHV/XHV vacuum system with a low-flow viscous element with mixture prepared by volume expansions to retain composition.

where Q_0 is the calibrated flow rate of the calibration reference source, t is the elapsed time of flow, P_{res} and V_{res} are the fill pressure and volume of the reservoir, respectively. Fig. 5 shows $P_{\text{RGA}}(t)$ decrease has a good fit with Eq. (21) (heavy dashed line) for the calibration reference source in use for this experiment. The gas supply is in a reservoir of 130 cm^3 filled to $\leq 275 \text{ kPa}$ which is considered a non-compressed gas (which simplifies shipping). This quantity of gas is designed to allow 5 min of flow per day for 1 year which produces 10% depletion of supply. The user can keep track of flow time for calibration checks and compute the flow rate as it depletes the supply for more accurate predictions of partial pressures in the RGA.

4.3. *In situ* calibration systems for XHV: total pressure $< 10^{-8} \text{ Pa}$

The same principle for introducing a viscous flow *in situ* calibration gas for UHV applications can be extended to very low partial pressures in XHV applications. In Fig. 6 the calibration reference source in Fig. 3 is replaced by a gas handling system that can deliver a low pressure mixture to a viscous leak which enters the ion source regions of the RGA and XHV ion (extractor) gauge. Instead of producing a calibration pressure of 10^{-3} Pa in the ionization region, a pressure of 10^{-9} Pa could be produced using a low gas pressure of 270 Pa through a viscous flow element with an equivalent flow rate to the calibration reference source shown in Fig. 3. Thus in Fig. 6 a series of volumes is shown that can be used to pipette gas to a desired pressure. The resulting flow rate to the RGA is calculated from $Q = AP_{\text{mix}}^2$, with mixture pressure, P_{mix} and a previous flow rate calibration of the viscous element to determine A. Pipetting gas mixtures avoids altering composition by fractionation that can occur with metering valves. Pipetting involves trapping a small quantity of the mixture in volume V1 and expanding it into $V2 \gg V1$ to produce a reduced pressure. If the pressure in V2 is higher than a few hundred Pa, the pressure can be further reduced by a series of expansions into the volume V3; isolation of V3 from V2; then evacuation of V3. Repeating this sequence lowers the pressure in V2 while leaving the composition the same as the original mixture. An isolation valve between the gas source and the XHV vacuum is closed during mixture pressure preparation to assure no unintended gas flow into the XHV system

occurs. As an example for a XHV application, a certified gas mixture with 88% H₂, 9% CO and 3% CO₂ produces (applying Eqs. (15) and (16)) a composition of 64.8% H₂, 24.8% CO and 10.4% CO₂ at the RGA ion source. This design presents the RGA composition at XHV pressure of 10⁻⁹ Pa to the local RGA/Extractor Gauge. The gas load to the XHV getter pumping system is small at 10⁻⁸ Pa-L/s with species that the system will getter pump. Accuracy of sensitivity calibrations using this *in situ* method can be traceable to national measurement standards through calibration of the absolute flow rate of the viscous element and calculations of the RGA/IG conductance to the XHV vacuum system.

4.4. Calibration system for low-pressure processes: 1 Pa < P(process) < 100 Pa

Many industrial and research and development (R/D) vacuum processes operate at pressures of 1 Pa–100 Pa where process gas densities enable sustained plasmas and/or chemical processes that lead to practical chemical vapor deposition (CVD) or chemical etch rates [23,24]. Any of these processes are at pressures significantly higher than the operating pressure of an open ion source (OIS) (10⁻³ Pa) or closed ion source (CIS)(0.1 Pa) such that a pressure reduction system is needed. The goal of the measurement of a process gas is to determine the composition of the gas being sampled. If partial pressures in the process need to be known, it is best to measure the composition in the process [molar fractions of the process, X_i(Process)] and multiply times a direct pressure measurement of the process, e.g. pressure from a capacitance diaphragm gauge (CDG), P_{CDG}:

