Ultimate limits in the gas composition determination within small sealed volumes by quadrupole mass spectrometry

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A B S T R A C T

Miniaturization of modern sealed vacuum devices and higher demands for their stable operation require accurate determination of the gas composition in the early stage of their operation as well as after a long operational period. Among a few highly sensitive gas methods, quadrupole mass spectrometry seems to be the most appropriate one for this task as gas amounts are well below $1 \cdot 10^{-4}$ mbar L. In this paper, a new approach, how to prepare a quadrupole mass spectrometer for routine quantitative analysis of small gas amounts, is described. In the first stage, it was calibrated by an innovative *in-situ* procedure using three different gases: nitrogen, argon and neon. Each gas was admitted into a chamber with a precisely determined volume equipped by a capacitance manometer. By opening the variable leak valve, ion current versus flow rate dependence was determined over three orders of magnitude. Non-linear response at very low flow rates was detected. In the next stage, gas quantities from $3 \cdot 10^{-5}$ mbar L to $6 \cdot 10^{-7}$ mbar L of pure gas were admitted, which proved that by numerical correction of non-linearity, the achieved accuracy of gas quantity determination could be noticeably improved. Rather poor results were on the contrary obtained when synthetic gas mixtures were analysed. Additional calibrations with gas mixtures revealed a strong interference provoked by argon. It enhanced the instrument's sensitivity for nitrogen for a factor of up to 2.3, depending on argon fraction. Considering this effect, further corrections led to a substantially improved accuracy of the nitrogen fraction determination in small gas amount mixtures. In general, quantification of very small gas amounts needs a careful analysis of all contributions influencing the accuracy, as the number of data points is limited and mostly recorded in the non-linear mode of the instrument's operation.

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1. Introduction

There are many modern vacuum devices where a required pressure over an extended period is mandatory. The total pressure in vacuum insulating panels with a typical volume of a few L should remain below 0.1 mbar for a few years [1]. In vacuum glazing elements, having a typical volume of ~0.1 L, a pressure below $1 \cdot 10^{-3}$ mbar should be kept for a decade [2]. In small optoelectronic devices, the tolerable pressure in a volume, even smaller than 0.001 L, should remain in the high vacuum range for some years [3].

During the developing stage of such devices, careful recording of the initial pressure is mandatory. Measurements of the absolute pressure in a small sealed enclosure is the first challenging task, as the vacuum gauge must be very stable and should not interfere with the gas. When composition of the gas, which had been accumulated over a certain time, is searched, this represents an even more challenging task. The investigated device is usually put into a batch inlet system and punctured by a suitable actuator. The released gas is admitted to the analytical part, equipped with a mass spectrometer. General procedures of the quadrupole mass spectrometer (QMS) calibration as partial pressure gauges are well described in the recommended practice [4]. The main specific problem, when working with small gas amounts, is that the analysis consists of a limited number of recordings of ion currents versus time, which means that the instrument, calibrated in the static mode, operates in the transient mode. Our literature survey revealed that only a few reports exist on the evaluation procedure and achieved accuracy of gas composition determination of small gas amounts. Calibration of the QMS against known quantities of pure gas (~10^{-3} mbar L) by integration of the QMS time response

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was described by Dobrozemsky [5]. Unfortunately, even if the main sources of errors are mentioned in the discussion, the achieved accuracy on the composition of synthetic gas mixtures is not presented. Another attempt on absolute calibration of even smaller gas amounts of only ~10^{-7} mbar L, applying a spinning rotor gauge, was reported by Winkler [6]. This method is suitable for quantification of pure gases but could not be adopted for the analysis of unknown gas mixtures. A different approach, described by Kendall for calibration, with advantages and drawbacks, is based on very fast admission of small gas pulses down to 10^{-7} mbar L [7].

In our slightly different approach described in Ref. [8], we calibrated the QMS as a partial gas flow analyser rather than as a partial pressure analyser [8]. Quantification of the gas mixture in the batch inlet with the QMS allowed a rather fast and accurate determination of mixtures containing ~0.1 mbar L of the gas. At low gas flow rates ($<10^{-6}$ mbar L/s), the impact of argon affected the accuracy of hydrogen determination.

In this paper, a detailed calibration procedure of the QMS as a partial gas flow meter for gas flow rates below 10^{-6} mbar L/s is presented. In the next stage, the accuracy of gas quantity determination by admitting the following gas amounts of pure gases is evaluated: $3 \cdot 10^{-5}$ mbar L, $6 \cdot 10^{-6}$ mbar L, $3 \cdot 10^{-6}$ mbar L and $6 \cdot 10^{-7}$ mbar L, respectively. Finally, small amounts of synthetic gas mixtures are analysed. Main sources of the inaccuracy in the evaluation of recorded data are presented and discussed.

