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Quantification of hydrogen in a gas mixture of noble gases

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ABSTRACT

Quantification of hydrogen fraction in the gas mixture with inert gases kept in a small enclosure of the gas surge arrester (GSA) is a challenging task. Hydrogen greatly influences device properties, but as an omnipresent gas it represents also the background of any mass spectrometer. Hydrogen fraction in a particular GSA was quantified after its puncture in an evacuated batch inlet and subsequent introduction to a pumped chamber housing a quadrupole mass spectrometer (QMS). Its calibration was performed by an innovative in-situ calibration procedure which should yield high accuracy. In the first stage, a pure gas (Ar, Ne, H_2) contained in a calibrated volume was set by a leak valve to flow into the UHV system. The pressure change reading of the capacitance manometer over time gives the flow rate which is directly correlated to the ion current of a specific mass peak in the span of 3 orders of magnitude. The extracted calibration curves of the QMS for each gas species are applied in the second stage of the calibration when known gas mixtures are prepared in the calibrated volume to verify the gas composition determination procedure based on the fractionation. Such procedure is revealed fairly accurate at high (above $\sim 6 \times 10^{-5}$ mbar L/s) flow rates, however a significant error appeared at lower flow rates. Possible explanations for erroneous hydrogen determination at very low fluxes by the QMS in the mixture with argon are presented.

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1. Introduction

Gas surge arresters (GSAs) are still the most reliable devices for over-voltage protection of various electronic devices. The selection of the gas, its ionization energy and its pressure are the main features that define the breakdown voltage across the gap between two metal electrodes. For a long-term stable operation, a gas mixture of inert gases and hydrogen is applied [1]. Hydrogen has a strong impact on the breakdown voltage in GSAs, much more than noble gases, and at the same time it prevents oxidation of the electrode surfaces after the surge. Its partial pressure in the GSA must be thus kept within narrow limits. During our manufacturing process applying a brazing material, the gas mixture is prepared and introduced into the vacuum furnace at high temperature. As the breakdown voltage at room temperature often exceeded the set value, it was hypothesized that the hydrogen fraction inside the GSA could be different comparing to the mixture applied in the furnace since hydrogen could dissolve into and permeate through metal electrodes due to high temperature.

To verify the actual gas composition, the quadrupole mass spectrometry seems to be the most appropriate option. Surprisingly, analyzing the gas mixture contained in the small volume of the GSA was found to be substantially more challenging than it had been assumed from the recommended practice for calibration of mass spectrometers [2]. For such analysis the approach with the batch inlet system [3] is most appropriate. Quantitative analysis of a static gas sample is typically performed by emitting this sample to the pumped quadrupole mass spectrometer (QMS) and measuring the instantaneous QMS response. To simplify the gas composition determination we decided to use the QMS as a partial flow analyzer rather than as a partial pressure analyzer. Quantification of partial flow rates from the batch inlet into the analytical chamber with the QMS allows determination of the gas composition in the batch inlet as described in the next section.

Our literature survey revealed only a few such attempts. Santeler [4] derived calibration equations for both direct (in-situ) and indirect calibration of partial pressures and partial flow rates and reports on equations required to convert between partial pressure calibrations and partial flow rate calibrations. Leckey and Boeckmann [5] developed a rather sophisticated method to analyze small concentrations of heavy gases in lighter gases, where the control valve was employed to maintain the constant low pressure in the QMS chamber which was required for linear response of the

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instrument. The QMS time response needed to be integrated in order to calculate the sample composition. Dobrozemsky [6] calibrated the QMS against known gas quantities, where the integration of the QMS time response was also needed. An application of an analogous calibration method was recently published by Erjavec and Šetina [7]. As none of the cited authors elaborated our approach, a detailed procedure is described below.

2. Theory

The batch inlet system [3] is particularly appropriate for small and precious samples of gas mixtures such as in various sealed devices. In our particular case we are dealing with a sufficiently low initial total pressure $p_{tot,0}$ in the batch inlet resulting in the molecular flow regime during the gas flow through a variable leak valve (VLV) to the analytical chamber with the QMS. The latter chamber is continuously pumped and kept at a pressure several orders of magnitude lower compared to the pressure in the batch inlet. Specific system pumping speeds for different gas species are not relevant in the present case because in the following we are not interested in partial pressures in the analytical chamber [4]. The molecular flow into the analytical chamber fractionates the sample gas predictably, because the partial gas flow rate Q_i of species i is proportional to its partial pressure p_i in the batch inlet in the following manner

$$Q_i = \frac{A}{\sqrt{2\pi\, m_i kT}} p_i = K\frac{p_i}{\sqrt{m_i}}, \tag{1}$$

where m_i is its molecular mass, k is Boltzmann constant and A is the effective cross-section of the VLV. In the rightmost term, the gas-independent terms are substituted by constant K containing the VLV conductivity and temperature T. In the following these two quantities will be assumed constant.

