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Abstract

A new model to describe the gas flow status inside the gas mass spectrometer (MAT271) inlet system has been developed and applied to the latest isotope amount ratio measurements. Starting from the consideration that the gaseous sample flow in the inlet system towards the ion source is a major contributor to the total combined uncertainty on gaseous isotope amount ratio measurements, especially for this particular instrument. The theoretical model elaborated here assumes a transitional flow regime - a mixing between molecular and viscous flow - and defines a mathematical procedure for treatment of the measurement data in order to quantify the viscous flow contribution in the gas flow. The model is entirely suited for the highly specific working conditions in this instrument being an IRMM modified MAT 271 IRMS to perform absolute isotope amount ratio measurements on gas sample. This model could be also applied to data obtained from other IRMS instruments with adequate adaptations. This quantification of the imperfectness of the gas flow to the ion source is materialized as a "viscous factor" and will affect as a correction directed to the data treatment for all isotope amount ratio measurements performed via this instrument.
A validation of the elaborated model has been demonstrated to a series of CO_2 measurements in calculating the isotope amount ratios of carbon and oxygen from measurements of the ion current ratios. These results obtained are discussed in the paper.

Introduction

The Avogadro II Amount Comparator inlet consists of a spherical reservoir having a volume of two liters (Fig.1). When performing ion current ratio measurements on CO_2 by means of this machine, the vessel is filled with about $2 \cdot 10^{17}$ molecules of CO_2 resulting to a total pressure in the vessel of about 1 Pa [1,2].

The gas effusion process of the CO_2 molecules from the vessel through the gold foil to the ion sources obeys kinetic gas theory, with a mean free path λ in the range much larger than the molecular leak dimensions. This molecular leak consists of 15 holes made by a laser beam through the foil. The diameter of the holes is about 20 μm, to be compared with the mean free path of the CO_2 molecules in the inlet. While in the apparatus the pressure is measured, the mean-free path values on the low pressure side of the gold leak pinholes can be calculated:

$$\lambda = \frac{k \cdot T}{\sqrt{2} \cdot \pi \cdot P \cdot d_i^{\,2}} \quad = 1.2 \text{ cm} \qquad [1]$$

k = Boltzmann Constant = $1.380\,7 \cdot 10^{-23}$ J·K^{-1}
T = 75^0C = 348 K
P = 1 Pa
d_i = diameter of a CO_2 molecule ≈ $3 \cdot 10^{-8}$ cm

For the case of CO_2 molecules existing in the expansion vessel of the mass spectrometer, the ratio of the diameter d_i of the CO_2 molecules to the length of the holes L_h (about 30 μm), $\frac{d_i}{L_h}$ is of the order of 10^{-5} and the proportion of the molecules that bounce off the entrance to the pinholes can be neglected. Since the gold foil has a thickness of the same order as L_h, and also as the geometry of the holes are not really known, there could be a lingering suspicion that we are dealing in an effect with diffusion down the tube (connection of the expansion vessel to the ion source) where the flow regime is of an imperfect molecular flow (while minor viscous flow conditions take place as well) and where a small part of the inelastic wall collisions could be a significant source of uncertainty and so has to be verified [3,4]. In order to correct the measurements for mass fractionations effects taking place during sample inlet, and so apply kinetic gas theory to the observed ion current ratios, one has to be

sure that the change from viscous to molecular flow at the pinholes in the gold foil through which the molecules effuse into the spectrometer, is complete. Traces of viscous flow conditions in the molecular flow during this effusion would falsify the extrapolation of the measurement results back time $t = t_o$, the time at which the sample starts to leak into the ion source. Such an extrapolation is necessary to determine the initial isotopic composition of the sample [5,6].

The ultra-high precise ion current ratio measurements made by this instrument however are of such high quality that they allow calculating the viscous flow contribution in the molecular flow, which makes it able to correct for it when there is a need for.

Theoretical background

In the most general case, the dynamic conditions of a given molecule with isotopic species *i*, at the inlet system across the low pressure side of the gold membrane at the exit of the expansion vessel of the mass spectrometer (to prevent a too fast gas release from it) to its ion source, could be a combination of molecular and viscous gas flow conditions (Fig. 1).

Considering a gas pressure in the expansion vessel of about 1 Pa at a temperature $T = 75^oC$, the mean free path λ of the molecules effusing from the vessel into the ion source is in the range of a few centimeters, i.e. about three orders of magnitude larger than the diameter (20 μm) of the 15 holes in the gold foil. Therefore, there it can be assumed that the gas flow to the ion source is essentially of molecular origin and the presence of the viscous component is rather unlikely.

For the exact calculations of λ it must be considered that due to the roundness imperfections of the holes (laser beam made), a correct determination of their differing diameters is rather difficult. Therefore when isotope amount ratio measurement results performed on similar mass spectrometers (as on the Avogadro II and III amount comparator) are compared to each other, an experimental proof of the gas flow features in the inlet system must be considered, because of the different mean free paths (and of pumping speeds).

Roughly said, the inlet system of the Avogadro II Amount Comparator consists of 2 L spherical storage vessel (Fig.1) made of stainless steel, the gold membrane with 15 holes and a further circular channel until the ionization chamber ($P_2 \sim 10^{-6}$ Pa).

Prior to admission the gas to mass spectrometer, the expansion vessel ($T = 75^0C$ = 348K) is filled to a pressure P_1 of about 0.5 Pa (exactly measured by means of a membrane manometer) yielding an amount of gas sufficient for one CO_2 ion current ratio measurement lasting about 1.5 hours. Temperature and pressure readings are controlled by a carefully laid-out data-acquisition system built up for the re-determination of the Avogadro constant.