$$P_i(\text{Process}) = X_i(\text{Process}) P_{\text{CDG}} \quad (22)$$

An example of a pressure reduction from a low pressure chemical vapor deposition (CVD) or chemical etch process to the CIS RGA is shown in Fig. 7. A sampling tube flows gas by pressure difference from the process passing the molecular leak to the QMS and on to the interstage pumping port of the turbomolecular-molecular drag hybrid pump. The sampling system process probe i.d. and length is designed for a flow rate to produce a pressure at the molecular leak that is < one-half the process pressure. If the process involves a plasma, an alumina sampling tube should be used to be electrically neutral. Otherwise a metal sampling tube is used for robustness. The flow through the

sampling tube to the molecular leak region is typically in transition flow in this pressure range, whereas the flow through the small orifice(s) of the molecular leak into the QMS is in molecular flow. The orifice diameter of the molecular leak is designed to produce ≤0.1 Pa within the CIS with its 1 L/s exit conductance. Some fractionation of the process gas species probably occurs with this sampling system; typically a user is looking for repeatability of the process rather than absolute partial pressures.

Fig. 7 also shows a means for *in situ* calibration of the CIS RGA using the same Calibration Reference Source (labeled Cal Ref Gas in Fig. 7) as was used in Fig. 3 for the OIS RGA with its nominal flow rate of 1.4 × 10⁻² Pa-L/s. The gas enters between the molecular leak and the CIS. With this flow rate into the CIS with its exit conductance of ~1 L/s, a stable pressure of 1.4 × 10⁻² Pa is developed in the CIS whenever the Calibration Reference Source valve is opened and the CIS turbomolecular hybrid pump is running. This pressure is within the linear operating range indicated in Fig. 1 for the CIS. The gas flow dynamics are again viscous flow into the CIS and molecular flow out of the CIS region. Using the partial pressure for a species, P_i from Eq. (15) and its associated ion current, I_i, the sensitivity, S_i, for the CIS is given by Eq. (20). This repeatable calibration of the CIS can show the stability of the CIS RGA over time or provide the data on which to update sensitivities. Thus variations in the data from the process are real indications of process drift which is the information the user needs.

4.5. Calibration system for atmospheric pressure processes: 50 kPa < P(process) < 200 kPa

Many industrial and research processes involve supply gases and the process itself operating at pressure from 50 kPa up to 200 kPa. To analyze the composition of such gases a major reduction of sample pressure to introduce into a QMS is needed. Fig. 8 shows an example of such an analysis system. The CIS RGA used with this inlet system is an INFICON CPM with 100 amu mass range and Faraday cup ion detection. The yttria-coated iridium filament (for oxygen tolerance) is operated in the Lo (40 eV/200 μA) emission mode to minimize fragmentation interferences. The gas sampling system in Fig. 8 [25,26] is based on a traditional sampling scheme of two-stage pressure reduction by capillary/interstage pumping/orifice sampling method [12]. The capillaries are selected with i.d. and length controlling flow rate to a level the pumping

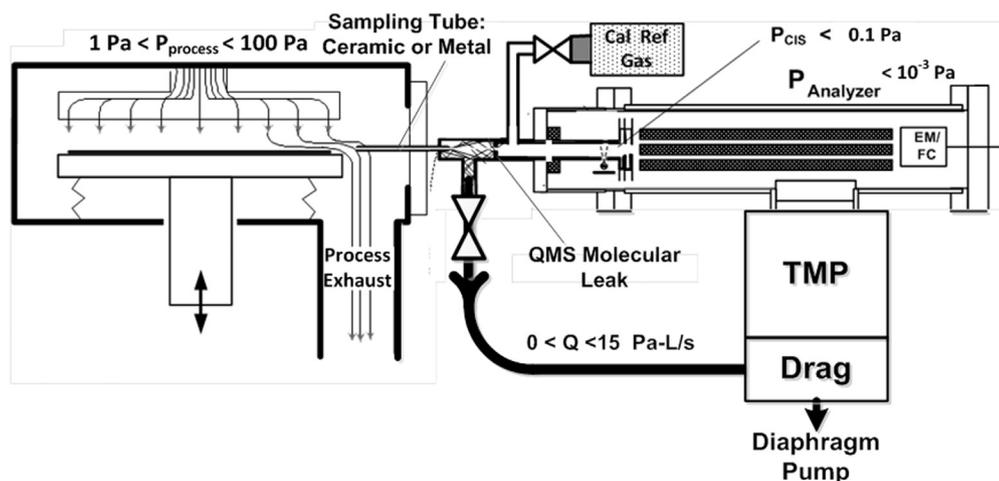


Fig. 7. Pressure reduction from 1 Pa < P_{process} < 100 Pa by a sampling tube with viscous or transition flow to drop the pressure at the molecular leak to < 1/2 P_{process}. The flow through the orifice leak to the CIS is molecular as is the gas exiting the CIS. The composition of the process gas is preserved with viscous flow but altered if transition flow occurs. An *in situ* calibration reference gas with composition given as in Table 2, can flow into the CIS.

