International Journal of Mass Spectrometry xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Quantification of small gas amounts with an ion trap mass spectrometer

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ARTICLE INFO

Article history:
Received 25 November 2015
Received in revised form 22 February 2016
Accepted 22 February 2016
Available online xxx

Keywords:
Ion trap mass spectrometer
Gas quantification
In situ calibration

ABSTRACT

Accurate quantification of the composition in small amounts of gas is a challenging task, since there are a limited number of analytical methods having a highly sensitive and fast response. A recently introduced ion trap mass spectrometer (ITMS) was preliminarily studied as a candidate for routine quantitative analysis of small gas amounts detected as gas bursts. The ITMS was calibrated by an innovative in situ procedure using three pure gases: nitrogen, argon and hydrogen. Total pressure versus flow rate dependence was determined over three orders of magnitude, while the gas fraction pattern was simultaneously recorded by the ITMS. The obtained specific gas sensitivities of the ion gauge and pertaining ITMS fraction patterns were applied for quantification of synthetic binary gas mixtures with a composition ratio equal to 1:1, ranging from 3.17×10^{-3} mbar L to 6.7×10^{-5} mbar L. The error in quantification was substantially higher than for pure gases and depended on the amount and gas type. Argon was noticeably overestimated, while hydrogen was highly underestimated. At smallest gas amounts, the disproportion was as high as 1:0.36. The origin of error for low mass ions seems to be related to the ITMS's intrinsic principle of ion generation, separation and detection.

1. Introduction

There are many modern vacuum sealed devices where a stable residual pressure with unchanged composition should remain in the high vacuum range for prolonged periods. Quantification of accumulated gases is an important issue in the early stage of the device operation as it may predict its good or bad performances on the long-term scale [1,2]. Unfortunately, extremely small gas amounts are very difficult to analyze correctly due to the limited number of datapoints, collected close to the detection limit of a suitable residual gas analyzer. In the last few decades, quadrupole mass spectrometers (QMSs) were considered as the most sensitive gauges for gas composition analysis [3,4]. Linearity over a wide pressure range is usually tested by noble gases but this parameter itself does not reveal the potential dependence of sensitivity on the presence of other gases. The sensitivity of the instrument for each species of interest as a function of the concentration of other species present in the gas sample was studied intensively as it greatly determines quantification inaccuracy [5]. Recently, a detailed study of a representative QMS instrument and its true performance on the quantification of very small gas amounts was reported [6]. A relatively slow response, non-linearity, and interference even at low ion current readings were recognized as its main drawbacks.

The ion trap mass spectrometer (ITMS) is covering the same area of selective gas detection as the QMS. Its operational principle, capability to present contaminants in various environments, and particularly fast scanning, being the main advantages compared to the QMS, has been described in Refs. [7,8]. The response to known leak rates flowing into the ITMS simultaneously, and its capability to quantify small gas amounts, has not been reported yet.

In this paper, a detailed calibration procedure of an ITMS in combination with an ion gauge (IG), applied as a partial gas flow meter for flow rates below 10^{-4} mbar L/s, is presented. Experimentally acquired total pressure versus known throughput relations of pure hydrogen, nitrogen and argon were applied in the subsequent quantification of known amounts of synthetic binary mixtures consisting of these gases. The main sources of errors in this process are presented and discussed in comparison to the QMS.

2. Calibration experiment

2.1. Calibration of the ion gauge

The native output of the ITMS is expressed as ratiometric data, meaning that it determines each ion peak in relation to the sum of all ion peaks. It can express the partial pressure of each gas only

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http://dx.doi.org/10.1016/j.ijms.2016.02.012
1387-3806/

when the pertaining sum of ion peaks is related to the IG output. For such an expression, correction factors K_j of the ion gauge for individual gases are required. This means that in situ calibration of the ion gauge by pure gases is the first required step.

We adopted the method proposed by Winkler [9], who introduced a small amount of a very pure gas (down to $p \cdot V \sim 10^{-7}$ mbar L), prepared in an extremely well outgassed glass chamber by using a spinning rotor gauge as an absolute pressure sensor. By opening the connecting valve, the gas was admitted to the analytical UHV chamber, pumped by a known pumping speed S and equipped with an IG. By integration of the total pressure burst over time and multiplying by S, the admitted gas amount $p \cdot V$ was reconstructed rather accurately.

In our case, a much larger gas amount was prepared inside a volume with a leak where the pressure was measured by capacitance manometers, recorded until it dropped toward the offset value. From this pressure decay curve, the gas flow rate was calculated and correlated to the total pressure p_{tot}, expressed in nitrogen equivalent units.

The correction factor K_j, which is used when other gas species j than nitrogen is measured, is specified by the basic equation [10]:

$$p_j = \frac{K_j}{K_{N_2}} p_{tot}. \tag{1}$$

K_j/K_{N_2} is sometimes termed as the ratio of ion gauge constants, R_j, as in Ref. [10]. Due to many details which influence the ion gauge response, it is recommended to calibrate the ion gauge in situ just before it is applied for particular precise measurements [10].