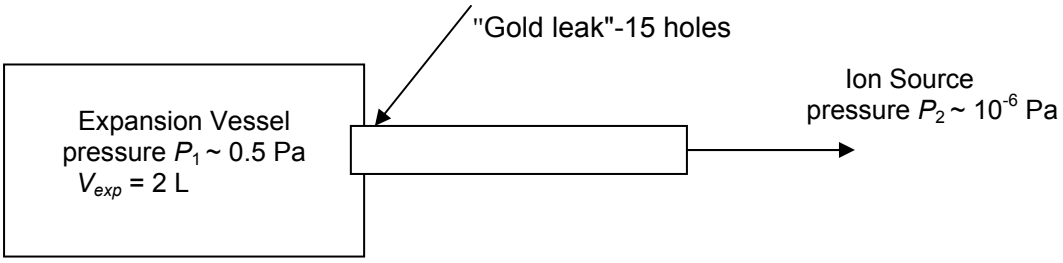

Fig.1: Schematic show of the inlet system

The adequate abstract concept that describes the gas flow dynamics when evacuating a fixed volume *V* in such a relative simple vacuum system is given by the throughput value Q of the gas flow effusing from the expansion vessel into the ion source:

$$Q = \frac{d(P \cdot V_{exp})}{dt} = V_{exp} \cdot \frac{dP}{dt} = C \cdot (P_2 - P_1) \qquad [2]$$

C is the conductance value (expressed in $m^3 \cdot s^{-1}$ or $L \cdot sec^{-1}$) under molecular flow conditions and is defined as a measure of ease with which *abstract volumes* can pass from one place in a vacuum system to another place due to a pressure difference, in this specific case between P_1 and P_2 (Fig. 1) values and expressed in $L \cdot sec^{-1}$. The throughput value *Q* is defined as a measure of the gas flow rate (in $Pa \cdot L \cdot sec^{-1}$). When considering ideal gas [7,8] behavior in the expansion vessel, is the pressure *P* in the vessel:

$$P = \frac{n \cdot R \cdot T}{V} = \frac{n \cdot R \cdot T \cdot N_A}{V_{exp} \cdot N_A} = \eta \cdot k \cdot T \qquad [3]$$

n = number of moles gas in the vessel (≈ $5 \cdot 10^{12}$ moles$\cdot cm^{-3}$)
R = molar gas constant = 8.314 47 $J \cdot mol^{-1} \cdot K^{-1}$
N = number of molecules in the vessel (≈ $2 \cdot 10^{14}$ molecules$\cdot cm^{-3}$)
N_A = Avogadro constant = $6.022\ 136\ 7 \cdot 10^{23}$ mol^{-1}
k = Boltzmann Constant = $\frac{R}{N_A}$ = $1.380\ 7 \cdot 10^{-23}$ $J \cdot K^{-1}$
η = number density = $\frac{N}{V_{exp}} = \frac{n \cdot N_A}{V_{exp}}$

In this way equation [2] can be re-written as:

$$Q = V_{exp} \cdot \frac{dP}{dt} = V_{exp} \cdot k \cdot T \cdot \frac{d\eta}{dt} = -C \cdot P$$

or

$$\frac{d\eta}{dt} = -\frac{C}{V_{exp} \cdot k \cdot T} \cdot P = -\frac{C}{V_{exp}} \cdot \eta = -\beta \cdot \eta \qquad [4]$$

Because the pressure in the expansion vessel of the spectrometer (P_1) is in the order of 1 Pa, so much larger than the ion source pressure ($P_2 < 10^{-6}$ Pa), their difference ($P_2 - P_1$) ≅ - P_1 ≅ - *P*. β is the proportionality factor between the release of gas molecule from the vessel and the gas amount present in the vessel [9].

For regular shapes of inlet systems as in the Avogadro II Amount Comparator with gas under molecular flow conditions, the total conductance *C* of the whole inlet is obtained by addition of the conductance of the gold leak (C_{leak}) and the conductance of the channel ($C_{channel}$):

$$\frac{1}{C} = \frac{1}{C_{leak}} + \frac{1}{C_{channel}} = \frac{C_{leak} + C_{channel}}{C_{leak} \cdot C_{channel}} \qquad [5]$$

Substitution of equation [5] in [4] gives:

$$\frac{d\eta}{dt} = -\frac{1}{V} \cdot \frac{C_{leak} \cdot C_{channel}}{C_{leak} + C_{channel}} \cdot \eta \qquad [6]$$

Where C_{leak} is in equation [7] the molecular flow conductance of the gold membrane, with S_1 the total area (total surface of the 15 holes) of the aperture ($4.71 \cdot 10^{-5}$ cm^2), *T* and $M_{(CO2)}$ respectively the temperature and the molar mass of the CO_2 gas in the expansion vessel.

$$C_{leak} = 3.64 \cdot S_1 \cdot \left(\frac{T}{M}\right)^{1/2} \qquad [7]$$

In equation [8] is the conductance $C_{channel}$ of the tube between the expansion vessel and the ion source (Fig. 1) calculated, with S_2 the aperture diameter of the tube, D_2 the diameter (0.3 cm) and *L* the length (10 cm) of the tube.

$$C_{channel} = 6.18 \cdot \frac{S_2^2}{D_2 \cdot L} \cdot \left(\frac{T}{M}\right)^{1/2} \qquad [8]$$

Introducing equation [7] and [8] in [6] gives:

$$\left(\frac{d\eta}{dt}\right)_{mol} = -\frac{22.495\cdot\left(\frac{T}{M}\right)^{1/2}\cdot S_2^2}{V\cdot(3.64\cdot S_1\cdot D_2\cdot L + 6.18\cdot S_2^2)}\cdot\eta = -\beta_{mol}\cdot\eta \qquad [9]$$

As it is demonstrated by equation [9], the molecular flow regime in the gas inlet system of the Avogadro II Amount Comparator or the speed at which the gas concentration ($d\eta/dt$) decreases in the vessel (Fig.1), is proportional to the gas concentration in the vessel (number density η) at any time and a proportionality factor being a function of the molar mass of the gas in the vessel, of the temperature in the inlet system (T = 75 ± 0.1 ^{0}C) and of the geometry of the entire inlet system.

The equation for the conductance of viscous flow regime in the inlet system of the mass spectrometer is given by, where γ is the gas viscosity :

$$C_{vis} = \frac{\pi\cdot D_2^4}{128\cdot\gamma\cdot L}\cdot\left(\frac{P_1+P_2}{2}\right) \qquad [10]$$

By considering equation [10], the decreasing rate of the gas concentration in the expansion vessel $\left(\frac{d\eta}{dt}\right)_{visc}$ due to possible viscous flow conditions in the inlet tube between the gold foil and the ion source (Fig. 1) can be calculated as well:

$$\left(\frac{d\eta}{dt}\right)_{visc} = -\frac{1}{V}\cdot C_{vis}\cdot\gamma = -\frac{\pi\cdot D_2^4}{128\cdot V\cdot\gamma\cdot L}\cdot\left(\frac{P_1+P_2}{2}\right)\cdot\eta \qquad [11]$$

Taking into account the pressure difference $P_1 - P_2 \cong P_1 = P = \eta\cdot k\cdot T$, equation [11] becomes:

$$\left(\frac{d\eta}{dt}\right)_{visc} \cong -\frac{\pi\cdot D_2^4\cdot k\cdot T}{256\cdot V\cdot\gamma\cdot L}\cdot\eta^2 = -\beta_{visc}\cdot\eta^2 \qquad [12]$$

and demonstrates that decreasing rate of the gas molecules under viscous flow conditions are independent of molar mass of the gas in the expansion vessel, but proportional to the square of concentration (number density η) of the gas in the vessel.

