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Method to test linearity of quadrupole mass spectrometers by use of a flowmeter and a standard leak

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ABSTRACT

A linearity test of the quadrupole mass spectrometer signal can be performed by using the pressure generated by the flow rate of a secondary leak as a fix point and varying the flow rate by a primary gas flowmeter around this value. Applying this method, we have investigated three different quadrupole mass spectrometer in a range of helium partial pressures between 10^{-9} Pa and 10^{-4} Pa, corresponding to flow rates of 10^{-7} Pa L s^{-1} to 10^{-2} Pa L s^{-1} in our system. Our preliminary results indicate significant non-linearities for even modest partial pressure changes.

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1. Introduction

When quadrupole mass spectrometers (QMS) are used for quantitative measurements e.g. for the calibration of standard leaks by using a calibrated set of standard leaks [1,2], it has to be assumed that the signal of quadrupole mass spectrometer has a linear response to partial pressure and flow rate through a vacuum system. Also when comparing outgassing rates this has to be assumed.

Non-linearity has been defined in ISO 14291 [3] as extent to which the change in ion current is not proportional to the corresponding change in partial pressure. The non-linearity is equal to the change of sensitivity in a given range. According to ISO 14291, the linear response range of a QMS is the partial pressure range over which the non-linearity is within a specified limit.

Investigations have shown [4–6] that the linear response range may not only depend on the partial pressure but also on the total pressure and gas mixture. This was not the focus of our investigation and we also did not investigate which parameters of the QMS settings influence the linearity as it was done e.g. in Ref. [4]. Instead, the focus of our investigation was the development of a method which allows an accurate test of linearity of a QMS. It is a by-product of our calibrations of standard leaks by a primary gas flowmeter. Standard leaks are leak elements which emit a constant flow of gas [7,9], usually of only one gas species which is helium. They may be of the permeation type [1,7,8], where the gas is diffusing through a solid (e.g. helium though quartz glass), or of the capillary type [1,9,10], where the flow is determined by the conductance of the capillary or a crimped part of it.

Our experimental method will be described in the following section; Section 3 discusses the influences of the methodology which may contribute to the uncertainty of the non-linearity, Section 4 will give preliminary results for three types of QMS that were in usage on our laboratory before we draw some conclusions.

2. Experimental set-up and method

The experimental set-up of our calibration system for standard leaks is shown in Fig. 1. The calibration is carried out by a direct comparison of the unknown flow rate from the standard leak with the known flow rate from the primary gas flowmeter. The QMS signal serves to compare the two flow rates. For this, the secondary leak and the flowmeter are mounted at equivalent places on the vacuum system with respect to the QMS. The length of the tube which is about 1 m from the gas source to the QMS, the diffuser and the position of the QMS, ensure that equal flows from both sources generate the same signal on the QMS.

The flowmeter is a primary measurement device and was described in Ref. [11]. It generates known gas flow rates from

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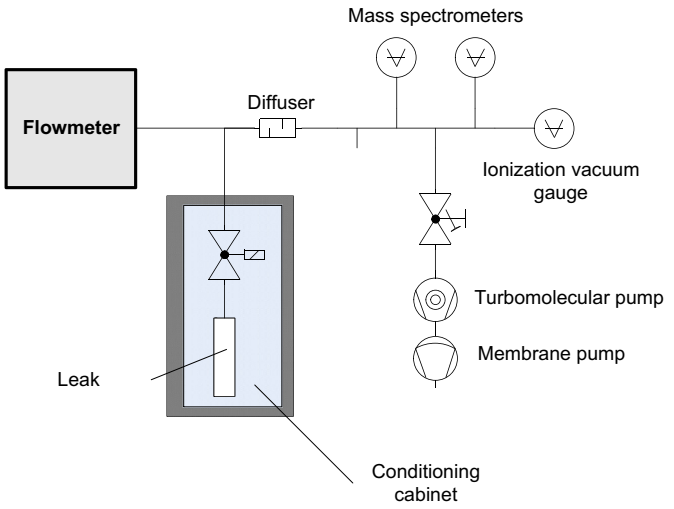

Fig. 1. Scheme of the experimental set-up of the calibration system for standard leaks.

10^{-7} Pa L s^{-1} to 10^{-2} Pa L s^{-1} at 23 °C. A very similar flowmeter in our laboratory was described in Ref. [12] with an extended measurement uncertainty discussion of the flow rate. The flowmeter was modernized since the publication [11], but the measurement method remained the same.

