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Time Stability Characterization of Quadrupole Mass Spectrometers

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Quadrupole Mass Spectrometers (QMSs) are widely used in industry for many applications such as leak detection, diagnostic purposes, qualitative and quantitative measurements in vacuum processes. This study focuses on the measurements of time stability of metrological characteristics including sensitivity using Faraday cup as a detector, mass scale, mass resolution, secondary electron multiplier (SEM) gain and minimum detectable partial pressure (MDPP) of QMSs. Time stability of sensitivity of eight different commercial QMSs was investigated by seven national metrology institutes at three different nominal calibration pressures of 5×10^{-6} Pa, 5×10^{-5} Pa and 5×10^{-4} Pa for N₂ and He. A common measurement protocol was adopted in order to compare results from different participants. The measurements were carried out with a periodicity of about three months for about two years. The usage history of the instruments was recorded between the measurements. To generate the reference pressures determined either by calibrated ionization gauges or by primary methods, each participant used its own system. In the case of ionization gauges, they were periodically recalibrated to ensure their traceability to a primary pressure standard. This study was conducted in the framework of EMRP IND12 project that was funded by the European Metrology Research Program [1]. The preliminary results obtained during the first year of the study were presented in [2]. The obtained final results will be discussed in the present work.

Key words: Quadrupole Mass Spectrometer, Sensitivity, Time Stability, Mass scale and resolution, MDDP, SEM Gain

1. Introduction

Time stability of sensitivity of nine different commercial QMSs was investigated by seven national metrology institutes and one industrial partner at three different nominal calibration pressures of 5×10^{-6} Pa, 5×10^{-5} Pa and 5×10^{-4} Pa. We have selected nitrogen and helium as the test gases for our investigations. Nitrogen is selected because it is mostly used for calibrating residual gas analyzers (RGAs), helium is selected as it is generally used for leak detection. A common measurement protocol was adopted in order to compare results from different participants. Subsequent measurements were carried out at intervals of about three months during two years. The test instruments used in this study are identified by the QMS- i , $i=[1..8]$. Additionally, this study focused on the measurements of time stability of metrological characteristics including mass scale, mass resolution, secondary electron multiplier (SEM) gain and minimum detectable partial pressure (MDPP) of selected QMSs. We have attempted to get information about the performance for commercial QMSs from different manufacturers. The operation of RGAs requires optimal selection of the several functional parameters and proper use of RGAs has been discussed in previously published studies [3-6]. Participant-6 studied two identical QMSs equipped with two filaments identified as QMS6-1, QMS6-2 and QMS7-1 and QMS7-2. For the purpose of the study, each QMS was studied independently with both filaments. Instrument details are presented in **table 1**. Methods used in this study by participants are presented in **table 2**.

Table 1 Instrument details

	Participant 1	Participant 2	Participant 3	Participant 4	Participant 5	Participant 6	Participant 7
	QMS1	QMS2	QMS3	QMS4	QMS5	QMS6-1/6-2 (QMS7-1/7-2)	QMS8
Mass range /amu (atomic mass unit)	1-200	1-200	1-200	1-300	1-100	1-100	1-100
Filament Type	Thorium oxide iridium	Tungsten	Tungsten	Tungsten	Twin Tungsten	HS Yttria	Oxide coated iridium
Type of ion source	open	grid ion source	open, radial	axial	open	open, radial	open
Quadrupole rod diameter /mm	6.35	6	6.35	8	6	6	6.35
Emission Current (mA)	2	2	1	1	1	2	1
Electron energy (Cathode) (eV)	102	90	70	90	70	68.5	70
Field axis potential (V) (ion energy in mass filter)	10	12	5.5	10.50	5.5	6.13 /5,88 (8,38 /8,63)	NA

2. Measurement procedures

2.1. Procedure for characterization measurements

Settings of the QMS instrument:

First demand for the measurements was to setup the QMSs according to manufacturer's recommendations. In order to optimize their QMS performance, each participant was allowed to make any adjustment prior to first measurement.

It is well known that ion sources may have different parameters including emission current, electron energy, extraction voltage, and field axis potential, SEM voltage, resolution setting and any other parameter that can be adjusted by the user. For each QMS, the operational parameters remained unchanged along the time stability study.

He and N₂ gases were selected for stability tests. Sensitivity measurements of the QMS were performed at three different nominal calibration pressures: 5×10^{-6} Pa, 5×10^{-5} Pa and 5×10^{-4} Pa. At pressure of 5×10^{-5} Pa, measurements were taken both with Faraday and SEM detector. At the beginning of the project, only Faraday detector was used at 5×10^{-6} Pa and 5×10^{-4} Pa, but after the measurement no.1, it was decided to add SEM measurements for those pressure points. Emission current I_e was the manufacturer pre-set default value.