Let $\eta_i(t)$ the concentration of the gas molecules with different isotopic species *i* present in the expansion vessel (Fig. 1) at measurement time *t*. Based on the equations [9] and [12], the flow rate $\frac{d\eta_i}{dt}$ can be calculated for the molecules effusing from the expansion vessel, through the gold foil into the ion source under molecular AND viscous flow conditions:

$$\frac{d\eta_i}{dt} = (1-\chi)\cdot\left(\frac{d\eta_i}{dt}\right)_{mol} + \chi\cdot\left(\frac{d\eta_i}{dt}\right)_{visc}$$

$$\frac{d\eta_i}{dt} = -(1-\chi)\cdot\beta_{mol}\cdot\eta_i - \chi\cdot\beta_{visc}\cdot\eta_i^2 \qquad [13]$$

where χ is the "contribution" factor (sub-unitary) of viscous flow contribution to the total gas flow in the inlet system, and (1-χ) the molecular part.

When integrating equation [13] to time $t = t_0$, i.e. the time that the measurements of the ion current ratios start and the time that the gas is still in its original isotopic composition so not yet suffering from isotope fractionation effects during sample, the new equation becomes:

$$\frac{d\eta_i}{dt} = -\eta_i\left[(1-\chi)\cdot\beta_{mol} + \chi\cdot\beta_{visc}\cdot\eta_i\right]$$

or

$$-dt = \frac{\frac{1}{(1-\chi)\beta_{mol}}d\eta_i}{\eta_i} - \frac{\frac{d\eta_i\cdot\chi\cdot\beta_{visc}}{(1-\chi)\beta_{mol}}}{\chi\cdot\beta_{visc}\cdot\eta_i + (1-\chi)\beta_{mol}}$$

or

$$-dt = \frac{1}{(1-\chi)\beta_{mol}}\cdot\frac{d\eta_i}{\eta_i} - \frac{\chi}{(1-\chi)}\cdot\frac{\beta_{visc}}{\beta_{mol}}\cdot\frac{d\eta_i}{(1-\chi)\beta_{mol}+\chi\cdot\beta_{visc}\cdot\eta_i} \qquad [14]$$

and after integration, equation [14] becomes:

$$-dt = \frac{1}{(1-\chi)\beta_{mol}}\cdot\int_{\eta_0}^{\eta_i}\frac{d\eta_i}{\eta_i} - \frac{\chi}{(1-\chi)}\cdot\frac{\beta_{visc}}{\beta_{mol}}\cdot\int_{\eta_0}^{\eta_i}\frac{d\eta_i}{(1-\chi)\beta_{mol}+\chi\cdot\beta_{visc}\cdot\eta_i}$$

$$\frac{\eta_i}{\eta_{o_i}}\cdot\left(\frac{(1-\chi)\cdot\beta_{mol}+\chi\cdot\beta_{visc}\cdot\eta_{o_i}}{(1-\chi)\cdot\beta_{mol}+\chi\cdot\beta_{visc}\cdot\eta_i}\right) = \exp\left[-(1-\chi)\cdot\beta_{mol}\cdot t\right] \qquad [15]$$

A simulation of equation [15] is visualized in Fig. 2 and 3. Starting from a theoretical amount of gas molecules ($5\cdot10^{18}$ molecules) in the expansion vessel of the spectrometer or a theoretical number density η_0, for different viscous flow contributions χin the gas flux from the vessel to the ion source is the molecular flow (decrease rate (η_i) in function of time) calculated.

For χvalues between $0 < \chi < 0.3$ were taken, responsible for viscous flow contributions in the gas flux to the ion source between 0 and 3%. The latter would be of course extremely high, but is only used for the simulation (Fig.3)

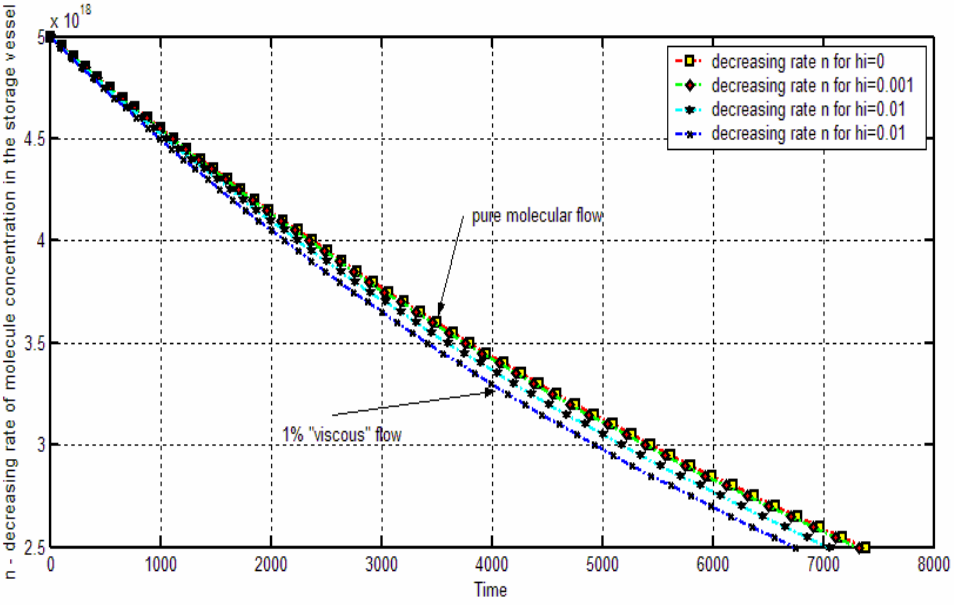

Fig.2: Theoretical estimation of molecular density decreasing during a "mixed" flow. The decrease of the number density η_i for CO_2 gas in function of time (hours).

A theoretical simulation is made by applying equation [15] and considering in the gas flow from the expansion vessel through the gold foil to the ion source, a mixture of molecular and viscous gas conditions. In the simulation, four different contributions for viscous flow in the gas flux are considered with $0 < \chi < 0.3$.

