Mass Spectrometry for Real-Time Gas Analysis

Andrew Mezo and Rodrigo Mitishita

Coanda Research & Development Corporation,
Burnaby, BC, Canada

Abstract

This paper presents a calibration approach for quadrupole mass spectrometry used in real-time gas analysis, with emphasis on correcting species-dependent ionization effects through empirically determined relative sensitivity factors. Using a certified span gas containing nitrogen, oxygen, argon, and helium, the method shows that calibrated measurements converge closely to known gas compositions and reproduce expected ambient air concentrations. The results demonstrate improved accuracy and reliability in time-resolved gas concentration measurements for industrial and research applications.

Introduction

Mass spectrometry (MS) is one of the most versatile and sensitive analytical techniques available for identifying and quantifying chemical species. Its fundamental principle is the separation of charged particles (ions) according to their mass-to-charge ratio (m/z), allowing for the detection and quantification of components in complex mixtures with high precision.

At its core, a mass spectrometer consists of three primary stages: ionization, mass analysis, and detection. In the ionization stage, neutral molecules are converted into ions by removing or adding electrons, often through electron impact, chemical ionization, or field ionization. The resulting ions are then accelerated through electric or magnetic fields within a high-vacuum environment. In the mass analyzer, ions are spatially or temporally separated based on their m/z ratio, since lighter ions travel differently than heavier ones. Finally, a detector measures the abundance of ions striking it, typically producing a signal proportional to their concentration.

There are multiple types of mass analyzers, including quadrupole, time-of-flight (TOF), ion trap, and magnetic sector instruments, each optimized for different applications. For real-time gas analysis, such as monitoring process gases, leak detection, or environmental sampling, the residual gas analyzer (RGA) type of quadrupole mass spectrometer is commonly employed. It offers a compact design, rapid response, and the ability to monitor multiple species simultaneously.

The signal intensity for each detected m/z value is proportional not only to the number of ions but also to the ionization efficiency, which varies among species. Therefore, accurate quantification requires calibration against known reference mixtures to determine relative sensitivity (RS) factors. These account for differences in ionization cross-section, fragmentation patterns, and detector response.

The mass spectrometer's ability to deliver real-time, multi-species concentration data makes it indispensable for a wide range of applications. In industrial and research contexts, it is used for analyzing combustion gases, studying catalytic reactions, characterizing vacuum systems, and verifying gas purity. When properly calibrated, it provides rapid, quantitative insights into chemical environments where traditional analytical instruments may be too slow or insufficiently sensitive.

Residual Gas Analysis and Measurement Principles

A mass spectrometer used for residual gas analysis measures the partial pressures of gases by separating ions according to their mass-to-charge ratio (m/z). The sample gas is ionized (commonly by electron impact), and the resulting ions are extracted and guided into a mass analyzer. Depending on the instrument design, electric and/or magnetic fields are used to selectively transmit, trap, or separate ions so that only ions of a given m/z reach the detector at a given time. The detector then converts the arriving ion flux into an electrical signal, which can be related to the amount of each species after accounting for ionization efficiency, fragmentation, and instrument sensitivity.

The system is maintained under high vacuum conditions, typically in the range of 10^{-5} to 10^{-8} Torr, ensuring that gas molecules have mean free paths much longer than the physical dimensions of the spectrometer. In this molecular flow regime, collisions between gas molecules are exceedingly rare compared to interactions with the chamber walls. As a result, ions generated in the ionization region travel essentially unimpeded through the acceleration and deflection fields, following well-defined trajectories determined by their mass-to-charge ratios The ions are then detected as an electrical current, with the measured signal directly proportional to their abundance at each selected mass-to-charge ratio.

Larger molecules sometimes fragment into smaller ions. If there are more ions, the current (and signal) increases. The current can increase for a given mass-to-charge ratio if there are more species or fragments with the same mass-to-charge ratio present, or if they are easier to ionize compared to other components. Consequently, the signal strength at a given mass-to-charge ratio may not necessarily indicate the relative abundance of components in a mixture, especially when they exhibit complex fragmentation patterns.

Calibration Procedure Example

When dealing with gas mixtures of relatively simple components (compared to larger organic compounds, for instance), one of the best ways to accurately measure relative abundances is through calibrations with different known mixtures of the species of interest. Commercial calibration gas mixtures are typically produced by specialty gas suppliers using gravimetric blending techniques, where each component gas is added to a high-pressure cylinder by weight using precision balances. The process is performed under controlled temperature and pressure conditions to minimize uncertainty. This method yields mixtures with certified accuracies often better than ±1% relative uncertainty.