Identification of the ITMS's peaks belonging to the same gas species can be done during calibration of the ion gauge for an individual gas j. The ITMS's output at each sweep consists of 300 peak fractions, starting at mass number 1, and giving the sum equal to 1.

The formalism of conversion of the ITMS's output and total pressure p_{tot} into partial pressures for simple gas mixtures with non-overlapping peaks is described by an equation for each gas component j as:

$$p_j = \sum_{j\,min}^{j\,max} frac(j) \cdot \frac{K_j}{K_{N_2}} \cdot p_{tot}, \tag{2}$$

where *frac* means the fraction of a particular ion mass, while the sum runs over all fractions related to the gas species j. The sum of all partial pressures in the mixture thus generally differs from p_{tot}, expressed by the IG in nitrogen equivalent units.

2.2. Measuring of small gas amounts by the ITMS

After getting all the K_j values, the capability for quantification of small amounts of selected pure gas can be verified. This method was applied for quantitative evaluations of small gas amounts which are relevant in gas interaction with pure metal surfaces in Ref. [11]. Similar calibration procedure is described by McCulloh [12] for much larger quantities of pure gas, $p \cdot V \sim 0.85$ mbar L, where nitrogen, argon and helium were leaked into the calibration chamber for half an hour.

When a small amount of a gas mixture is to be analyzed, the corresponding ion fractions recorded by the ITMS are needed too. We describe below in detail the procedure for quantification of gas amounts by using ratiometric data from the ITMS correlated to the p_{tot}. There is a noticeable difference compared to the QMS. The ratiometric data contain ion fractions, which cannot be simply converted to partial pressures, as they need first to be expressed as corrected fractions of the p_{tot}, and then only integrated over time.

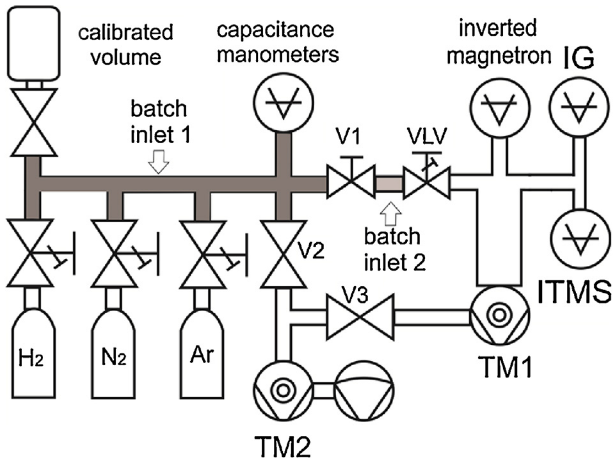

Fig. 1. Experimental set-up of the all-metal UHV system. A known amount of gas is leaked through the VLV into the analytical section with the ITMS.

2.3. Measuring apparatus and calibration procedure

The ITMS tested in this study was the commercially available 835 Vacuum Quality Monitor (VQM), which runs simultaneously with the ion gauge Series 390 Micro-Ion, both manufactured by Granville-Phillips (MKS Instruments). Both were mounted on an all-metal UHV system, capable to achieve a base pressure of ~1 × 10^{-10} mbar, recorded by the inverted magnetron gauge (IMG Varian 524), Fig. 1. The ITMS was applied in the native ratiometric mode, as advised by the manufacturer. The option at which raw data would be recorded instead was not applicable in our case as the amount of data would exceed the capability of a standard desktop PC. The pumping system consisted of two turbo-molecular pumps in-line with the membrane pump as a fore pump. The preparation procedure, how to reach a low outgassing rate, was described in Ref. [6], with the exception that the bakeout was performed at 105 °C due to the limitations of ITMS's ion gauge.

The first part of the experiment comprised of the calibration of the ion gauge with three pure gases, while the ITMS was recording their ion fractions [12]. The selected gas was admitted to batch inlets 1 and 2 to reach the fill pressure of $p_{tot,0} = 0.01$ mbar. By opening the variable leak valve (VLV, model 951-51906 Varian), the capacitance manometer (CM, 0.05 mbar full scale, model 627BU5MCD1B, MKS) and the ion gauge recorded simultaneously the exponential pressure decay. Precisely known volume of the batch inlets ($V = 0.317$ L) enables calculation of the instant gas flux $Q(t)$, which generates $p_{tot}(t)$ over ~3 decades when leaking of the gas quantity $p \cdot V = 3.17 \times 10^{-3}$ mbar L takes about 4 min for hydrogen and ~15 min for argon. The variable leak valve conductance in each new cycle need not to be the same as in the previous one, as it is each time calculated anew by fitting of the pressure decreasing $p_{tot}(t)$ graph. In doing so, its stability, which is an important parameter, is also proved. The molecular flow regime during the whole gas flow range through the variable leak valve to the analytical chamber is preserved, due to the sufficiently low initial fill pressure in the batch inlets. 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, $\lambda/d > 5$.

We introduce a useful new parameter: the "apparent pumping speed" S_j for a particular gas from the basic formula, $S_j = Q_j/p_j$, where p_j is the uncorrected p_{tot} of the ion gauge for gas j and Q_j the corresponding flow rate. As time is eliminated from this correlation, S_j is expressed as the inverse slope of the p_j versus Q_j relation in each