The standard leak is installed in a temperature-controlled cabinet, since the flow rate from a standard leak depends on temperature, particularly for permeation type standard leaks. The cabinet may accommodate three standard leaks at a time and shows a temperature drift of less than 0.005 K/min.

The QMS is mounted on a 6-way DN63CF cross. Two QMS may be installed on this at equivalent positions. The cross is pumped by a 180 L/s (for helium) turbomolecular pump with Holweck stage backed by a membrane pump (Balzers Typ TCM180). The conductance to the DN63 cross is 100 L/s, so that the effective pumping speed for helium is about 64 L/s.

To understand the following section, we will briefly describe the principal measurement method of the flowmeter.

In the upper range of the generated flow ($>10^{-5}$ Pa L s^{-1}) the flowmeter is used in the constant pressure mode. The gas flow exits via a leakage with a conductance of about 10^{-6} L/s. The pressure decrease can be compensated by changing the volume by squeezing a bellows displacer volume. The pressure is measured by a differential capacitance diaphragm gauge with respect to a constant pressure reference volume. The volume change ΔV by the displacer to keep the pressure constant within a measured time interval gives the conductance of the leakage at the prevailing pressure p in the flowmeter:

$$C = \frac{\Delta V}{\Delta t} \tag{1}$$

The flow rate is obtained by multiplying C with the pressure p.

In the lower range of the generated flow ($\leq 10^{-5}$ Pa L s^{-1}) the flowmeter is used in the constant conductance mode. Here, the flow through the leakage is molecular and the conductance independent of pressure which is below 80 Pa. The conductance is measured at higher pressure and the fill pressure is reduced to give the desired flow rate.

In both measurement modes, the molar gas flow rate of the flowmeter $q_{\nu,\mathrm{FM}}$ is determined by

$$q_{\nu,\mathrm{FM}} = \frac{pC}{RT_{\mathrm{FM}}} \tag{2}$$

where R denotes the molar gas constant and T_{FM} the temperature in the flowmeter.

In a calibration of a standard leak, the unknown flow rate $q_{\nu,\mathrm{SL}}$ from the standard leak can be determined by

$$q_{\nu,\mathrm{SL}} = q_{\nu,\mathrm{FM}} \cdot \frac{I_{\mathrm{SL}} - I_0}{I_{\mathrm{FM}} - I_0} \tag{3}$$

where: I_{SL} is the signal of the QMS for the relevant gas species, when this is exposed to the unknown flow from the standard leak, I_{FM}, when it is exposed to the known flow from the flowmeter of the same gas species, and I_0 the offset at residual pressure. If the ratio

$$Z = \frac{I_{\mathrm{SL}} - I_0}{I_{\mathrm{FM}} - I_0} \tag{4}$$

is different from 1, any non-linearity of the mass spectrometer will affect the measurement results. For this reason $q_{\nu,\mathrm{FM}}$ is varied around $q_{\nu,\mathrm{SL}}$, so that Z varies around 1 by typically ±20% (Fig. 2) and $q_{\nu,\mathrm{SL}}$ can be determined for $Z = 1$ by linear interpolation of the values $q_{\nu,\mathrm{SL}}(Z)$. The final value

$$\overline{q}_{\nu,\mathrm{SL}} = q_{\nu,\mathrm{FM}}(Z = 1) \tag{5}$$

is not affected by the non-linearity of the mass spectrometer. Typically, 5 measurements are taken with different $q_{\nu,\mathrm{FM}}$.

The methodology to evaluate the non-linearity of the QMS signal is as follows: The ratio

$$S' = \frac{I_{\mathrm{FM}} - I_0}{q_{\nu,\mathrm{FM}}} \tag{6}$$

can be identified as sensitivity S' of the QMS at flow rate $q_{\nu,\mathrm{FM}}$. In principle, the non-linearity could be simply determined by changing $q_{\nu,\mathrm{FM}}$ and observing the corresponding change of $(I_{\mathrm{FM}}-I_0)$. In this case, however, a timely change of the sensitivity or of the pumping speed in the system could be confused with a non-linear response. The always constant flow from the standard leak $q_{\nu,\mathrm{SL}}$ gives us the possibility to eliminate this effect.

