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Absolute isotope amount ratio measurements on gases
Part I: Measurements of isotope amount ratios—Basic theory

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Abstract

A basic measurement model and corresponding measurement function for measuring isotope amount ratios on various gases is described and discussed, as the measurand is different from the one used in differential measurements (δ values).

Performed on similar types of 'hardware' (a gas isotope ratio mass spectrometer) Isotope Amount Ratio Measurements ('IARM') are not intended to replace the traditional (delta) isotope measurements but to complement them: providing "absolute" isotope amount ratio values when there is a need for them. The basic theory is discussed while in a subsequent paper, illustrations by experimental values will be described.

The measurement functions used in performing 'IARM' describe a transparent and metrologically traceable relationship between an isotope amount ratio of an element (the quantity intended to be measured i.e. the 'measurand') to its measured ion current ratio (the quantity subject to measurement), based on the gas flow dynamics in the gas inlet system of the mass spectrometer and due consideration of isotope fractionation effects.

Keywords: Isotope ratio mass spectrometry; Kinetic gas theory; Isotope amount ratios; SI-traceability

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1. Introduction

Molar mass values $M(\mathrm{E})$ (or mean relative atomic weights) of elements are determined at IRMM by measuring the isotopic composition of an element E (Eq. (1)) as for instance on Si in a near perfect ^{28}Si single crystal [1,2].

In general:

$$M(\mathrm{E}) = \sum f({}^{i}\mathrm{E})M({}^{i}\mathrm{E}) = \sum \left[\frac{R_{\mathrm{i/j}}({}^{i}\mathrm{E})}{\sum R_{\mathrm{i/j}}({}^{i}\mathrm{E})}\right] M({}^{i}\mathrm{E}) \qquad (1)$$

The 'quantity intended to be measured' (i.e., the measurand [23]) is R. The quantity *amount of substance*, or rather the *amount-of-substance ratio*, R, must be "absolute" in order to arrive at an 'absolute' value for the molar mass and an 'absolute' value for the Avogadro constant where the kilogram then would be defined as the mass of a fixed number N_{kg} of atoms ^{12}C. Since the factor to connect atomic mass standards with the macroscopic mass is the Avogadro constant, in a first step it has to determined within the framework of the SI with a relative uncertainty of 2×10^{-8}. For R-values to be 'absolute', they must have been 'calibrated' by means of synthetically prepared ratios embodied in synthetic mixtures of enriched isotopes. Molar mass values for various elements (Xe, C, S, etc.) have been determined at IRMM over the last decades in this way [3–5].

As an offshoot of the Avogadro project, another concept has gradually emerged: direct measurements of R under near-ideal gas conditions and measuring the 'degree of imperfectness' of the (measurement) procedure against values derived from kinetic gas theory [6] assuming gases behave as ideal. Central in both approaches is *not* the concept of measuring amount-of-substance, but of measuring *ratios* of amount-of-substance: observed ratio values are calibrated by means of measurements of synthesized amount ratios and it can be checked against kinetic gas theory. In addition, *measurement* is a comparison of an indication generated by an unknown value of a quantity to an indication generated by a known value of the same quantity, a measurement of amount-of-substance, hence that is always a measurement of a *ratio of amount-of-substance*, ultimately to

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the realization or embodiment of a known (sub-) multiple of the mole. The unit for this measurement is mol/mol i.e., 'one' symbol '1'. This unit is considered to be a base unit in the SI system. The knowledge gained from the measurements of silicon isotope amount ratios for a more accurate Avogadro constant, is consistent with that description of a measurement [7–9].

The procedure for measuring *R* values in near-ideal gas conditions, leads to a value for the Avogadro constant which is consistent in its interrelationship with other fundamental constants (Planck, Boltzmann, universal gas constant) to within 10^{-6} relative (this implies measurements of isotope amount ratios to 10^{-4} relative [1,2]).

The amount measurements needed in the pathway to the Avogadro constant [7–9], have enabled us to better understand the ratio character of any *amount* measurement (to the amount contained in one mole) as described above.

2. Measurements of isotope amount ratios

Measured isotope amount ratios are sensitive to effects in nature and, as a consequence, show (very) small variations. To measure these, ultra-high precision measurements are required. Fortunately, in most cases, valuable information can be obtained from the measurement of *differences* in isotope amount ratios and most of the related analytical instrumentation (mass spectrometers) has been developed accordingly [10–15].

Based on Nier's original configuration, more and more sophisticated 'delta' isotope ratio mass spectrometers (IRMS) were designed and built in the mass ranges needed and enabling to attain an impressive measurement precision and accuracy (of the δ values).