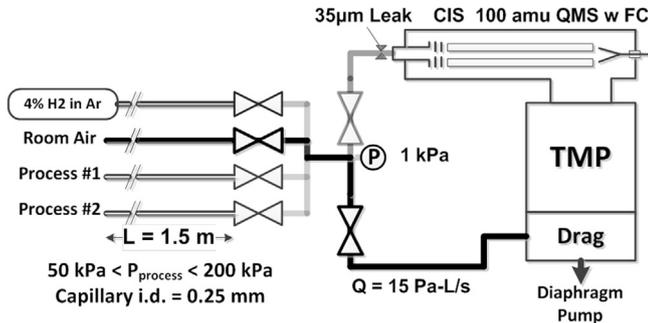


Fig. 8. An analytical sampling system designed for pressures $50 \text{ kPa} < P < 200 \text{ kPa}$ using capillaries producing $\sim 1 \text{ kPa}$ at the 35 micron orifice leak to the CIS. Calibration reference gases are sampled through capillaries for system calibration. Heavy line indicates flow from Room Air as a calibration gas to the drag stage of the TMP.

system can accommodate. For example the capillaries in Fig. 8 are 1.5 m in length with an i.d. of 0.25 mm. The flow of room air shown by the dark line in Fig. 8 shows the major pressure drop from atmospheric pressure (100 kPa) to 1 kPa at the tee leading to the 35 μm diameter molecular leak into the CIS RGA. Capillaries are mated with small dead volume valves; the molecular leak is common to any capillary selected as gas flows to the interstage pumping port of the drag stage of a compound turbomolecular pump. The flow rate by design is $\leq 15 \text{ Pa-L/s}$ which is tolerated by the hybrid turbomolecular pump. Multiple sampling points are achieved by selecting a different capillary from the four choices shown. In Fig. 8, the two reference mixtures used for a fuel cell analysis project are Room Air (at 35% relative humidity (RH)) and safe hydrogen (4% H_2 in Ar). These mixtures are sampled to determine and validate the air components and H_2 sensitivity for the CIS RGA. After flow is established (which displaces the previous sample), the gas is analyzed.

5. Results and discussion

5.1. Sensitivity verification

Verification of sensitivity over time can be done using the four *in situ* calibration methods provided by the hardware in Figs. 3 and 6–8. Those three systems using the Calibration Reference Source have available repeatable partial pressures to check mass scale and sensitivity values. Traceability to SI units of flow rate of the Calibration Reference Source can be established by calibration at national metrology institutions. This flow device is portable and can be shipped as needed to allow intercomparisons of calibrations of various RGAs. This enables industry to have a common reference gas for RGAs for use in different locations. Calibration of the conductance to the main vacuum system for this appendage device requires a calibrated ion gauge at least initially to establish accurate partial pressures at the RGA and ion gauge (see Eqs. (18) and (19)).

An example of regular measurement of sensitivity vs time is shown in Fig. 10 for a CIS RGA similar to system in Fig. 7 using 70 eV and 2 mA electron emission and a Calibration Reference Source with 95% Ar as principle gas component (see Table 2). The Ar sensitivity determined over a period of 44 days shows stability regions and an abrupt change. During day 26, a power failure shut down the CIS RGA and the vacuum system vented to atmosphere. On restart, the sensitivity is lower by 25% probably due to erosion of the tungsten filament or shift to a new position. The new lower sensitivity however is stable so the data would say use the new Ar sensitivity for subsequent analyses. This is the purpose of *in situ* calibration which is to determine normal operation, operational upsets and