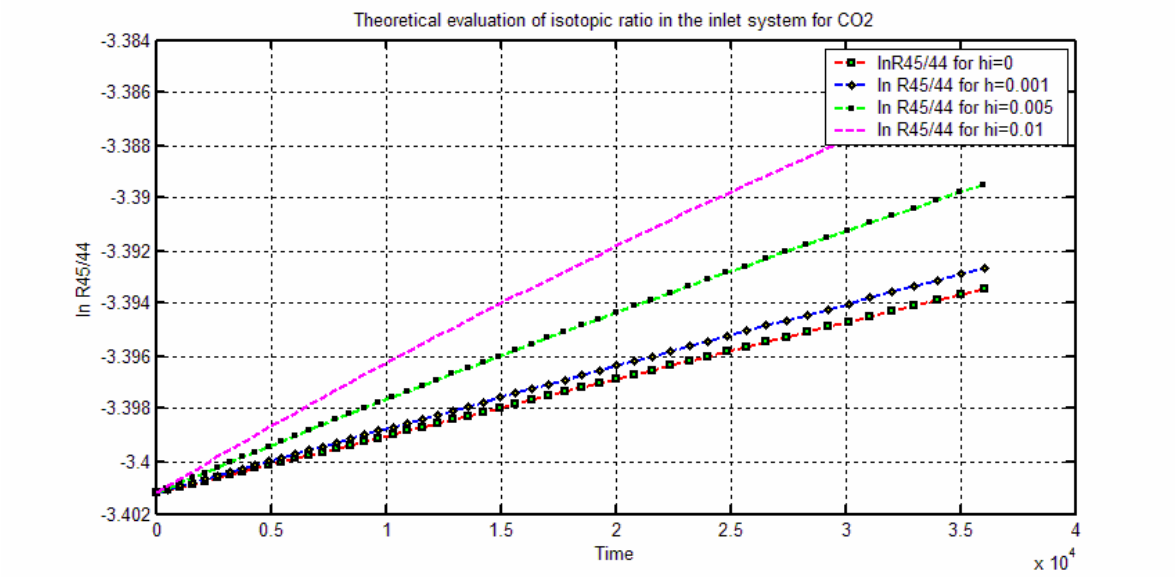

Fig.3:
A theoretical estimation of ln $R_{45/44}$, based on equation [15], versus time (hours) for different viscous flow contributions (χ -values) in the CO_2 gas flow to the ion source. For the calculations is considered that the gas flow from the expansion vessel through the gold leak into the ion source is a mixture of molecular and viscous gas conditions. In the simulation, four different contributions of the viscous flow in the gas flow are considered with $0 < \chi < 0.3$.

The simulations made via equation [15] clearly demonstrate (as shown in Figs. 2 and 3) that when the molecular flow in the inlet tube to the ion source of the gas mass spectrometer is contaminated, even slightly, by small amounts of the gas under viscous flow conditions, the entire gas behavior deviates strongly from a pure molecular flow regime, and will substantially change the whole flow regime in the inlet system.

As an example: for a χ value of 0.05, the experimental leak rate (i.e. the slope of the linear interpolation ln(I) versus time, in the case presented $I(^{44}CO_2)^+$ over time) deviates about 2.5×10^{-2} (rel) from its theoretical value.

As earlier indicated only β_{mol} is mass dependent and could therefore create a mass fractionation effect during the gas flow. Equation [15] is written for two isotopic species of the same molecule able to estimate the variation of the isotope amount ratio.

Starting from the equation [15] as basis, applied for both isotopic species i and 1, it follows for the species i, with i = 45 or 46 in the case of $^{i}(CO_2)^+$:

$$\ln\left[\left(\frac{\eta_i}{\eta_{oi}}\right)\cdot\frac{\left[1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_i}}\cdot\eta_{oi}\right]}{\left[1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol\,i}}\cdot\eta_i\right]}\right]=-(1-\chi)\cdot\beta_{mol_i}\cdot t \qquad [16]$$

and for the most abundant species 1 or $^{44}(CO_2)^+$:

$$\ln\left[\left(\frac{\eta_1}{\eta_{01}}\right)\cdot\frac{\left[1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_1}}\cdot\eta_{01}\right]}{\left[1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_1}}\cdot\eta_1\right]}\right]=-(1-\chi)\cdot\beta_{mol_1}\cdot t \qquad [17]$$

In case the viscous contribution χ is very small:

$$\left[1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol}}\cdot\eta\right]\approx\left[1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol}}\right]^{\eta} \qquad [18]$$

equation [16] can be re-written as:

$$\ln\left(\frac{\eta_i}{\eta_{oi}}\right)+\left(\frac{\eta_{oi}}{\eta_i}\right)\cdot\ln\left[\frac{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_i}}}{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_i}}}\right]=-(1-\chi)\cdot\beta_{mol_i}\cdot t \qquad [19]$$

and equation [17] as:

$$\ln\left(\frac{\eta_1}{\eta_{01}}\right)+\left(\frac{\eta_{01}}{\eta_1}\right)\cdot\ln\left[\frac{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_1}}}{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_1}}}\right]=-(1-\chi)\cdot\beta_{mol_1}\cdot t \qquad [20]$$

which is practically as well as for equation [19] as for [20] a linear decreasing rate of the versus time, because χ is very close to 0 (in the case of pure viscous flow ln 1 = 0):

$$\ln\left[\frac{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol}}}{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol}}}\right]\cong\ln\left[\frac{1+\left(\frac{0}{1-0}\right)\cdot\frac{\beta_{visc}}{\beta_{mol}}}{1+\left(\frac{0}{1-0}\right)\cdot\frac{\beta_{visc}}{\beta_{mol}}}\right]\cong\ln 1\cong 0\,.$$

By extracting equation [17] from equation [16], the variation of the isotope ratio *R* versus time, R_t , can be calculated.

$$\left(\frac{\frac{\eta_i}{\eta_{oi}}}{\frac{\eta_1}{\eta_{01}}}\right)\cdot\left[\frac{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_1}}\cdot\eta_1}{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_i}}\cdot\eta_i}\right]\cdot\left[\frac{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_i}}\cdot\eta_{oi}}{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_1}}\cdot\eta_{o1}}\right]=\exp\left[(1-\chi)\cdot\left(\beta_{mol_1}-\beta_{mol_i}\right)\cdot t\right]$$

or

$$\left(\frac{(R_{i,1})_t}{(R_{i,1})_{t0}}\right)\cdot\left[\frac{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_1}}\cdot\eta_1}{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_i}}\cdot\eta_i}\right]\cdot\left[\frac{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_i}}\cdot\eta_{oi}}{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_1}}\cdot\eta_{o1}}\right]=exp\left[(1-\chi)\cdot\left(\beta_{mol_1}-\beta_{mol_i}\right)\cdot t\right] \qquad [21]$$

Equation [21] is a very powerful tool to quantify the contribution of viscous flow in the gas flux to the ion source of the mass spectrometer. This knowledge of this contribution is of high importance because small amounts of viscous flow will strongly deviate the molecular flow conditions from kinetic gas behavior, and so falsify the correction for mass fractionation of the measurements during sample inlet.