If the sensitivity of the QMS signal changes in time, the ratio

$$S = \frac{I_{\mathrm{SL}} - I_0}{q_{\nu,\mathrm{SL}}} \tag{7}$$

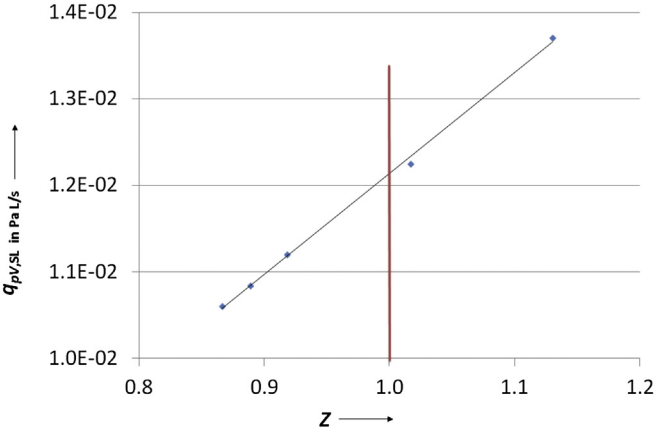

Fig. 2. Example for a measurement of leak rate $q_{\nu,\mathrm{SL}}(Z)$ with QMS A. Linear interpolation for $Z = 1$ yields $\overline{q}_{\nu,\mathrm{SL}}$ (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1
Description of some properties and overall ratings of the quadrupole mass spectrometers A, B and C used in our laboratory for standard leak calibrations.

QMS	Mass range	Ion source	Length quadrupole	Detector	Overall rating
A	1–200	Open/Radial	159 mm	Faraday/SEV	Cheap, simple device
B	1–300	Open/Radial	125 mm	Faraday/SEV	Medium priced
C	1–200	Open/Grid	200 mm	Faraday/SEV	expensive, high level

would change accordingly. The $q_{\nu,\mathrm{FM}}$ is varied around the value of $q_{\nu,\mathrm{SL}}$, as described above. For each $q_{\nu,\mathrm{FM}}$ there is a corresponding $q_{\nu,\mathrm{SL}}$ measured within a short period of time, so that the quantity D

$$D = \frac{S'}{S} - 1 = \frac{I_{\mathrm{FM}} - I_0}{I_{\mathrm{SL}} - I_0} \cdot \frac{q_{\nu,\mathrm{SL}}}{q_{\nu,\mathrm{FM}}} - 1 \tag{8}$$

describes the non-linearity of the QMS signal, where the time dependence of the sensitivity S is eliminated, except for the short period of 15 min to take the signal from the standard leak, the flowmeter and at residual pressure.

$D = 0$, when the QMS signal is linear, but $D \neq 0$, otherwise.

For a clear representation, we will use the QMS signal at $\overline{q}_{\nu,\mathrm{SL}}$ (where $Z = 1$) as a reference point.

Three QMS in use at our laboratory for standard leak calibrations were tested (Table 1) over a wide range of helium gas flow rates and associated helium partial pressures. Since this was no systematic investigation of QMS, but a proof of test of the method, we prefer not to reveal the product/manufacturer. Each QMS was equipped with both Faraday detector and secondary electron multiplier.

3. Uncertainty of the evaluated non-linearity

There are 5 influences that may contribute to the uncertainty of the determined non-linearity D (Eq. (8)).

1. a systematic error of $q_{\nu,\mathrm{FM}}$ that depends on fill pressure or flow rate
2. a time dependence of $q_{\nu,\mathrm{SL}}$
3. a drift in time of I_0
4. a drift of the sensitivity of the QMS due to a shift on the mass/charge scale within the measurement period of 15 min
5. a change of the partial pressure not related to the flow from the standard leak or flowmeter but due to a change of effective pumping speed with pressure or time.

To 1: Any systematic uncertainty of $q_{\nu,\mathrm{FM}}$ does not affect D because it would affect in the same manner $q_{\nu,\mathrm{SL}}$ as well (see Eq. (3)). So, due to the ratio (Eq. (8)), such errors drop out. Only a fill pressure dependent error would not cancel out. This could be the pressure dependent change of the conductance and an incorrect calibration of the device measuring the fill pressure in the flowmeter. Since the conductance is measured each time with a typical random uncertainty of 0.3%, this is also the possible uncertainty for D. The pressure dependent calibration uncertainty of the capacitance diaphragm gauges used for the fill pressure measurement is typically 0.1%.

To 2: The standard leaks are installed in the cabinet 24 h at the desired temperature before being measured to assure that the helium density profile is constant. The temperature drift in the cabinet is less than 0.05 K within the measurement period for the leak. In the worst case, for a permeation leak with 4%/K change in flow rate, this may cause an uncertainty of 0.2%. There are no other sources which may cause a change in the flow rate from a helium standard leak within the measurement period.