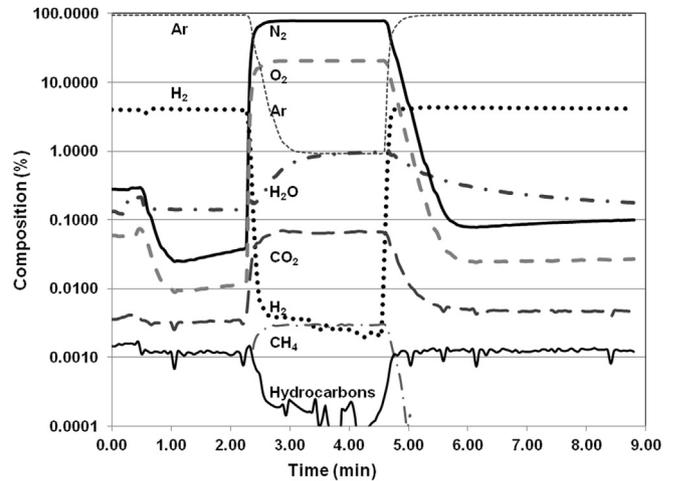


Fig. 9. Composition vs time from Fig. 8 system. Left: 4% H_2 in Ar; Middle: Room Air (35% RH); Right: 4% H_2 in Ar again. Transient to new composition is rapid; displacement of previous species is longer due to diffusion times proportional to mass.

long-term drift. Along with the Ar shift shown in Fig. 10, the user can look at the minor components of the gas mixture like H_2 , He and N_2 to see if their sensitivities have shifted by the same factor or different. If different, a new calibration profile with a new sensitivity for each minor component can be calculated using Eqs. (15) and (16) for the CRS mixture used. Other sensitivities can be scaled by interpolation and thus save a total recalibration with pure gases.

The analytical system shown in Fig. 8 enables sampling from near atmospheric pressure processes to provide compositional analysis. The major pressure drop from 50–200 kPa to 1 kPa is accomplished by the capillary selected and the new gas flows passing the channel to the molecular leak. Species from the flowing gas diffuse into the channel leading to the molecular leak going to the CIS RGA. The diffusion process is a random walk through the length of the channel (6 cm in the system shown in Fig. 8). Indications of that diffusion are shown in Fig. 9 where the two reference gas mixtures (Room Air and 4% H_2 in Ar) are alternated. In Fig. 9, the concentration changes to the new composition have shorter time constants than the displacement of the previous species. The diffusion of the new species is driven by the new composition whereas the diffusive depletion of the previous composition is driven by an ever decreasing concentration of previous gas remaining. It is still evident in Fig. 9 that the species depleting have a time constant that is proportional to mass: Hydrogen at mass 2 depletes to a new constant value faster than 40-Ar in the first composition change and 28- N_2 , 32- O_2 and 44- CO_2 take long times to reach a new asymptote when the composition goes back to 4% H_2 in Ar. In the cases of water vapor changing from 100 ppm in the H_2 –Ar mix to 10,000 ppm in air and back to 100 ppm, the time constant is even longer than other species because of the strong interaction of water vapor with the walls of the sampling system. Changing composition of H_2O requires a new equilibrium concentration on the walls plus the diffusion time, thus the long time constant. Note also in Fig. 9 that there is evidence of $\sim 10 \text{ ppm}$ of hydrocarbons ($43\text{-C}_3\text{H}_7^+$ fragments) in the 4% H_2 in Ar gas. In air the hydrocarbons go away; however in lab air, about 30 ppm of methane is observed along with elevated levels of CO_2 (700 ppm) due to breathing of lab occupants. The gas composition in the ion source for this sampling design is the same as in the composition of the reference mixture. This occurs because the viscous flowing gas stream at the interstage creates a sample pressure that supports molecular flow through the small channel(s) of the molecular leak. Thus the flow into the CIS region is molecular