The ion currents measured on the Faraday cup of the mass spectrometer are proportional to the molecule density η_i of the investigated isotopic species *i* in the ion source. The proportionality factor k_{eff} however is mass *independent* and *identical* for each isotopic species *i*.

Assuming that the isotope fractionation during fragmentation is negligible than are at any time, the ion currents measured proportional to the number density η_i in the source. Therefore, it could be stated that:

$$I_i = k_{eff} \cdot \eta_i \qquad [22]$$

and, replacing η_i in the previous equations [16] and [17] by equation [22] we will get:

$$\frac{I_i}{I_{oi}} \cdot \frac{1+\left(\frac{\chi}{1-\chi}\right) \cdot \frac{\beta_{visc}}{\beta_{mol\,i}} \cdot \frac{1}{k_{eff}} \cdot I_{oi}}{1+\left(\frac{\chi}{1-\chi}\right) \cdot \frac{\beta_{visc}}{\beta_{mol\,i}} \cdot \frac{1}{k_{eff}} \cdot I_i} = exp\left[-(1-\chi) \cdot \beta_{mol\,i} \cdot t\right] \qquad [23]$$

and,

$$\frac{I_1}{I_{01}} \cdot \frac{1+\left(\frac{\chi}{1-\chi}\right) \cdot \frac{\beta_{visc}}{\beta_{mol1}} \cdot \frac{1}{k_{eff}} \cdot I_{01}}{1+\left(\frac{\chi}{1-\chi}\right) \cdot \frac{\beta_{visc}}{\beta_{mol1}} \cdot \frac{1}{k_{eff}} \cdot I_1} = exp\left[-(1-\chi) \cdot \beta_{mol1} \cdot t\right] \qquad [24]$$

From equations [23] or equation [24], k_{eff} can be calculated, when putting $A = \exp\left[-(1-\chi) \cdot \beta_{mol_i} \cdot t\right]$ for sake of simplification, therefore:

$$\ln A = -(1-\chi).\beta_{mol_i} \cdot t$$

or

$$-(1-\chi).t = \frac{\ln A}{\beta_{mol_i}} \qquad [25]$$

By introducing equation [25] in [23], k_{eff} becomes:

$$k_{eff} = \frac{\left(\frac{\chi}{1-\chi}\right) \cdot \frac{\beta_{visc}}{\beta_{mol,i}} \cdot I_i \cdot I_{0i} \cdot (1-A)}{A \cdot I_{0i} - I_i} \qquad [26]$$

Substitution of equation [26] in [23] gives:

$$ln\left[\frac{I_1}{I_{01}}\cdot\frac{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol1}}\cdot\left[\frac{A\cdot I_{0i}-I_i}{\left[\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{vis}}{\beta_{mol_i}}\cdot(1-A)\right]\cdot I_i\cdot I_{0i}}\right]\cdot I_{o1}}{1+\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{visc}}{\beta_{mol_i}}\cdot\left[\frac{(A\cdot I_{0i}-I_i)}{\left[\left(\frac{\chi}{1-\chi}\right)\cdot\frac{\beta_{vis}}{\beta_{mol_i}}\cdot(1-A)\right]\cdot I_i\cdot I_{0i}}\right]\cdot I_1}\right]=\left[-(1-\chi)\cdot\beta_{mol1}\cdot t\right]$$

or:

$$ln\left[\frac{I_1}{I_{01}}\cdot\frac{1+\frac{\beta_{mol_i}}{\beta_{mol_1}}\cdot\left[\frac{A\cdot I_{0i}-I_i}{(1-A)\cdot I_i\cdot I_{0i}}\right]\cdot I_{o1}}{1+\frac{\beta_{mol_i}}{\beta_{mol_1}}\cdot\left[\frac{(A\cdot I_{0i}-I_i)}{(1-A)\cdot I_i\cdot I_{0i}}\right]\cdot I_1}\right]=\left[-(1-\chi)\cdot\beta_{mol1}\cdot t\right] \qquad [27]$$

Introducing equation [25] in [27] gives:

$$ln\left[\frac{I_1}{I_{01}}\cdot\frac{1+\frac{\beta_{mol_i}}{\beta_{mol_1}}\cdot\left[\frac{A\cdot I_{0i}-I_i}{(1-A)\cdot I_i\cdot I_{0i}}\right]\cdot I_{o1}}{1+\frac{\beta_{mol_i}}{\beta_{mol_1}}\cdot\left[\frac{(A\cdot I_{0i}-I_i)}{(1-A)\cdot I_i\cdot I_{0i}}\right]\cdot I_1}\right]=\frac{\beta_{mol_1}}{\beta_{mol_i}}\cdot ln\,A \qquad [28]$$

or:

$$\frac{I_1}{I_{01}}\cdot\frac{I_i\cdot I_{0i}\cdot(1-A)+\frac{\beta_{mol_i}}{\beta_{mol_1}}\cdot I_{01}\cdot(A\cdot I_{oi}-I_i)}{I_i\cdot I_{0i}\cdot(1-A)+\frac{\beta_{mol_i}}{\beta_{mol_1}}\cdot I_1\cdot(A\cdot I_{0i}-I_i)}=A^{\frac{\beta_{mol1}}{\beta_{moli}}} \qquad [29]$$

or

$$\frac{\frac{I_i\cdot I_{0i}}{I_{01}}\cdot(1-A)+\left(\sqrt{\frac{M_1}{M_i}}\right)\cdot(A\cdot I_{0i}-I_i)}{\frac{I_i\cdot I_{oi}}{I_1}\cdot(1-A)+\left(\sqrt{\frac{M_1}{M_i}}\right)\cdot(A\cdot I_{0i}-I_i)}=A^{\sqrt{\frac{M_i}{M_1}}} \qquad [30]$$

For CO_2 for instance, equation [30] can be solved numerically for A as a function of time, using as input values the measured ion currents at *m/e* 44 (index 1), 45 and 46 (index *i*). In this way, the functions $A_{45/44}(t)$ and $A_{46/44}(t)$ can be estimated ($A=exp\left[-(1-\chi)\cdot\beta_{mol_i}\cdot t\right]$), and the value χ or the viscous flow contribution factor for the gas flow to the ion source, can be determined for both ion current ratios $I\,[{}^{i}(CO_2)^{+}]/\,I\,[{}^{44}(CO_2)^{+}]$ with i = 45 or 46.