2. Theory

2.1. Ideal case

The batch inlet system [4] is particularly appropriate for small and precious samples of gas mixtures which are released from a sealed device after the puncture inside the chamber with a known volume.

In our particular case we are dealing with a sufficiently low initial total pressure $p_{tot,0}$ in the batch inlet after the puncture, which is resulting in the molecular flow regime during the whole gas flow range through a variable leak valve (VLV) to the analytical chamber equipped with the QMS. The proof follows from the fact that the mean free path λ is greater than the characteristic dimension. This is calculated from the effective cross-section area and expressed as a circular aperture with diameter d. Even at $p_{tot,0} = 0.01$ mbar and measured flow rates, $\lambda/d > 5$. The benefit of our setup is that it is not necessary to open the VLV to the same position each time. As the quantity of the analysed gas is often unknown, the VLV enables to set the maximum ion current of a selected gas to a safe, preset value. The only restriction is that while opened it should stay fixed during an individual calibration procedure. An orifice with exactly known conductance, equipped with a simple valve, seems to be a better and a cheaper choice at first glance. As the pressure in the small volume is in principle unknown, a set of orifices should be available to reach the optimized ion current of the QMS. Such a set is not an acceptable option for a practical work as the quantity of the gas is very limited. Our goal is to determine the gas composition of small, unknown quantities of gases that have been accumulated for a long time (typically months or years), so it's impossible to experiment with different orifices to finally find a matching one.

The analytical 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 the partial pressures in the analytical chamber, but only in the QMS response [9]. The molecular flow into the analytical chamber fractionates the sample gas

predictably, because the partial gas flow rate Q_i of gas 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 the Boltzmann constant and A is the effective cross-section of the VLV. In the rightmost part, the gas-independent terms are substituted by a constant K, containing the VLV conductance and temperature T. In the following, these two quantities will be assumed as constant for a particular cycle.

For the purpose of calibrating, the QMS response to a particular gas flow rate Q_i, the batch inlet has been filled with a pure gas, whereupon the VLV was rapidly opened to a constant conductance. The pressure in the batch inlet was decreasing as an exponential function, and consequently, with the corresponding flow rate $Q_i(t)$:

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

The time constant τ_i of pressure decrease for each gas with a molecular mass m_i is defined by the batch volume, temperature and conductance of the VLV, $\tau_i = (V \cdot \sqrt{m_i})/K$. This type of calibration gives a continuous diagram of the ion current I_i versus gas flow rate Q_i, otherwise determined in discrete points [4]. The calibration procedure presents in fact "digitizing" of the continuous gas flow rate Q_i into a set of discrete ion current readings I_i by the QMS, recorded in equal time sequences. A linear response of I_i versus Q_i is expected. The slope is termed as the dynamic sensitivity (DS), in units, As/mbar L. This instrument's property is somehow analogue to the commonly defined sensitivity S in A/mbar, as for the partial pressure gauge [4]. The dynamic sensitivity is more appropriate for this study as it eliminates the need to know the actual pumping speed. To make the quantification feasible, when using the sensitivity S in the case of an individual gas, the pumping speed was assumed to be constant [6].

The basic problem exposed in the present study is first presented in an idealised case of the QMS determination of three gas flow rates. Initially, all three gases are contained in a small batch inlet volume in equal proportions. By a quick opening of the VLV, ion currents are sampled and displayed in a table or in a graphical form, Fig. 1. The sweep number j for the time interval is presented
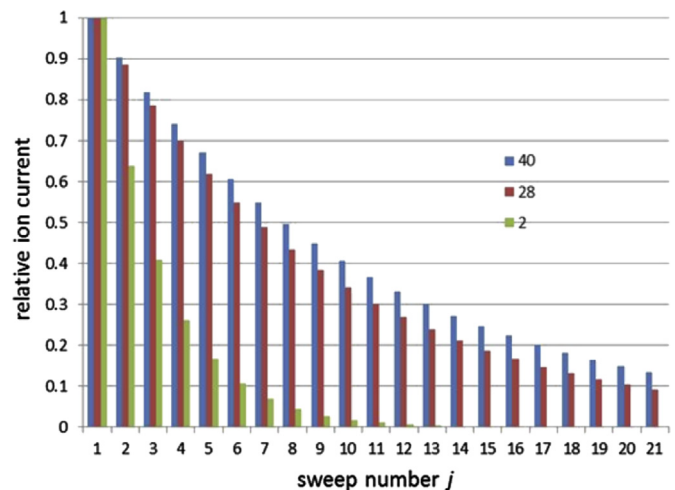

Fig. 1. Concept of the gas flow rate Q sampling by the QMS presented for three common masses: 2, 28, and 40.