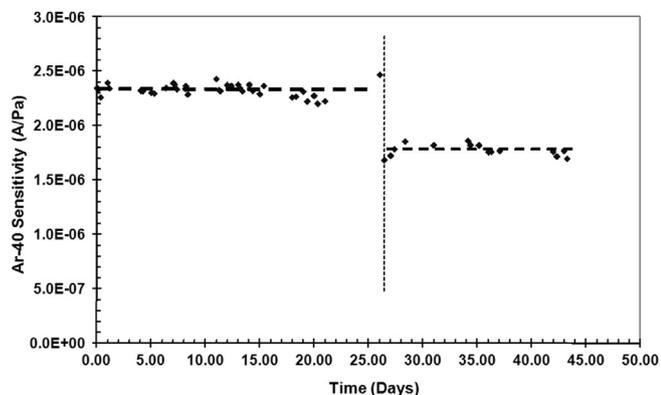


Fig. 10. The FC sensitivity of a CIS RGA operated at 70 eV/2000 μ A over 45 days shows two periods of stability. A shutdown of the CIS vacuum due to power failure occurred on Day 26 with a 23% average sensitivity loss due to oxidation and probable warping of the W filament during event. In each period the relative standard deviation of sensitivity is 2.4% and 2.8%, respectively.

and the flow exiting the CIS is also molecular; the mass dependence of species cancels [12]. This makes the relevant reference gas mixture available by just opening the appropriate capillary valve on this system.

5.2. Quality assurance

When the need for accuracy is important for making process decisions, there is a need for monitoring performance of a mass spectrometer or RGA measurement system. Analyzing reference mixtures that are pertinent to the process and comparing results to their known composition at the ion source is a traditional quality assurance (QA) approach. Examples of significant use of this QA approach were previously reported [16,17] by the author.

The same QA concept is embodied in the designs presented here by the inclusion of *in situ* calibration reference sources to provide data for QA assessment. An example is the system in Fig. 8 sampling two reference mixtures: 4% H_2 in Ar and Room Air, sampled over an extended period of time. Fig. 11 shows the measured values of the 4% H_2 and 96% Ar in a H_2 /Ar binary mixture by the CIS RGA system over 23 days. The data show near complementary differences for these two components with minor variations due to differing amounts of impurities measured with each sample. When there are multiple components in the reference mixture, the differences can vary independently such that plotting the deviations of each component is diagnostic. This is seen in Fig. 12 where the components of Room Air (35% Relative Humidity) are measured over 162 days show normal variations that are summarized in Table 3. The data in Fig. 12 suggests that the calibration done on Day 0 is still appropriate 162 days later where measurements show acceptable variations. This implies no recalibration is needed until the values ΔX_i indicate biases trending larger than two standard deviations from normal operation. The source of these biases can be operational upset (see Fig. 10) or drift from filament aging or contamination, etc. The actual data that shows the differences from the reference mixture can be used to make minor adjustments to sensitivities to minimize these differences. This amounts to re-calibration accomplished without removal of the RGA from the system.

6. Conclusions

Accurate measurements of partial pressures in vacuum systems or compositions of process gas require some planning for the analytical system. The process application and its pressure range

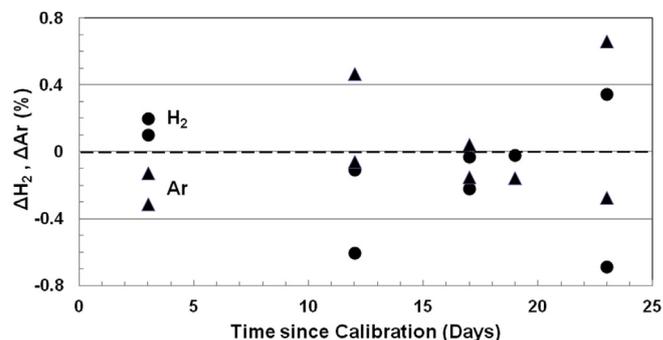


Fig. 11. Measured differences in molar fractions $X_i - X_{ref}$ expressed as % difference for $\bullet \Delta H_2$ (%) and $\blacktriangle \Delta Ar$ (%) are shown over time for a 4.0% H_2 in Ar binary mixture. Initial calibration for H_2 was done with 2% H_2 in N_2 certified mixture on Day 0.