The method of 'absolute' isotope amount ratio measurements is basically different from usual δ-measurements because the measurand is different. Instead of concentrating on minimizing systematic errors (by cancellation processes) and assuring identical conditions in the mass spectrometer for reference and sample, the approach is to maximize, but know and control the isotope fractionation process in the molecular gas flow from the inlet system to the ion source. Therefore, the concept is to relate the dynamics of the ionization and subsequent measurement of the ion currents to known physical processes as well as to measure under extremely stable and known conditions.

In an 'absolute' isotope amount ratio gas mass spectrometer [4–8], ion currents arising from isotopically distinct molecules are measured using a single Faraday cup in peak jumping mode (in combination with different high ohmic resistors) and calculating mean ratios of measured ion currents, collected at well defined mass (to charge) positions [15,16]. These measurements are calibrated by means of synthesized isotope amount ratios.

During the measurement, the sample in the expansion vessel of the spectrometer changes in isotopic composition over time because the effusion out of the expansion vessel through the gold foil at the inlet of the spectrometer is mass dependent. Extrapolation of the ion current ratios measured to the start of the measurement ($t = 0$) is therefore required to determine the initial isotopic composition of the sample. One of the most sensitive parameters in such measurements is the gas flow with associated physical (and chemical) processes between the gas and the inlet system of the mass spectrometer. The resulting ultra-high precision ion current ratio measurements are very well suited for studying effects related to adsorption/desorption processes in the inlet system and for isotope exchange reactions at surfaces [17].

2.1. The gas mass spectrometer

Measurements are made using a Finnigan MAT 271 mass spectrometer modified at IRMM and named the "Avogadro II Amount Comparator". The modification was mandatory in order to attain a triple aim: more accurate isotope amount measurements over larger dynamic ranges with smaller measurement uncertainties. Basically, it is a conventional gas isotope ratio mass spectrometer with an electron impact ion source and a magnetic beam deflection. The detection system, originally only Faraday cups, was enlarged with an additional Secondary Electron Multiplier detector system, used for detection of small ion currents ($<10^{-13}$ A). Also, to expand the dynamic range of measured ratios, the detection chain was split into two different amplification channels. One stable ion current, being measured on the Faraday cup as well as on the SEM each with their own amplification channel, enables to connect the two measurement scales. The channels are usually measuring ion currents of very different magnitudes and a dynamic calibration against each other is inserted within the measurement. This arrangement enables to measure ion current ratios down to 10^{-6} (or currents down to 10^{-16} A) with measurement uncertainties of 10^{-3} relative and has led to significantly improved measurements of isotope amount ratios and molar mass values for several elements (e.g., Si, Pt, Kr, Xe) [3–8].

The unique part of this mass spectrometer is its inlet system. It consists of an inlet vessel (Fig. 1) with a volume of about 2 L, where the gaseous sample to be measured is introduced via a computer controlled valve system. When ion current ratios are measured on for instance CO_2, the vessel contains about 2×10^{18} CO_2 molecules, resulting in a total pressure of about 10 Pa. The gas sample is admitted from the vessel to the ionization chamber through a small aperture (15 holes) made in a thin gold foil (a "gold leak") each of about 20 μm diameter.

The mean free path λ of the gas molecules (Eq. (2)) is much larger than the molecular leak dimensions; the gas effusion pro-

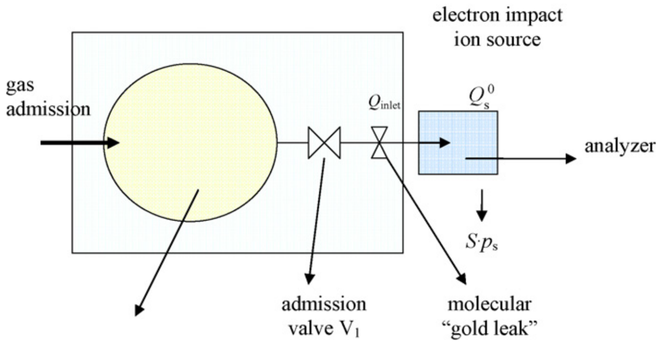

Fig. 1. Gas inlet system of the gas mass spectrometer.

cess from the expansion vessel through the gold foil to the ion source obeys in a first approximation kinetic gas theory:

$$\lambda = \frac{kT}{\sqrt{2}\pi P d_i^2} \tag{2}$$

k, Boltzmann constant = 1.380 $7 \times 10^{-23}\,\mathrm{J\,K^{-1}}$; $T = 75.0 \pm 0.1\,°\mathrm{C} = 348.0 \pm 0.1\,\mathrm{K}$, the temperature of the entire inlet system; $P = 10\,\mathrm{Pa}$, inlet pressure but depending of the gas type; d_i: diameter of the gas molecule (exemplified for a CO_2 molecule $\approx 3 \times 10^{-8}$ cm).