EXPERIMENTAL RESULTS

Two sets of data from the 'Avogadro amount comparators' were considered for the calculation of the viscous flow contribution in the (molecular) gas flow to the ion source. Two CO_2 samples of natural isotopic composition [10] were selected for the measurements: sample S1 and S2. The main results of the calculations are shown in Table 1.

On both CO_2 gases the ion currents $I(^iCO_2^+)$, resp. at *m/e* 44 to 46, were measured. The experiments have been defined in this way that for each of the 30 scans (from *m/e* = 44 to 46 and backwards) the mean intensity I_{44}, I_{45}, and I_{46} at the same time within a scan could be calculated. These values are stored in a data file and are considered as *N* vectors $\vec{I}_{44}$, $\vec{I}_{45}$ and $\vec{I}_{46}$ (with *N* = 30 = number of scans). A fourth *N*-dimensional vector has been considered as the "time" vector $\vec{t}$ for the times at which the 30 mean scans are calculated.

Starting from these four vectors ($\vec{I}_{44}$, $\vec{I}_{45}$, $\vec{I}_{46}$ and $\vec{t}$) and taking into account equation [30], a data treatment could be developed for calculating the χ factor as a quantitative deviation from the pure molecular gas flow in the mass spectrometer inlet system.

With the notations I_i for the ion currents $I(^{45}CO_2^+)$ and $I(^{46}CO_2^+)$, and I_1 being the ion current $I(^{44}CO_2^+)$, equation [30] can be re-written as follows:

$$\frac{I_i \cdot I_{0i}}{I_{01}} \cdot (1-A) + \left(\sqrt{\frac{M_1}{M_i}}\right) \cdot (A \cdot I_{0i} - I_i) = A^{\sqrt{\frac{M_i}{M_1}}} \cdot \frac{I_i \cdot I_{0i}}{I_1} \cdot (1-A) + A^{\sqrt{\frac{M_i}{M_1}}} \cdot \left(\sqrt{\frac{M_1}{M_i}}\right) \cdot (A \cdot I_{0i} - I_i)$$

where the I_{01} and I_{0i} values are obtained from the extrapolation of $\ln(I_1)$ and $\ln(I_i)$ versus time, at t = 0 respectively, or:

$$\frac{I_i \cdot I_{0i}}{I_{01}} - \sqrt{\frac{M_1}{M_i}} \cdot I_i = A \cdot \left(\frac{I_i \cdot I_{0i}}{I_{01}} - \sqrt{\frac{M_1}{M_i}} \cdot I_{0i}\right) + A^{\sqrt{\frac{M_i}{M_1}}} \left(\frac{I_i \cdot I_{0i}}{I_1} - \sqrt{\frac{M_1}{M_i}} \cdot I_i\right) + A^{\sqrt{\frac{M_i}{M_1}}+1} \left(\sqrt{\frac{M_1}{M_i}} \cdot I_{0i} - \frac{I_i \cdot I_{0i}}{I_1}\right)$$

[31]

When re-writing equation [31] as a power of A, real polynomial function can be obtained:

$$a1 \cdot A^{1+\sqrt{\frac{M_i}{M_1}}} + b1 \cdot A^{\sqrt{\frac{M_i}{M_1}}} + c1 \cdot A + d1 = 0 \qquad [32]$$

with:

$$a1 = \sqrt{\frac{M_1}{M_i}} \cdot I_{0i} - \frac{I_i \cdot I_{0i}}{I_1} \qquad [33]$$

$$b1 = \frac{I_i \cdot I_{0i}}{I_1} - \sqrt{\frac{M_1}{M_i}} \cdot I_i \qquad [34]$$

$$c1 = \frac{I_i \cdot I_{0i}}{I_{01}} - \sqrt{\frac{M_1}{M_i}} \cdot I_{0i} \qquad [35]$$

and

$$d1 = \sqrt{\frac{M_1}{M_i}} \cdot I_i - \frac{I_i \cdot I_{0i}}{I_{01}} \qquad [36]$$

The polynomial expression [32] can be resolved for each time t during the ion current ratio measurements on CO_2, and this for $I_{45}/I_{44} = I\,[\,^{45}(CO_2)^+]/\,I\,[\,^{44}(CO_2)^+]$ as well as for $I_{46}/I_{44} = I\,[\,^{46}(CO_2)^+]/\,I\,[\,^{44}(CO_2)^+]$.

When the ion currents I_{44}, I_{45} and I_{46} continuously are measured over time, at each time t a value $I_{44(t)}$, $I_{45(t)}$ and $I_{46(t)}$ can be obtained. From the fittings of all these current measurements, the intensities $I_{44(t0)}$, $I_{45(t0)}$ and $I_{46(t0)}$ at sample inlet (time t_0) can be obtained.

In Fig. 4 an example of $I_{45(t)}$ versus t is given. These currents, together with the square roots of the mass ratios $\sqrt{\frac{M_{45}}{M_{44}}}$ and $\sqrt{\frac{M_{46}}{M_{44}}}$, taken as input values for the equations [33] to [36], at each time (t) a value a_1, b_1, c_1 and d_1 can be deduced and the polynomial expression [32] resolved. The result is an $A(t)$ value over time from which by applying of equation [25], the viscous flow contribution in the gas flow to the ion source or $\square_{(t)}$ over time can be calculated.
The results are shown in Figs. 5 and 6.