dictate the sampling interface between process and RGA ion source. The goal of each sampling interface is to establish a predictable composition at the ion source. Measuring the residual partial pressures in a vacuum system is best done with an OIS RGA with an ion source operated at conditions that produce stable sensitivity. Once stable conditions are determined, the settings must remain constant to expect that sensitivities will also remain constant. Typically the calibration of an RGA from a vendor is provided for N_2 or Ar. Other sensitivities are given as historical values that are useful but not necessarily accurate. Ion detection with a FC is straight forward where ion current measurement with an electrometer is direct and stable. The use of an electron multiplier extends the detection limit about two orders of magnitude lower in partial pressure which is needed for UHV/XHV applications. Monitoring of gain can be done by measuring gain using Eq. (2) and scaling FC sensitivities using Eq. (3). Or an EM sensitivity can be measured directly (solving Eq. (4) for $S_i(EM)$) using the known minor components of the Calibration Reference Source. Initial sensitivities for an RGA can be measured on a test stand using pure gases for the species expected. When the RGA is mounted into an analytical system, a means for introducing an *in situ* Calibration Reference Source with an appropriate mixture is recommended to verify the initial calibration over time. This assures the user accuracy of the partial pressures reported for use in evaluating the vacuum at that location and qualifies physically separated RGAs for inter-comparison of results for large-dimension vacuum systems like accelerators. The portability of the Calibration Reference Source enables certification of flow rate and the potential for inter-comparison of process measurements between industrial sites. Full calibration does require a calibrated ion gauge for determination of

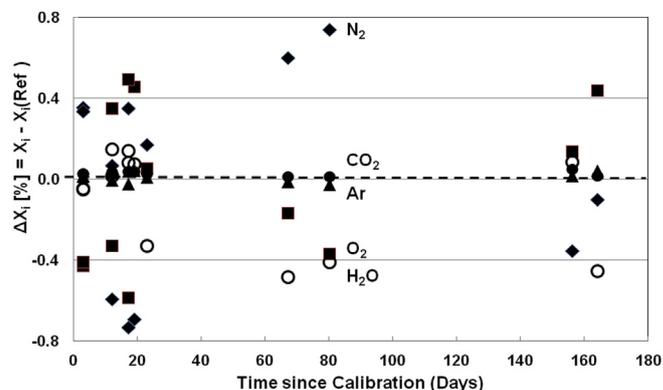


Fig. 12. Room Air (35% RH) component differences in molar fractions $X_i - X_{ref}$ expressed as % difference ΔX_i [%] over 162 days. Components (Reference Value) are $\blacklozenge N_2$ (77.3%), $\blacksquare O_2$ (20.74%), $\blacktriangle Ar$ (0.9%), $\circ H_2O$ (1.0%), $\bullet CO_2$ (0.04%).

Table 3

QA summary data on Composition of Reference Mixtures sampled through Capillary lines. Individual data points are shown in Figs. 11 and 12 for H₂ in Ar and Air, respectively. Results ΔX_i for all mixtures were randomly distributed over time.

Standard mixture	Duration (days)	Component	Average of $\Delta X_i = X_i - X_i(\text{Ref})$ (%)	ΔX_i Std deviation (%)	Relative Std deviation (%)
H ₂ in Ar	23	H ₂ (4 mol-%)	-0.05	0.34	8.50%
		Ar (95.8 mol-%)	0.01	0.33	0.35%
Room air	162	N ₂ (77.3 mol-%)	0.01	0.50	0.65%
		O ₂ (20.75)	0.00	0.40	1.9%
		Ar (0.91%)	0.02	0.02	2.2%
		CO ₂ (0.03 mol-%)	0.04	0.01	25%

the conductance of the RGA/IG appendage to the main vacuum system. Repeatability measurements can come from repeated use of the Calibration Reference Source by itself.

Many vacuum processes have gases introduced to accomplish a coating or etch process. For these processes where the composition of the process gas is the goal of analysis, a CIS RGA is recommended. If partial pressures in the actual process are desired, the $P_i(\text{Process})$ is given by Eq. (22) where the P_{Process} is the best process pressure from a CDG or strain gauge and X_i are the composition mole-fractions measured by the RGA analytical system. The introduction of a calibration gas at the CIS by sampling a known mixture or with an *in situ* Calibration Reference Source is necessary to check sensitivities over time. The advantage of the viscous flow Calibration Reference Source is that the composition does not change over time and the flow rate is stable for more than a year with recommended use. The disadvantage is the composition in the ion source is different from the composition in the reservoir due to the gas dynamics of flow regimes. Thus to achieve the desired composition in the ion source, some planning for the composition of the reference mix is needed in the design of the analytical system. For processes near atmospheric pressure, capillary samples of a tank with a reference mixture is recommended; the sampling system described delivers compositions to the ion source that are the same as the mixture in the tank.

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