As can be seen, the mean free path λ is at least two orders of magnitude larger than the diameter of the holes in the gold foil. Therefore it can be stated that the gas flow to the ion source is mainly of molecular nature. Its degree of imperfection (i.e., a possible small viscous contribution, adsorption, etc.) was subject of an earlier study [14,17] which has shown proof that this effect is within measurement uncertainty.

The isotope ratio measurements are performed in a peak-jumping mode, built-up in a symmetrical sequence to enable corrections for time drift. Thus all ion currents are detected at exactly the same moment. The software is treating the data such that all corrections are applied at exactly the same time of measurement.

2.2. Gas dynamics in the MAT271 mass spectrometer

In the mass spectrometer, complete molecular gas flow conditions from the inlet system to the ion source ionization chamber through the 'gold leak' have been demonstrated for particular gases. For each ion current measurement only a small part of the gas is ionized and used for the measurement, whilst the major part is pumped off by the pumps on the analyzer system. This implies that the gas in the ion source and in the inlet vessel (Fig. 1) behaves under *dynamic* conditions. Under these circumstances and using vacuum science terminology we will use the basic concept 'gas throughput' Q (equivalent of the flow rate in vacuum terminology) which can be defined as $Q = p\mathrm{d}V/\mathrm{d}t$. The gas dynamics for the ion source can then be expressed as the difference between the gas input – gas throughput from the inlet vessel through the 'gold foil' (Q_{inlet}) with an additional but small contribution from adsorption/desorption process at the surfaces (Q_s^0) and the gas output – gas pumped off from the ion source at a flow rate Sp_{s} (S being the pumping speed parameter and p_{s} the pressure in the ion source):

$$\frac{\mathrm{d}(V_{\mathrm{s}}p_{\mathrm{s}})}{\mathrm{d}t} = V_{\mathrm{s}}\frac{\mathrm{d}(p_{\mathrm{s}})}{\mathrm{d}t} = Q_{\mathrm{inlet}} + Q_{\mathrm{s}}^0 - Sp_{\mathrm{s}} \tag{3}$$

where V_{s} is the volume of the ionization box inside the ion source ($V_{\mathrm{s}} = 2\,\mathrm{mL}$); p_{s} is the partial pressure in the ionization box of the ion source, gradually decreasing from 10^{-6} to 10^{-4} Pa during the measurement. Q_{inlet} is the gas throughput from inlet system vessel through the holes in the gold foil.

It must be pointed out that the pumping speed parameter S (in the molecular flow range) is inversely proportional to the square root of the molar mass of the gas pumped. Because the amount of ionized gas is too small ($\ll 0.1\%$) when compared to the other parameters, its contribution to Eq. (3) is neglected: its size it has no significance on the balance.

A similar equation (Eq. (4)) can be set up for the inlet reservoir (Fig. 1). Here, the balance equation is the relation between gas effusing via the 'gold leak' and gas entering via desorption from the inner surface. Over the years, large efforts have been made to inhibit adsorption/desorption by electro-polishing the inner surface of the inlet system, made of high purity stainless steel. During operation, the inlet system is kept at $(75.0 \pm 0.1)\,°\mathrm{C}$. Hence, the equation for the gas dynamics in the inlet reservoir can be expressed as:

$$\frac{\mathrm{d}(V_{\mathrm{inlet}}p_{\mathrm{inlet}})}{\mathrm{d}t} = V_{\mathrm{inlet}}\frac{\mathrm{d}p_{\mathrm{inlet}}}{\mathrm{d}t} = -Q_{\mathrm{inlet}} + Q_{\mathrm{inlet}}^0 \tag{4}$$

with V_{inlet}, the volume of the inlet reservoir (2 L); p_{inlet}, partial pressure of the gas in the vessel (at time t), decreasing in time during the measurement; Q_{inlet}^0, gas released by desorption processes in the inlet vessel.

The quantity Q_{inlet} in both Eqs. (3) and (4), although of opposite signs, refers to the flow rate of the gas leaving the inlet reservoir to the ion source. Both equations are valid for the entire period of measurement, independent of the gas type or of the inlet parameters, as long as admission valve V_1 (Fig. 1) is open and there is still gas left in the inlet vessel.