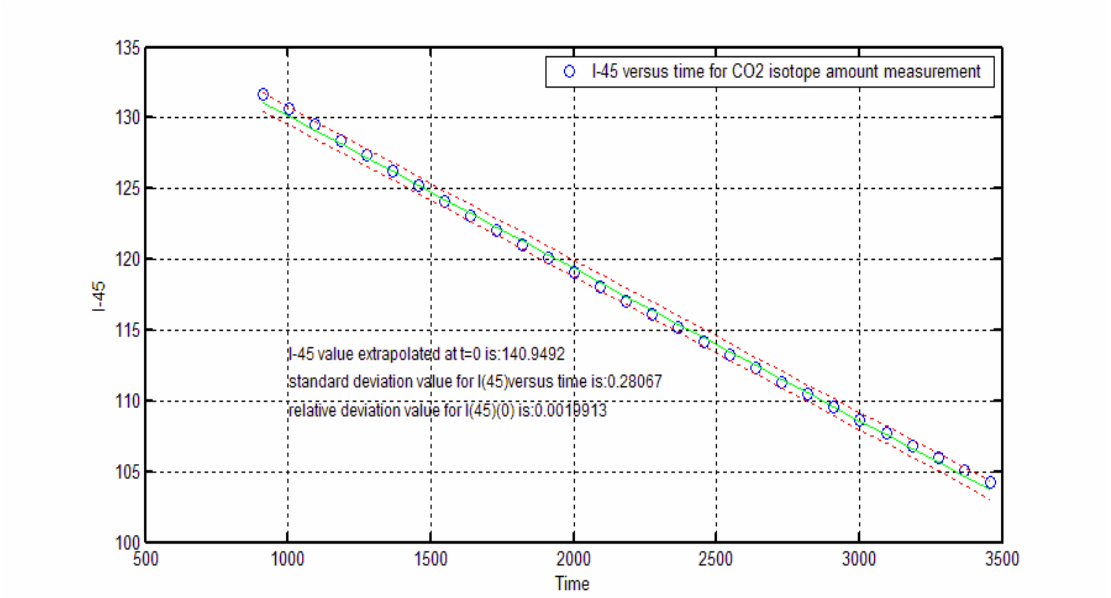

Fig.4:

A linear fit of $ln(I_{45})$ versus time t_0 resulting in $ln(I_{45(t0)})$ needed to solve equation [32]. The standard deviation on the leak rate k (with $\ln I = -k\cdot t + \ln I_0$) or on the slope of the fitted line is in the order of $2\cdot10^{-3}$ (relative).

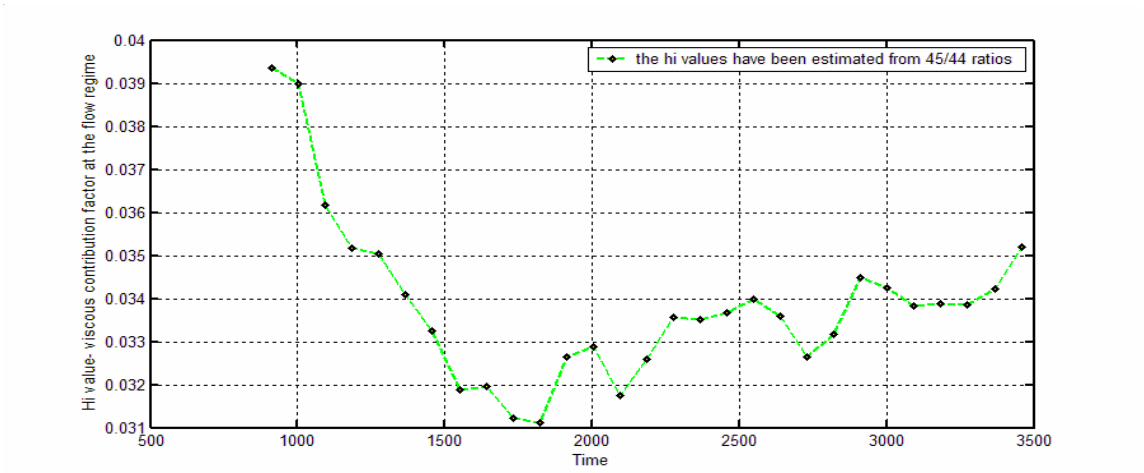

Fig.5:

Experimental χ factors within one ion current ratio measurement on high purity CO_2 versus time, $R_{45} = I_{45}/I_{44} = I\,[\,^{45}(CO_2)^+]/I[^{44}(CO_2)^+]$ versus t.
In this measurement a mean χ value of 0.033 8 ± 0.001 8 (1s) could be obtained.

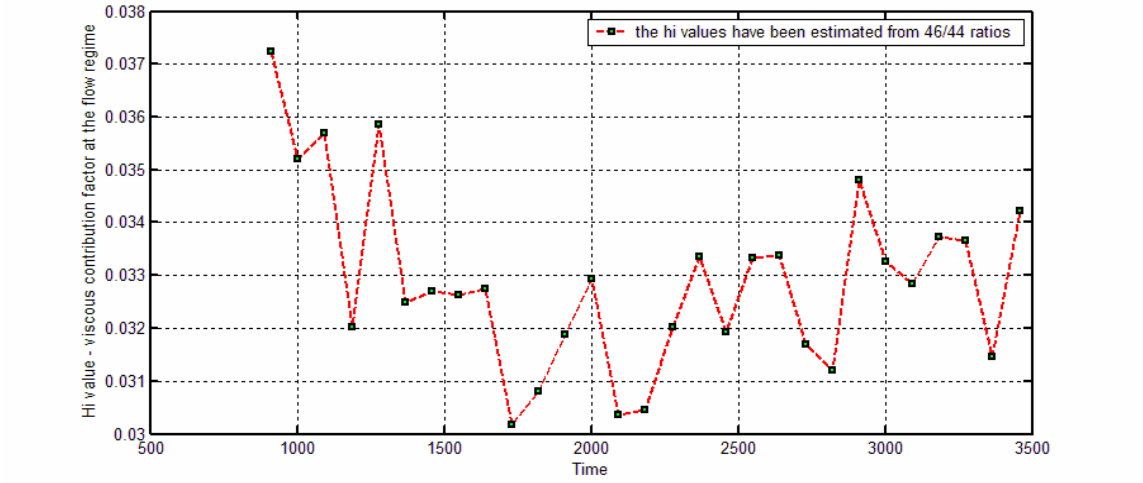

Fig.6:

Experimental □ factors within one ion current ratio measurement on high purity CO_2 versus time, $R_{46} = I_{46}/I_{44} = I\,[\,^{46}(CO_2)^+]/I[^{44}(CO_2)^+]$ versus t . In this measurement a mean χ value of 0.032 9 ± 0.001 7 (1s) could be obtained.