The Hiden HPR-20 Residual Gas Analyzer (RGA) quadrupole mass spectrometer that we use at Coanda features a mass-to-charge ratio detection range of up to 200 m/z. We can use a multiple ion detection (MID) scan method to focus on a few mass-to-charge ratios. An example calibration mixture used for precise detection of argon tracer in a reactor containing air and helium consisted of 17% nitrogen (N_2), 5% oxygen (O_2), 1% argon (Ar), and balance helium (He). The mass spectra of these individual components show dominant peaks at the same mass-to-charge ratio values as their molecular mass (e.g. O_2 has molecular mass of 32 g/mol, and parent peak at 32 m/z). Therefore, we require an MID scan of 4, 28, 32, 40 m/z for He, N_2, O_2 and Ar, respectively.

Figure 1 is a plot of the detected partial pressure as a function of time at the above m/z, obtained for a sample MID scan of our calibration gas mixture. At $t < 2620$ s the instrument was sampling ambient air, with relative concentrations of 0% He, 78% N_2, 21% O_2, and 0.93% Ar. Sampling of the calibration gas mixture began at $t = 2620$ s, producing a sharp increase in helium partial pressure and a smaller increase in argon, while the partial pressures of nitrogen and oxygen decreased accordingly.

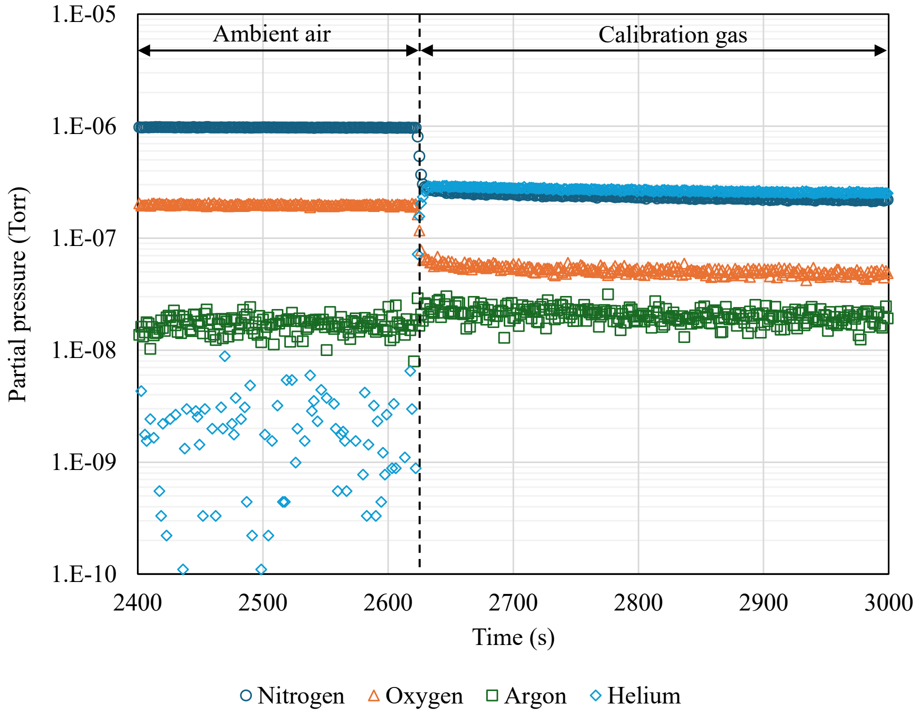

Figure 1: **Log-linear plot showing partial pressures of a calibration gas mixture containing 5% oxygen, 1% argon and 17% nitrogen, balance helium at t > 2620 s. Ambient air was sampled at t < 2620 s.**

As discussed above, ionization of gas molecules occurs at a different rate for each species, which means that the ratio of partial pressure and total pressure does not directly translate to a concentration measurement. A correction factor is therefore required for each species of interest to account for this phenomenon. The calibration parameter used with the mass spectrometer instrument is the relative sensitivity (RS) factor. It is related to the probability of ionizing a molecule of a given species "x", relative to the probability of ionizing a nitrogen molecule. The corrected partial pressure is calculated as:

$$P_{corr,x} = \frac{P_x}{RS_x}, \qquad (1)$$

where P_x is the uncorrected partial pressure of each species, i.e. N_2, O_2, Ar or He in this case. Although RS guideline values are provided for many species of interest by the mass spectrometer manufacturer, these can change with environmental conditions, instrument age, relative concentration of the species present in the sample gas, and therefore, empirical determination of these relative sensitivities is usually recommended to achieve the best accuracy possible.