In the absence of any gas in the vessel and, hence, lack of any gas flow to the ion source (designated as 'background' measurement experiment), Eqs. (3) and (4) can be considered as describing a 'steady-state' condition in the inlet vessel; gas effusion to the ion source ionization chamber is caused by desorption processes on the inlet vessel surface: $Q_{\mathrm{inlet}}^{\mathrm{backg}} = Q_{\mathrm{inlet}}^0$ or steady-state condition obeyed in Eq. (4), which changes Eq. (3) into Eq. (5):

$$V_{\mathrm{s}}\frac{\mathrm{d}p_{\mathrm{backg}}}{\mathrm{d}t} = Q_{\mathrm{s}}^0 + Q_{\mathrm{inlet}}^0 - Sp_{\mathrm{backg}} \tag{5}$$

with p_{backg} the background pressure in the ion source ($\approx 10^{-6}$ Pa).

The background equation (Eq. (5)) could be a matter for discussion, especially because of the way the desorption term Q_{inlet}^0 is treated. Assumed here is that the gas desorbed, i.e., is independent of the residual gas pressure in the inlet vessel and that Q_{inlet}^0 is identical in Eqs. (4) and (5). Experiments however have shown that this assumption is not entirely correct but via calibrations against synthetic isotope mixtures all such (small) systematic effects of unknown origin ($<10^{-5}$ rel on the amount ratio) will be corrected.

Much work has been done in the past on adsorption/desorption processes in the inlet reservoir [16–22]. However a general treatment has not (yet) been achieved. In a first approximation, it can be assumed that the desorption term is constant over small pressure ranges. A same reason is appropriate for the adsorption/desorption term in the ionization box ($T = 175\,°\mathrm{C}$ and pressure 10^{-4} Pa); under these circumstances the adsorption/desorption process is reduced so much as to have negligible effect.

Introducing Eqs. (4) and (5) in Eq. (3) will give the *basic equation* for the gas dynamics between inlet vessel and ionization box in terms of partial pressures:

$$V_{\text{s}}\left[\frac{\mathrm{d}p_{\text{s}}}{\mathrm{d}t}-\frac{\mathrm{d}p_{\text{backg}}}{\mathrm{d}t}\right]=-V_{\text{inlet}}\frac{\mathrm{d}p_{\text{inlet}}}{\mathrm{d}t}-S(p_{\text{s}}-p_{\text{backg}}) \qquad (6)$$

It is well-known that the ideal gas law (Boltzmann) is perfectly applicable at working conditions of the spectrometer: i.e., pressure ranges between 10 and 10^{-6} Pa and temperatures ranges from 100 to 180 °C:

$$\eta_{\text{inlet}}=\frac{N_{\text{inlet}}}{V_{\text{inlet}}}=\frac{n_{\text{inlet}}N_{\text{A}}}{V_{\text{inlet}}}=\frac{p_{\text{inlet}}}{kT_{\text{inlet}}} \qquad (7)$$

with η_{inlet} being the number density, N_{inlet} the number of gas molecules present at a given moment in the vessel volume V_{inlet}, k the Boltzmann constant, T_{inlet} and p_{inlet} respectively the temperature and the pressure, and n_{inlet} the moles of the gas.

A similar relationship is valid for the ion source:

$$\eta_{\text{s}}=\frac{N_{\text{s}}}{V_{\text{s}}}=\frac{n_{\text{s}}N_{\text{A}}}{V_{\text{s}}}=\frac{p_{\text{s}}}{kT_{\text{s}}} \qquad (8)$$

By introducing Eq. (8) in Eq. (6) it can be modified as:

$$T_{\text{s}}\left(\frac{\mathrm{d}(n_{\text{s}})}{\mathrm{d}t}-\frac{\mathrm{d}(n_{\text{backg}})}{\mathrm{d}t}\right)=-T_{\text{inlet}}\frac{\mathrm{d}(n_{\text{inlet}})}{\mathrm{d}t}-\frac{S}{V_{\text{s}}}T_{\text{s}}(n_{\text{s}}-n_{\text{backg}}) \qquad (9)$$

It was noticed that Eq. (9) does not involve any measured quantity such as ion currents; therefore this equation is of minor importance i.e., it is only a relation between the two compartments (inlet and ion source). Nevertheless the ion currents measured are directly proportional to the amount n_{s} (in mol) present in the ionization chamber with proportionality factor called the ionization efficiency, ε_{eff}. Assuming further that the ionization efficiency is mass *independent*, Eq. (9) becomes:

$$\frac{T_{\text{s}}}{\varepsilon_{\text{eff}}}\frac{\mathrm{d}(I-I_{\text{backg}})}{\mathrm{d}t}=-T_{\text{inlet}}\frac{\mathrm{d}(n_{\text{inlet}})}{\mathrm{d}t}-\frac{S}{V_{\text{s}}}\frac{T_{\text{s}}}{\varepsilon_{\text{eff}}}(I-I_{\text{backg}}) \qquad (10)$$

with I and I_{backg} being the ion currents measured for sample and background, respectively.