Measurement procedure:

The emission of the QMS was switched on for a minimum period of 12 hours prior to measurement. Degassing of the QMS was not required after this run-in time. After the run-in time of the QMS, the following measurement procedure value was followed:

Noise and residual spectra: System is pumped down to the residual pressure conditions. In order to evaluate minimum detectable partial pressure, initially noise level measurement is taken by selecting the mass to charge ratio, $m/z=5$, and setting the QMS to perform continuous ion current measurement. Integration time is set to get approximately 1 reading/s. Minimum of 100 readings are recorded and saved. One measurement is done with Faraday detector and another with SEM detector Standard deviation of the readings is used in post processing data evaluation to calculate MDPP.

The QMS software is set to perform an analog spectrum. Two spectra of residual gas at ultimate pressure over the mass range from $m/z=0$ amu to $m/z=50$ amu are recorded. One spectrum is taken with Faraday detector and another one with SEM detector. This measurement is not directly related QMS stability measurement, but was added to the measurement protocol to record the status of the calibration system prior to the sensitivity measurements. Participants could see from this measurement what is dominant gas in the system, if there is a leak present, or how much water vapor is in the system, etc...

Gas selection: For sensitivity measurements gas species j at the desired partial pressure p_j is introduced into the system. An optimum scan range is set in order to get stable pressure regarding the peaks to be scanned. Spectrum ranges are in the mass range $m/z=0$ amu to $m/z=6$ amu for He and $m/z=10$ amu to $m/z=30$ amu for N_2 with a scan speed 1 s/amu.

Zero scan: One scan is recorded in the selected mass range at ultimate pressure using Faraday detector and repeated with SEM detector to get zero signal. Total pressure indicated by the ionization gauge is also recorded.

Calibration scan: Once the first calibration pressure (5×10^{-6} Pa) is stabilized, five scans using Faraday detector are performed in the selected mass range. Measurement is repeated with SEM detector. The calibration pressure shall not change more than 0.5 % between the beginning and the end of scan for each separate scan. Total pressure with ionization gauge preferably at the time of recording the main peak of gas is measured. If a primary method is used to determine calibration pressure, then mean generated pressure is used during the scan. The same scan procedure is applied to the next upper calibration pressure levels (5×10^{-5} Pa and 5×10^{-4} Pa). The zero and calibration scan procedures are applied for the other gas species.

Calibration methods: Calibrated ionization gauge considered to be adequate for this study to determine reference pressure for measurement of sensitivity. Ionization gauge calibrations were performed by a SRG before each calibration of the QMS. SRG was periodically calibrated at least once a year.

Post processing of data:

An adopted excel spreadsheet was provided to all participants for the collection of results. Post processing of data from recorded scans contains evaluation of saved spectra using

software from manufacturers of the QMS instruments. Determination of zero ion currents $I_{+i,0}$, where i means fragment of gas molecule, for instance 14 and 28 for N_2 , and of peak ion currents $I_{+i,n}$, where n means scan number (1 to 5) were used for sensitivity and SEM gain calculations. These data sets were also used for evaluation of fragmentation factors for N_2 which has a fragment in ion spectra at $m/z=14$.

Post processing of ion current noise measurement involves determination of standard deviation of 100 successive readings. Standard deviation of noise is necessary for the determination of minimum detectable partial pressure.

The zero scan spectrum is subtracted from the calibration scan spectrum measured. The sensitivity is calculated according to

$$S_{jk} = \frac{(I_{jk} - I_{0k})}{P_j}, \quad (1)$$

where I_{jk} is the peak signal of gas species j at $(m/z)_k$ at zero-corrected p_j and I_{0k} is the background signal at $(m/z)_k$.

Table 2 Methods used in this study

	Participant 1	Participant 2	Participant 3	Participant 4	Participant 5	Participant 6	Participant 7
Number of completed meas.run	8	8	7	6	8	8	7
Method	Comparison	Comparison	Comparison	Primary	Comparison	Primary	Primary
QMS connected to	Comparison calibration chamber	Comparison calibration chamber	Comparison calibration chamber	Continuous expansion system (primary standard, fix conduct.)	Comparison calibration chamber	Continuous expansion system (primary standard, fix conduct.)	Dynamic vacuum system (fix conduct.)
Reference pressure	EXG gauge calibrated against SRG traceable to Static Expansion System. EXG N_2 and He sensitivity coefficients measured	EXG gauge calibrated against SRG (N_2 and He sensitivity coefficients measured)	BAG gauge calibrated with N_2 at the primary standard applying the continuous expansion method	N_2 and He total pressure calculated through gas flow rate measurements and effective pumping speed value	Measured with a SRG and a BAG in-situ calibrated with SRG (7×10^{-5} to 1×10^{-3} Pa). SRG calibrated with both nitrogen and helium.	N_2 and He total pressure calculated through gas flow rate measurements and effective pumping speed value. Background residual pressure using the BA gauge.	Calculated through gas flow rate measurements and effective pumping speed value
Room Temp.	$(20 \pm 1)^\circ\text{C}$	$(23 \pm 2)^\circ\text{C}$	$(23 \pm 0.3)^\circ\text{C}$	$(21 \pm 1)^\circ\text{C}$	$(20 \pm 1)^\circ\text{C}$	$(20 \pm 1)^\circ\text{C}$	$(20 \pm 1)^\circ\text{C}$