To 3: The drift in I_0 is random and must be considered. Its influence depends strongly on the measured flow rate, the QMS, the detector and the gain (Tables 2 and 3). Both I_{SL} and I_{FM} were greater by a factor of 100–1000 and their standard deviations could therefore be neglected compared to I_0.

To 4: For all QMS, the mass stability is ±0.1 amu over 8 h according to the manufacturer specifications. So, the signals should be stable within our measurement period of 15 min. Therefore we decided to neglect this influence. If the specifications are not true, they will appear as a non-linearity of the QMS, but in a random manner.

To 5: The helium partial pressure in the chamber was $<10^{-4}$ Pa at a residual pressure of about $5 \cdot 10^{-6}$ Pa. In this pressure range, the pumping speed is independent of the pressure according to the manufacturer. Temperature changes are less than 0.2 K within 15 min, which means that the relative change of the effective pumping speed due to a change of conductance is $<3.5 \cdot 10^{-4}$. The frequency of the rotor of the turbomolecular pump which is averaged over several minutes for each signal

Table 3
Uncertainty budget for D in %. The contribution of the offset depends on the partial pressure signal caused by $\boldsymbol{q_{pV,\mathrm{SL}}}$. To reduce the number of lines, only approximate values were given for three ranges of $\boldsymbol{q_{pV,\mathrm{SL}}}$ given in Pa L s^{-1}.

Uncertainty contribution	Influencing	Relative contribution		
		QMS A	QMS B	QMS C
Conductance	$\boldsymbol{q_{pV,\mathrm{FM}}}$	0.25%	0.25%	0.25%
Fill pressure	$\boldsymbol{q_{pV,\mathrm{FM}}}$	0.1%	0.1%	0.1%
Temperature drift cabinet	$\boldsymbol{q_{pV,\mathrm{SL}}}$	0.2%	0.2%	0.2%
Offset drift on QMS Range: $q_{pV,\mathrm{SL}} = 10^{-7}$	I_0	1.0%	0.7%	0.4%
Offset drift on QMS $q_{pV,\mathrm{SL}} = 10^{-6}$	I_0	0.1%	0.5%	0.3%
Offset drift on QMS $q_{pV,\mathrm{SL}} > 10^{-5}$	I_0	0.01%	0.05%	0.1%
Temperature drift in cross chamber	Z	0.035%	0.035%	0.035%
Change of rotor frequency of the turbomolecular pump	Z	0.1%	0.1%	0.1%
Total uncertainty $q_{pV,\mathrm{SL}} = 10^{-7}$ ($k = 2$)	D	2.1%	1.6%	1.1%
Total uncertainty $q_{pV,\mathrm{SL}} = 10^{-6}$ ($k = 2$)	D	0.74%	1.22%	0.92%
Total uncertainty $q_{pV,\mathrm{SL}} > 10^{-5}$ ($k = 2$)	D	0.7%	0.71%	0.74%

Table 2
Relative offset $\Delta I_0/I$ (I either I_{SL} or I_{FM}) and relative standard deviation of offset $u(\Delta I_0/I)$ for different standard leaks with rates $\boldsymbol{q_{pV,\mathrm{SL}}}$ and corresponding helium partial pressure in the cross chamber for the 3 QMS within the maximum measurement period of 15 min. Total pressure p_{tot} is given in the 2nd column.

$q_{pV,\mathrm{SL}}$	p_{tot}	p_{helium}	QMS A		QMS B		QMS C	
(standard leak) Pa L s^{-1}	Pa	Pa	$\Delta I_0/I$ %	$u(\Delta I_0/I)$ %	$\Delta I_0/I$ %	$u(\Delta I_0/I)$ %	ΔI_0 %	$u(\Delta I_0/I)$ %
$2 \cdot 10^{-7}$	$5.2 \cdot 10^{-6}$	$3.0 \cdot 10^{-9}$	9.1	1.0	3.2	0.7	0.7	0.4
$2 \cdot 10^{-6}$	$5.2 \cdot 10^{-6}$	$3.0 \cdot 10^{-8}$	3.7	0.1	–	–	0.4	0.3
$6 \cdot 10^{-6}$	$5.3 \cdot 10^{-6}$	$8.3 \cdot 10^{-8}$	–	–	2.0	0.5	–	–
$1 \cdot 10^{-5}$	$5.4 \cdot 10^{-6}$	$1.6 \cdot 10^{-7}$	0.1	0.01	–	–	0.3	0.1
$6 \cdot 10^{-5}$	$6.1 \cdot 10^{-6}$	$9.4 \cdot 10^{-7}$	–	–	0.02	0.05	–	–
$>1 \cdot 10^{-4}$	$>7.4 \cdot 10^{-6}$	$>1.6 \cdot 10^{-6}$	>0.1	>0.01	>0.01	>0.01	>1.0	>0.01