Eq. (10) relates the quantity measured – ion currents – to the quantity which *is intended* to be measured. The equation however cannot be used in its primary form because of the large number of quantities that require measurement. Therefore conductance C is introduced and defined in vacuum terminology as a measure (expressed in L s^{-1}) of the flow rate of a gas through a given flow geometry created by a pressure difference:

$$C=\frac{Q}{\Delta p}$$

Eq. (4) can be re-written as:

$$Q_{\text{inlet}}-Q^{0}_{\text{inlet}}=C_{''\text{gold leak}''}(p_{\text{inlet}}-p_{\text{s}})=-V_{\text{inlet}}\frac{\mathrm{d}(p_{\text{inlet}})}{\mathrm{d}t} \qquad (11)$$

where Q_{inlet} has been replaced by the product of the conductance of the 'gold leak' and the pressure difference across it. A similar equation can be written for the case of absence of any gas in the inlet reservoir, with $C_{\text{gold leak}}$ being the conductance of the aperture in the gold foil:

$$Q^{0}_{\text{inlet}}=C_{\text{gold leak}}(p_{\text{bg inlet}}-p_{\text{s}}) \qquad (12)$$

where $p_{\text{bg inlet}}$ is the pressure in the inlet reservoir without gas (background level) and released only by desorbing from the surfaces.

According to Eqs. (11) and (12), a typical equation for the inlet vessel with gold leak can be given:

$$C_{\text{gold leak}}(p_{\text{inlet}}-p_{\text{bg inlet}})=-V_{\text{inlet}}\frac{\mathrm{d}(p_{\text{inlet}})}{\mathrm{d}t} \qquad (13)$$

Assuming 'pure molecular' gas flow conditions (i.e., complete absence of viscous flow) in the inlet system, the conductance is proportional to $\sqrt{T_{\text{inlet}}/M}$ (Knudsen law) with T_{inlet} and M respectively temperature and molar mass of the gas, and C_0 a proportionality constant depending on the geometry of the gold leak but independent of any type of gas:

$$C_{\text{gold leak}}=C_0\sqrt{\frac{T_{\text{inlet}}}{M}}$$

Therefore Eq. (13) becomes:

$$-V_{\text{inlet}}\frac{\mathrm{d}(p_{\text{inlet}})}{\mathrm{d}t}=C_0\sqrt{\frac{T_{\text{inlet}}}{M}}(p_{\text{inlet}}-p_{\text{bg inlet}}) \qquad (14)$$

Applying the Boltzmann relationship, Eq. (14) becomes

$$-\frac{\mathrm{d}(n_{\text{inlet}})}{\mathrm{d}t}=\frac{C_0}{V_{\text{inlet}}}\sqrt{\frac{T_{\text{inlet}}}{M}}(n_{\text{inlet}}-n_{\text{bg inlet}}) \qquad (15)$$

For the background experiment, steady-state conditions have been considered in the inlet vessel and therefore the following relationship is valid:

$$-\frac{\mathrm{d}(n_{\text{inlet}})}{\mathrm{d}t}=-\frac{\mathrm{d}(n_{\text{inlet}}-n_{\text{bg inlet}})}{\mathrm{d}t} \qquad (16)$$

Substituting Eq. (16) in Eq. (15), a differential equation is obtained, which has a straightforward solution:

$$\ln\frac{(n_{\text{inlet}\,t}-n_{\text{bg inlet}\,t})}{(n_{\text{inlet}\,t0}-n_{\text{bg inlet}\,t0})}=-\frac{C_0}{V_{\text{inlet}}}\sqrt{\frac{T_{\text{inlet}}}{M}}t \qquad (17)$$

By substituting Eq. (15) into Eq. (10), a relationship between the amount of gas present in the vessel and its measured ion currents can be obtained:

$$\frac{T_{\text{s}}}{\varepsilon_{\text{eff}}}\frac{\mathrm{d}(I-I_{\text{backg}})}{\mathrm{d}t}=\frac{C_0}{V_{\text{inlet}}}T_{\text{inlet}}\sqrt{\frac{T_{\text{inlet}}}{M}}(n_{\text{inlet}}-n_{\text{bg inlet}})-\frac{S}{V_{\text{s}}}\frac{T_{\text{s}}}{\varepsilon_{\text{eff}}}(I-I_{\text{backg}}) \qquad (18)$$