To calibrate the instrument using this span gas blend, we first compute the mean (uncorrected) system pressure (P_{total}) at steady state:

$$P_{total} = P_{N_2} + P_{O_2} + P_{Ar} + P_{He}. \qquad (2)$$

We then multiply the total pressure by the relative concentration of each species in the mixture to obtain their reference partial pressures:

$$\begin{aligned} P_{ref,N_2} &= 0.17\, P_{total} \\ P_{ref,O_2} &= 0.05\, P_{total} \\ P_{ref,Ar} &= 0.01\, P_{total} \\ P_{ref,He} &= 0.77\, P_{total} \end{aligned} \qquad (3)$$

The reference partial pressures are the target values that the mass spectrometer should be measuring. These target values are used to correct the actual measurement by computing new RS values for each species:

$$\begin{aligned} RS_{N_2} &= \frac{P_{N_2}}{P_{ref,N_2}} \\ RS_{O_2} &= \frac{P_{O_2}}{P_{ref,O_2}} \\ RS_{Ar} &= \frac{P_{Ar}}{P_{ref,Ar}} \\ RS_{He} &= \frac{P_{He}}{P_{ref,He}}. \end{aligned} \qquad (4)$$

The final step is to divide all corrected RS values by RS_{N_2}, making all sensitivity values relative to nitrogen, and setting $RS_{N_2} = 1$. We then use Equation 1 to obtain P_{corr} values for all components over the experimental duration. The sum of all corrected partial pressures over time is $P_{corr,total}$.

Calibrated Results

The calibrated results shown in Figure 2 illustrate the time-resolved volume concentrations of nitrogen, oxygen, argon, and helium following application of the empirically determined relative sensitivity (RS) factors. After calibration, the measured concentrations of the calibration gas mixture converge closely to the certified composition of 17% N_2, 5% O_2, 1% Ar, and 77% He, confirming the validity of the applied correction factors. Prior to calibration, the uncorrected signals underestimated the oxygen and argon fractions due to their lower ionization efficiencies relative to nitrogen. The improved agreement post-calibration demonstrates that the derived RS values effectively compensate for these differences in species-dependent ionization probability and detector response. Additionally, for the ambient air measurements preceding the calibration gas exposure ($t < 2620$ s), the corrected concentrations reproduce expected atmospheric proportions of approximately 78% N_2, 21% O_2, and 1% Ar, further validating the instrument's response stability and the robustness of the calibration procedure.

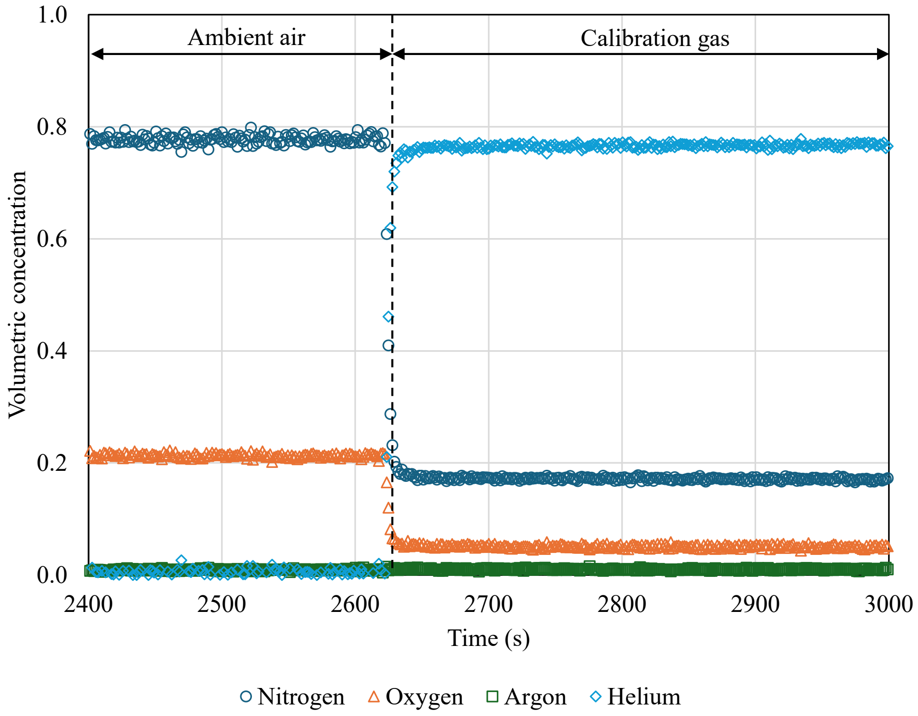

Figure 2: **Plot showing calibrated volume concentrations for span gas blend components at t > 2620s. Ambient air component concentrations shown at t < 2620s.**

Concluding Remarks

This work demonstrates a robust and repeatable calibration procedure for quadrupole mass spectrometry applied to real-time gas analysis. By empirically determining species-specific relative sensitivity factors, the accuracy of quantitative gas composition measurements can be significantly improved, even for mixtures containing species with widely varying ionization efficiencies. The calibration approach validated in this study ensures reliable detection and quantification across a broad dynamic range, enabling precise tracking of transient gas behaviours and composition changes.

At Coanda Research & Development, our ability to integrate high-vacuum mass spectrometry with advanced data acquisition and calibration methodologies allows us to deliver accurate, time-resolved gas concentration measurements. These sophisticated capabilities support our many industrial research applications, from process diagnostics and optimization to emissions characterization and advanced materials testing. Through our combined expertise in physical modelling and fluid dynamics, measurement science and custom instrumentation, Coanda provides innovative, science-based solutions to quantify and understand real-world flow phenomena.