The mathematical formalisms as described above, have been tested on 17 ion current ratio measurements $I_{45/44}$ and $I_{46/44}$. The measurements as presented in Table 1 were made on two different high purity CO_2 gases (with natural amount fractions) by means of "IRMM's Avogadro amount comparator".

Each such measurement took about 3500 seconds during which the 3 ion currents $I(^{44}CO_2^+)$, $I(^{45}CO_2^+)$ and $I(^{46}CO_2^+)$ successively were measured with integration times of 8 seconds for each ion beam.

From the extrapolation of the logarithms of the observed ion currents $\ln I(^{i}CO_2^{+})$ (with i = 44 to 46) versus time, the leak rates k_{44}, k_{45} and k_{46} could be calculated (Table 1). Whilst from the extrapolated ion current ratio values $R_{45} = I_{45}/I_{44} = I\,[\,^{45}(CO_2)^{+}]/I[^{44}(CO_2)^{+}]$ and $R_{46} = I_{46}/I_{44} = I\,[\,^{46}(CO_2)^{+}]/I[^{44}(CO_2)^{+}]$ versus time, the ratios at start of the measurements $R_{45(t0)}$ and $R_{46(t0)}$ could be calculated (Table1).

Especially the quantity value of the leak rates k is powerful tools for the estimation of the quality of each measurement. Not only k should be identical for one specific molecule, k_{44}= 9.210 ± 0.015 (1s) as for measurements of $I(^{44}CO_2^{+})$ on CO_2 sample IMEP-8-A/2, but also the value of k_i (i = 44 to 46) must decrease linearly with increasing molar mass: $\Delta(k_{44} - k_{45})$ should be equal to $\Delta(k_{45} - k_{46})$ as is the case in Table 1. When both conditions not are fulfilled is this a clear indication that something went wrong during the measurement.

When transferring the values obtained in Table 1 to equations [31] to [36], the mean □-value for each of the 17 ion current ratio measurements could be calculated, accompanied with their standard deviation. These χ-values are regarded as a quantitative estimation of viscous flow contribution in the gas flow to the ion source of the isotope amount comparator. For the calculation of these χ-values the MATLAB "*Visco-mol*" software had been used.

Additionally, all molecular and viscous conductances needed to solve the polynomial expression [32] had been calculated based on geometrical measurements of all single inlet system components at the mass spectrometer with the exception of gold foil dimensions; these dimensions were based on the values given by the manufacturer.

RESULTS AND DISCUSSION

The viscous flow contribution χ in the molecular gas flux to the ion source of the mass spectrometer has been determined on two different CO_2 samples via the ion current ratio measurements $I\,[\,^{45}(CO_2)^{+}]/I[^{44}(CO_2)^{+}]$ and $I\,[\,^{46}(CO_2)^{+}]/I[^{44}(CO_2)^{+}]$ versus time.

Whether the χ - values are determined via R_{45}-route or applying R_{46} as main input value, it does not make much difference on the χ - values (no significant difference within the given 1s-repeatabilities of $2 \cdot 10^{-2}$).

For all 34 measurements (two sets of 17 ion current ratios) a mean value for χ= 0.033 2 (15) (1s) could be obtained. This means that the gas flow is not consisting only of molecular conditions but that there is a 3.32 (15) % viscous contribution in the gas flux to the ion source.

As explained in equation [13], the viscous flow component $\dfrac{\pi \cdot D_2^4 \cdot k \cdot T}{256 \cdot V \cdot \gamma \cdot L} = \beta_{visc}$ is not mass dependent, which makes that the simple extrapolation of the measured ion current ratios to time t_0 (equation [4]) indeed need to be replaced by equation [13], using χ= 0.033 2 (15) (1s) as contribution from viscous flow conditions.

REFERENCES

[1] S.VALKIERS, Y.AREGBE, K.MAYER, P.DE BIEVRE. A Primary Isotopic Xenon Gas Standard for Isotopic and Molar Mass. ***Int.J.Mass Spectr.Ion.Proc.***173 (1998) 55-63.

[2] S.VALKIERS, H. KIPPHARDT, T. DING, P.DE BIEVRE, P. TAYLOR. A Primary Isotopic Gas Standard for sulfur in the form of sulfur hexafluoride with SI traceable values for isotopic composition and molar mass. ***Int.J.Mass Spectr.Ion.Proc***.193 (1999) 1-8.

[3] P.DE BIEVRE, S.VALKIERS, H.S.PEISER, P.SEYFRIED. High-accuracy isotope abundance measurements for metrology. ***PTB-Mitteilungen***, 4, 1994, 225-236.

[4] P.DE BIEVRE, T.MURPHY, G.LENAERS, S.VALKIERS, S.PEISER. The chemical preparation and characterisation of specimens for absolute measurements of molar mass of an element, exemplified for Silicon, for the determination of the Avogadro constant. ***Metrologia***, 32, 1995, 103- 110.

[5] P.DE BIEVRE, S.VALKIERS, P.TAYLOR, S.PEISER. Mass spectrometric methods for determining isotopic composition and molar mass traceable to SI, exemplified by improved values for nitrogen. ***Metrologia*****,** 33, 1996, 447 - 455

[6] R.GONFIANTINI, S.VALKIERS, P.TAYLOR, P.DE BIEVRE. Measuring the molar mass of Si for a better Avogadro Constant: reduced uncertainty. ***IEEE Trans. Instr. and Meas***., Vol.46, 2, April 1997, 566 - 571.

[7] E. JONES, R. CHILDERS, Addison-Wesley, 1990, 2nd Ed. 1993.

[8] J. JEANS, An introduction to the Kinetic Gas theory, Cambridge Univ. Press, pp. 51-55 (1944).

[9] R.ROARK, Formulas for Stress and Strain, McGraw-Hill (1998)

[10] Y.AREGBE, S.VALKIERS, K.MAYER, P.DE BIEVRE, R. WESSEL, A. ALINK. Measuring amount ratios of gas isotopes by two primary methods of measurements, ***Metrologia***, 35,1998,7-16.

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Quantification of the Imperfectness of the Molecular Flow Conditions of the Gas Entering the Mass Spectrometer Ion Source for Ionization: Exemplified for CO2 Isotope Amount Ratio Measurements

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Abstract
A new model to describe the gas flow status inside the gas mass spectrometer (MAT 271) inlet system has been developed and applied to the latest isotope amount ratio measurements

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