The majority of pumping systems are operating at molecular flow conditions and have pumping speeds S which are obeying the Knudsen law and are therefore proportional to $\sqrt{1/M}$ and to the temperature of the gas; this is also the case for turbomolecular pumping systems:

$$S = S_0\sqrt{\frac{1}{M}} \tag{19}$$

S_0 is constant for a pressure range varying from 10^{-3} to 10^{-7} Pa, however determined by the diameter of the flange at the pump. Introducing Eq. (19) in Eq. (18) yields:

$$(n_{\text{inlet}} - n_{\text{bg inlet}}) = \frac{V_{\text{inlet}}}{C_0}\sqrt{\frac{M}{T_{\text{inlet}}}}\frac{T_{\text{s}}}{T_{\text{inlet}}\varepsilon_{\text{eff}}} \times \left[\frac{\mathrm{d}(I - I_{\text{backg}})}{\mathrm{d}t} + \frac{S_0}{V_{\text{s}}}\frac{1}{\sqrt{M}}(I - I_{\text{backg}})\right] \tag{20}$$

From Eq. (20), the amount of gas in the vessel can be calculated at any time during the measurement via measurements of the ion currents at the collector system. In order to estimate the magnitude of $\mathrm{d}(I - I_{\text{backg}})/\mathrm{d}t$ and $S_0/V_{\text{s}}1/\sqrt{M}(I - I_{\text{backg}})$ in Eq. (20), the pumping parameter S_0/V_{s} was determined experimentally. During the measurement, the admission valve V_1 (Fig. 1) was closed promptly preventing that any gas would be subject to measurement. In this specific case Eq. (3) can be transformed to:

$$V_{\text{s}}\frac{\mathrm{d}(p_{\text{s}})}{\mathrm{d}t} = Q_{\text{s}}^0 - Sp_{\text{s}} \tag{21}$$

or after Boltzmann:

$$\frac{\mathrm{d}I}{\mathrm{d}t} = \frac{Q_{\text{s}}^0\varepsilon_{\text{eff}}}{N_{\text{A}}kT_{\text{s}}} - \frac{S_0}{\sqrt{M}V_{\text{s}}}I$$

or:

$$I = I_0\mathrm{e}^{-S_0/(\sqrt{M}V_{\text{s}})t} + \frac{Q_{\text{s}}^0\varepsilon_{\text{eff}}\sqrt{M}V_{\text{s}}}{S_0N_{\text{A}}kT_{\text{s}}} \tag{22}$$

where the ion current I_0 is the current immediately after closing valve V_1 (Fig. 1), i.e., at time $t=0$.

To measure the order of magnitude of the pumping characteristic S_0/V_{s}, the ion currents $I\,[^{44}(\mathrm{CO_2})^+]$ and $I\,[^{45}(\mathrm{CO_2})^+]$ were measured on $\mathrm{CO_2}$. After $\mathrm{CO_2}$ admission to the ion source, an ion current of 10^{-10} A was observed (via a 10^{11} Ω resistor). At time $t=0$, valve V_1 was closed and the decrease of the electric currents carefully measured over time (Fig. 2). The measured data have been treated via a 'non-linear least square regression'. Applying Eq. (22) that results in:

$$I = I_0\exp(-\beta_1 t) + \beta_2 \tag{23}$$

β_1 and β_2 have been obtained by a direct measurement of S_0/V_{s} hence a value for $\beta_1 = S_0/\sqrt{M}V_{\text{s}} = 0.9982\ \mathrm{s}^{-1}$ was obtained.

Applying S_0/V_{s} obtained for $\mathrm{CO_2}$ to Eq. (20), it is demonstrated that d $(I - I_{\text{backg}})/\mathrm{d}t$ is about five orders of magnitude smaller than $[(S_0/V)(1/\sqrt{M})](I - I_{\text{backg}})$, enabling it to be negligible in Eq. (20) (exemplified in Fig. 2).

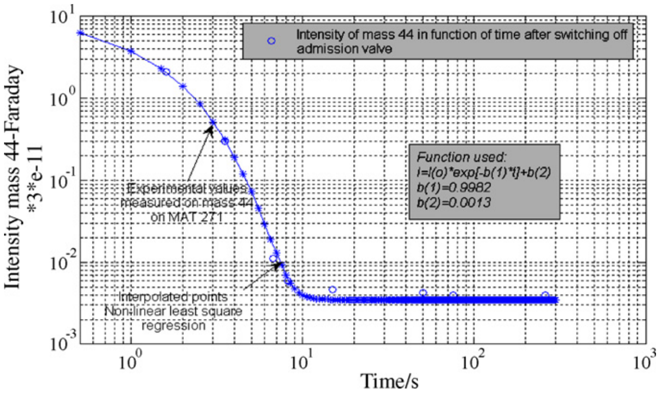

Fig. 2. Ion currents $I\,[^{44}(\mathrm{CO_2})^+]$ as a function of time (in s), after valve V_1 to the ion source was closed; the pumping characteristic S_0/V_{s} was calculated, applying a non-linear least squares fitting.