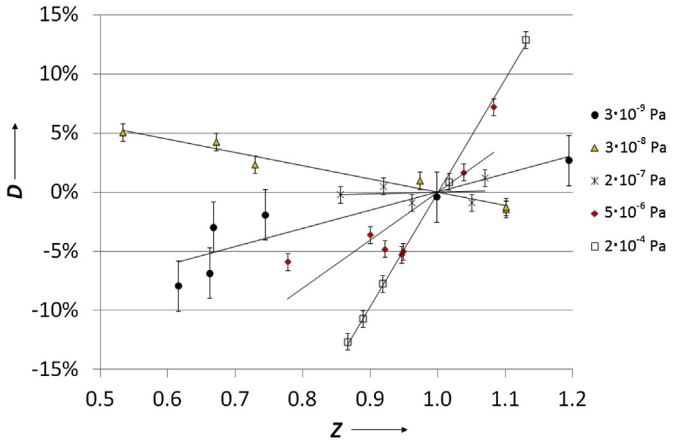

Fig. 3. The quantity D (Eq. (8)) as a function of the ratio Z (Eq. (4)) for QMS A and various helium partial pressures given to the right. The residual total pressure was typically $5 \cdot 10^{-6}$ Pa. Uncertainty bars ($k = 2$ or 95% probability) indicate the uncertainty of D when two values of D are being compared.

taken is stable within 10^{-3} as can be observed from the controller.

The uncertainty budget for D is summarized in Table 3.

4. Results and discussion

Figs. 3–5 show the results of D versus $Z = q_{\nu,\mathrm{SL}}/q_{\nu,\mathrm{FM}}$ around $Z = 1$ (see Eq. (5)) for the three QMS, separately for each of them. The results are given for flow rates varying by several orders of magnitude. The corresponding partial pressures in Pa for helium are given in the legend to the right. It should be noted that the uncertainty bars do not give the uncertainty of the measured value for leak rate but the uncertainty of D, hence the uncertainty of the *change* of sensitivity with Z. We also want to remind that these results are solely a by-product of standard leak rate calibrations and were not part of a systematic investigation of the QMS used in our laboratory. For this, we have no records, whether Faraday detector or secondary electron multiplier was used.

In Table 4 we quantified D for a 10% change of helium partial pressure in order to compare the data for the different partial pressures and QMS. The value for D at 10% was obtained from the slope of a linear least-square-fit of the observed values shown in Figs. 3–5. For this reason, random variations are reduced and the systematic uncertainty of D common to all values persists. The random scatter of D at 10% change of helium partial pressure was determined from the uncertainty of the slope. E.g., for QMS B at $6 \cdot 10^{-6}$ Pa Ls^{-1}, $D = (6.8 \pm 1.6)$ % means that the sensitivity changed by 6.8% for a helium partial pressure change of 10%, a rather high non-linearity. Those values which exceed the uncertainty showing significant non-linearity are marked as bold numbers.

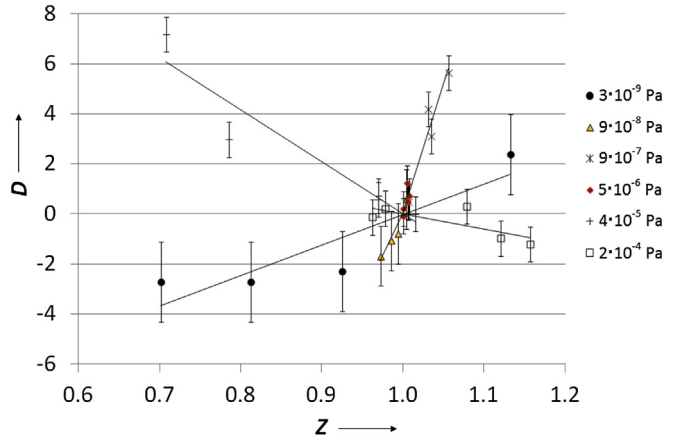

Fig. 4. The quantity D (Eq. (8)) as a function of the ratio Z (Eq. (4)) for QMS B and various helium partial pressures given to the right. The residual total pressure was typically $5 \cdot 10^{-6}$ Pa. Uncertainty bars ($k = 2$ or 95% probability) indicate the uncertainty of D when two values of D are being compared.