Suppose the batch inlet has been filled with a pure gas and the VLV is rapidly opened to a constant conductance. The pressure in the batch inlet is now decreasing and consequently also the corresponding partial flow rate

$$Q_i(t) = -V\frac{\mathrm{d}p_i}{\mathrm{d}t} = p_i(t)\frac{K}{\sqrt{m_i}}. \tag{2}$$

The same applies for any species i in the mixture of gases, since there is no interaction between the gas molecules. While the volume V of the batch inlet is known, this is not the case with the constant K since the VLV conductivity cannot be set reproducibly [3]. Nevertheless, if one can quantify the ratios of partial flow rates using the QMS (calibrated in-situ as a partial flow meter), the ratios of the corresponding partial pressures (i.e. gas composition) in the batch inlet can be obtained:

$$Q_i(t) : Q_j(t) : Q_k(t) : \ldots = \frac{p_i(t)}{\sqrt{m_i}} : \frac{p_j(t)}{\sqrt{m_j}} : \frac{p_k(t)}{\sqrt{m_k}} : \ldots. \tag{3}$$

When this is done at the moment $t = 0$ when the VLV is rapidly opened to a constant conductance and the initial total pressure $p_{tot,0}$ is known, the absolute values of partial pressures in the batch inlet can be calculated. This is what we called as the "first reading" method, where only the QMS reading immediately after opening the VLV is needed. There is no need to integrate the QMS time response for the entire gas depletion from the batch inlet, which is a common practice [6,7]. Nevertheless, the gases expected in the gas mixture need to be known.

In-situ calibration of the QMS as a partial flow meter yields calibration curve for chosen pure gas i that gives the relation between the flow rate Q_i and ion current I_i from the representative mass peak with the mass-to-charge ratio m/q. Unfortunately, the flow rate Q_i is not a directly measurable quantity in our experimental system, hence the calibration cannot be done in a straightforward way. When only pure gas i is filled in the batch inlet up to a pressure $p_{i,0}$ and the VLV is rapidly opened to a constant value at time $t = 0$, the total pressure p_{tot} in the batch inlet equals p_i which is exponentially decaying as

$$p_i(t) = p_{i,0}\exp(-t/\tau_i), \tag{4}$$

where $\tau_i = V\sqrt{m_i}/K$. From Eq. (2) follows that the partial flow rate Q_i is also decreasing exponentially with the same decay constant τ_i

$$Q_i(t) = \frac{Vp_{i,0}}{\tau}\exp(-t/\tau_i). \tag{5}$$

The in-situ calibration procedure thus requires a simultaneous measurement of $p_{tot}(t)$ and the conveniently selected indicator peak $I_i(t)$ of species i, after opening the VLV to the batch inlet, filled with the pure gas of interest. Instead of the numerical derivation of $p_{tot}(t)$ to obtain $Q_i(t)$ via Eq. (2), it is numerically more stable (and less sensitive to the noise) to fit the $p_{tot}(t)$ with an exponential decay function to obtain the unknown τ_i and then use Eq. (5) to calculate the flow rate for any time needed. Hence, for each $I_i(t)$ datapoint a corresponding $Q_i(t)$ can be calculated and the $Q_i(I_i)$ calibration curve for species i is obtained. There is no need to perform several calibration runs at various fixed flow rates, since a single calibration procedure inherently covers a broad range of Q_i's determined by the corresponding initial and final p_{tot}. If needed, the sensitivity can be introduced as $S_i = I_i/Q_i$. Constant K (VLV conductivity) does not need to be identical during the calibration and during composition determination of an unknown gas mixture, however it needs to be constant during each procedure.

Time needed to open VLV to the fixed position needs to be small compared to the characteristic decay constant τ_i for the lightest gas (usually hydrogen) contained in the mixture whose composition is being determined. If this condition is not fulfilled, the molar fraction of the lightest gas may change considerably during VLV adjustment.

When initial partial pressures for gas species i, j, k and their molecular masses are known, one can predict the composition of the remaining gas mixture in the vessel during depletion in the molecular flow regime. This can be done even without a known VLV conductivity (const. K unknown), as long as p_{tot} at the time of interest is known. The total pressure is namely a sum of partial pressures

$$\begin{aligned} p_{tot}(t) &= p_{i,0}\exp(-t/\tau_i) + p_{j,0}\exp(-t/\tau_j) + p_{k,0}\exp(-t/\tau_k) \\ &= p_{i,0}\exp(-w) + p_{j,0}\exp\left(-\sqrt{m_i/m_j}\,w\right) \\ &\quad + p_{k,0}\exp\left(-\sqrt{m_i/m_k}\,w\right). \end{aligned} \tag{6}$$

In the last expression a new variable $w = t/\tau_i$ was introduced, which is the only unknown and can be obtained by numerical solution of Eq. (6) for a known p_{tot}. Partial pressures of the remaining gas mixture can be thus calculated for any corresponding p_{tot}.

3. Experimental procedure

The all-metal UHV system, Fig. 1, consists of two main chambers separated by the VLV: the batch inlet and the analytical chamber where the QMS is mounted, i.e. single-stage pressure reduction configuration [3]. The general purpose batch inlet consists mostly of

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