The expression d $(I - I_{\text{backg}})/\mathrm{d}t$ in Eq. (20) is therefore not more then a small correction for deviation from steady-state condition of the gas pressure in the ion source, it can however not be rejected as the collection time is about 8000 s (Fig. 3).

The variation of isotope amount ratio with time for a gas consisting of two isotopes (and applying Eq. (20)) can now be given as:

$$R_{\text{inlet}}(t) = \frac{n_2(t) - n_{\text{bg}(t)}}{n_1(t) - n_{\text{bg}(t)}} = \sqrt{\frac{M_2}{M_1}}\frac{(\mathrm{d}(I_{2(t)} - I_2^{\text{backg}(t)})/\mathrm{d}t) + (S_0/V_{\text{s}})(1/\sqrt{M_2})(I_{2(t)} - I_2^{\text{backg}(t)})}{(\mathrm{d}(I_{1(t)} - I_1^{\text{backg}(t)})/\mathrm{d}t) + (S_0/V_{\text{s}})(1/\sqrt{M_1})(I_{1(t)} - I_1^{\text{backg}(t)})} \tag{24}$$

where I_1 and I_2 are the ion currents measured for the two isotopes.

Eq. (24) enables treating the measured ion currents in such a way that those 'absolute' isotope amount ratios can be obtained directly. This relationship (Eq. (24)) is valid at any point in time during the measurement and therefore the extrapolation to time $t=0$ gives the original isotope amount ratio of the sample, corrected for the isotope fractionation which took place permanently *during* the entire measurement.

It is useful to remind that measuring an absolute molar mass value (hence an absolute amount-of-substance ratio), is a real challenge as these values are continuously changing during the

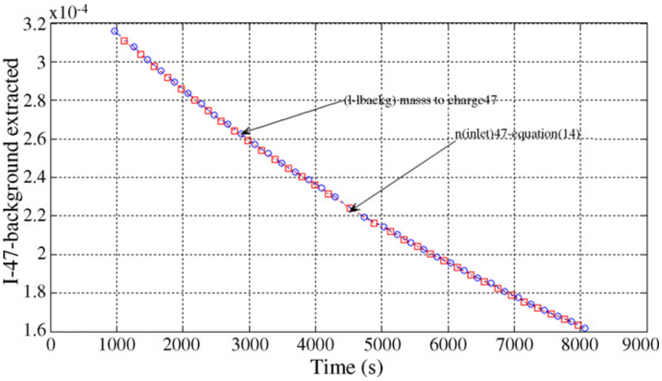

Fig. 3. The ion current $I\,[^{47}(\mathrm{CO_2})^+]$ measured over time (s): the small circles are measured ion currents (corrected for background), squares are calculations of $n[^{47}(\mathrm{CO_2})]$ (in mol.) at various times in the inlet vessel applying Eq. (20).

measurement itself and caused by the very act of measuring. In fact, at the moment the measurement is started, the measured value for the measurand is already different from the value of the measurand intended to be measured.

The isotope fractionation effect created by the molecular effusion process alters the isotopic composition of the remaining gas in the expansion vessel (Fig. 1) over time. This variation has been expressed in Eq. (17). It can be re-written in its exponentional form:

$$n_{\text{inlet}} - n_{\text{backg}} = (n_{\text{inlet}} - n_{\text{backg}})_{t0}\,\mathrm{e}^{-(C_0\sqrt{T_{\text{inlet}}})/(V_{\text{inlet}}\sqrt{M}t)} \tag{25}$$