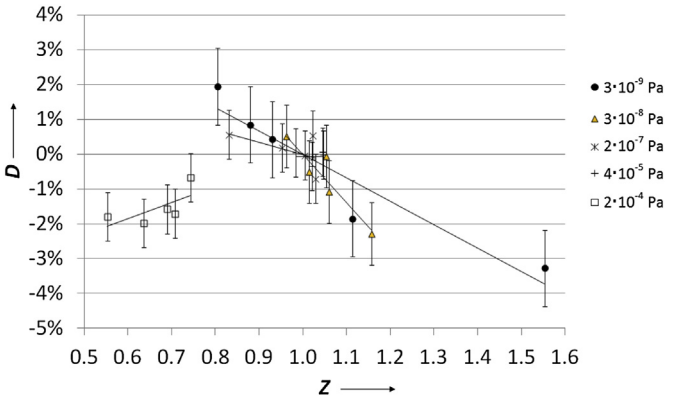

Fig. 5. The quantity D (Eq. (8)) as a function of the ratio Z (Eq. (4)) for QMS C and various helium partial pressures given to the right. The residual total pressure was typically $5 \cdot 10^{-6}$ Pa. Uncertainty bars ($k = 2$ or 95% probability) indicate the uncertainty of D when two values of D are being compared.

Table 4
D (Eq. (8)) at a 10% change of partial pressure for various helium partial pressures and for the three QMS (Table 1). The values are obtained from the slopes of the linear least-square fits through the data shown in Figs. 3–5, where each line represents another standard leak. The uncertainties given are obtained from the standard uncertainty of the slopes. Where the values exceed the uncertainty of D – hence show significant non-linearity-, they are in bold face. Total pressure corresponded to the 2nd column in Table 2.

$q_{pV,\mathrm{SL}}$ (standard leak) Pa L s^{-1}	p_{helium} Pa	QMS A %	QMS B %	QMS C %
$2 \cdot 10^{-7}$	$3 \cdot 10^{-9}$	1.5 ± 0.4	1.2 ± 0.4	0.7 ± 0.1
$2 \cdot 10^{-6}$	$3 \cdot 10^{-8}$	1.1 ± 0.1	–	**1.4** ± 0.3
$6 \cdot 10^{-6}$	$8 \cdot 10^{-8}$	–	**6.8** ± 1.6	–
$1 \cdot 10^{-5}$	$2 \cdot 10^{-7}$	0.2 ± 0.6	–	0.3 ± 0.3
$6 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	–	**10.3** ± 2.3	–
$3 \cdot 10^{-4}$	$5 \cdot 10^{-6}$	**4.0** ± 1.3	**11.7** ± 6.4	0.1 ± 0.01
$3 \cdot 10^{-3}$	$5 \cdot 10^{-5}$	–	**2.1** ± 0.4	0.0 ± 0.5
$1 \cdot 10^{-2}$	$3 \cdot 10^{-4}$	**9.6** ± 0.2	0.6 ± 0.3	0.5 ± 0.3

The QMS C of highest quality revealed the most linear response. Only one value was slightly non-linear. QMS A showed significant non-linearity beyond partial pressures of 10^{-4} Pa, while QMS B in the middle of the measuring range. QMS B also showed the largest uncertainties of the three QMS. It could be speculated that there is a correlation of non-linearity with quadrupole rod length (Table 1), but we do not support this, since we have not performed a systematic investigation.

5. Conclusion

The method of testing the linearity of QMS signals by use of a flowmeter and a standard leak proved successful. The non-linearity or change of sensitivity can be tested with an uncertainty of 0.7% when the offset has no significant influence ($p_{\mathrm{He}} > 10^{-7}$ Pa) and with an uncertainty of 2.1% when the offset is 10% of the signal ($p_{\mathrm{He}} = 3 \cdot 10^{-9}$ Pa). It was surprising to find relative large non-linearities or changes of sensitivity of the order of % up to 10%

when the helium partial pressure changed by 10% only, but further systematic investigations are needed to support these preliminaries observations.

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