As Eq. (25) only concerns the processes which take place in the inlet vessel and at the gold-leak, it has no physical link to the measured ion currents; in Eq. (24) it does. Hence, introducing Eq. (25) in Eq. (24) yields:

$$\sqrt{\frac{M_2}{M_1}}\,\frac{(\mathrm{d}(I_2(t) - I^{\text{backg}}(t))/\mathrm{d}t) + (S_0/V_\text{s})(1/\sqrt{M_2})[I_2(t) - I^{\text{backg}}(t)]}{(\mathrm{d}(I_1(t) - I^{\text{backg}}(t))/\mathrm{d}t) + (S_0/V_\text{s})(1/\sqrt{M_1})[I_1(t) - I^{\text{backg}}(t)]} = R_{\text{inlet}}(t) = \frac{n_2(t) - n_{\text{backg}}(t)}{n_1(t) - n_{\text{backg}}(t)}$$

or

$$R_{\text{inlet}}(t) = \frac{n_2(t_0) - n_{\text{backg}}(t_0)}{n_1(t_0) - n_{\text{backg}}(t_0)} \times \mathrm{e}^{-C_0(\sqrt{T_{\text{inlet}}})/V_{\text{inlet}}((1/\sqrt{M_2})-(1/\sqrt{M_1}))t} \tag{26}$$

or in logarithmic form:

$$\ln\left\{\sqrt{\frac{M_2}{M_1}}\,\frac{(\mathrm{d}(I_2(t) - I^{\text{backg}}(t))/\mathrm{d}t) + (S_0/V_\text{s})(1/\sqrt{M_2})[I_2(t) - I^{\text{backg}}(t)]}{(\mathrm{d}(I_1(t) - I^{\text{backg}}(t))/\mathrm{d}t) + (S_0/V_\text{s})(1/\sqrt{M_1})[I_1(t) - I^{\text{backg}}(t)]}\right\} = \ln[R^0_{\text{inlet}}] + \left[\frac{C_0\sqrt{T_{\text{inlet}}}}{V_{\text{inlet}}}\left(\frac{1}{\sqrt{M_1}} - \frac{1}{\sqrt{M_2}}\right)\right]t \tag{27}$$

Eq. (27) gives the full mathematical link between the measured ion current ratio and the initial isotope amount ratio in the inlet vessel at time $t = 0$. When explicated for R^0_{inlet}, it is the measured function as defined in the VIM [23]. Applying the linear time dependency of the right term in Eq. (26), an extrapolation to $t = 0$ will yield the initial isotope amount ratio of the sample in the inlet vessel. Taking into account that the mass spectrometer is measuring ion currents in a dissimilar time sequence, even over several hours, Eq. (27) is highly suitable for treating the data. A least square fitting in Eq. (27) will yield the original isotope amount ratio R^0_{inlet} in the gaseous sample. The slope is the quantitative proof that the measurement is dependent on the molar mass of the isotopes in the gas concerned.

The relationship in Eq. (27) is however subject to some supplementary assumptions:

- *pure* molecular gas flow conditions to the ion source are required;
- ionization efficiency is assumed to be identical for all isotopomers involved;
- with an empty inlet vessel (as required for the background measurements), gas flow conditions are supposed to be in ‘steady-state’ condition;
- stable temperature conditions are required in the source and in the inlet vessel;
- the isotope fractionation effects during *fragmentation* in the ion source need additional study, and are not yet taken into account;
- adsorption/desorption processes were supposed to be pressure independent, by assuming the relative small difference between an empty and a filled expansion vessel (a few Pa);
- for more complex gas molecules, potential ion-molecule reactions inside the ion source could disturb the ion current ratios measured; specific procedures have been developed for every particular case; they make the mathematical model developed in this paper even more complex.

All these assumptions could introduce small deviations from the mathematical model discussed in detail in this paper and could affect the measurement results. Hence, to quantify these *unknown systematic effects*, a calibration of the mass spectrometer through synthetically prepared mixtures of enriched isotopes (gravimetry) is required in order to obtain an ‘individual’ correction factor K for each measured ion current ratio. Thus absolute isotope amount ratios can be obtained, achieving metrological traceability [23] to the derived SI unit mol/mol. This will be the subject of another paper [24].

3. Conclusion

The measurement procedure to obtain “absolute” isotope amount ratio values as described in this paper is based on an established measurement procedure in the field of isotope research. In that prospect it was not the intention of this paper to search for new potential applications, but to explain in full detail the mathematical and physical backgrounds which underpin an ‘absolute’ isotope amount ratio measurement procedure. The basic theory is discussed while in a subsequent paper, illustrations by experimental values are described [24].

Through the application of gas kinetic concepts governing isotope fractionation of a gas (consisting of several isotopes) in the spectrometer, and subsequently by a calibration by means of synthetic isotope mixtures (Primary Measurement Standards for this measurand), it could be demonstrated that SI-traceable values in terms of the derived measurement unit mol/mol can be obtained.

The entire theoretical treatment which is the *keystone* of this type of measurement is based on pure physical principles with only minor assumptions, but the effects of which must be thoroughly evaluated and, eventually, taken into account.

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