2.2. Procedure for mass scale and mass resolution measurements

The mass resolution Δm depends mainly on the settings of the quadrupole voltages for the given geometry and RF-frequency of the quadrupole filter. Because of Δm is constant throughout the mass range of the QMS by setting the parameters, Δm was planned to be measured at two m/z value. Helium at $m/z=4$ and Nitrogen at $m/z=28$ were selected.

Mass scale and mass resolutions were determined from the scans taken for sensitivity measurement with Faraday detector at 5×10^{-5} Pa as given in the section of measurement procedure.

Background correction is applied to the taken spectrum and the peak position $(m/e)_{\text{peak}}$ was determined at the maximum of occurred experimental ion current I_{max} . Changes of the position of the peaks of ions He^+ (4), N^+ (14) and N_2^+ (28) were used for monitoring the stability of mass scale.

The expected 5%, 10% and 50% of the maximum ion current I_{max} were calculated respectively as $I_{5\%} = I_{\text{max}} * 0.05$, $I_{10\%} = I_{\text{max}} * 0.1$, $I_{50\%} = I_{\text{max}} * 0.5$. Then the (m/z) values for $I_{5\%}$, $I_{10\%}$, and $I_{50\%}$ on the left and right side of the peak were determined by interpolation between adjacent measurement points. The peak widths Δm at 5%, 10% and 50% were calculated as difference between left and right values. Changes of peak widths were used to assess stability of the resolution of QMS.

2.3. Procedure for SEM gain and minimum detectable partial pressure (MDPP) measurements

The SEM Gain is calculated as the ratio of the sensitivity of the SEM detector and the sensitivity of Faraday detector at 5×10^{-5} Pa, for a given gas species.

$$\text{SEM Gain} = \frac{S_{\text{SEM}_j}}{S_{\text{Faraday}_j}} . \quad (2)$$

The procedure to determine the MDPP of helium is the following: The sensitivity for helium at one partial pressure value, 5×10^{-5} Pa, is determined according to procedure given in **Section 2.1**. The noise level measurement at $m/z = 5$ with 100 values at residual pressure is taken each

with an integration time of 1s, and then the sample standard deviation of noise measurement values is determined, σ . The MDPP is given by the following equation:

$$\text{MDPP} = \frac{3\sigma}{S_{\text{He}}} . \quad (3)$$

Table 3 History of usage of the measurements

N o	Participant 1	Participant 2	Participant 3	Participant 4	Participant 5	Participant 6*	Participant 7
	QMS on lower chamber QMS wh: >50h p <5×10 ⁻⁷ Pa (EXG) only N ₂ and He used EXG no face to QMS UPS blackouts; P >700 Torr after outages;	Brand new QMS was mounted to the system on March 16, 2012. Manufacturer's settings of ion source were kept through all study. Filament switched on in UHV p<1×10 ⁻⁶ Pa for more than 1200 h operation in Faraday mode only	<u>for all:</u> QMS tuning done.QMS calibration to convert from pressure to current (CF). p <4×10 ⁻⁷ Pa (IG) <u>before 1st meas.:</u> QMS wh.: > 200h. Only N ₂ and He used. No QMS degas. Vented with air. 150 °C 24h. QMS cal	Vacuum QMS wh: 48h	Bakeout 1 week p is about 2×10 ⁻⁷ Pa	In every period between the measurements the QMS used for several times per month as comparators for the secondary helium leak standard calibrations.	p <3×10 ⁻⁷ Pa QMS wh: >22h
# 1	June 14-15, 2012	June 12, 2012	Aug 3-7, 2012	July 23-24, 2012	May 22 and 24, 2012	May 26, 2012	Aug 28-29, 2012
	QMS wh: >17h p <5×10 ⁻⁷ Pa (EXG) only N ₂ and He used vented to atm. SRG changed	Different measurements mainly in residual gas of unbaked vacuum system carried out. QMS wh: >1500 h. SEM working hours: 250h working pressure in the range from 5×10 ⁻⁷ Pa to 1×10 ⁻⁴ Pa	Vented with air. 100 °C 10h. QMS wh: 12h	Vacuum QMS wh: 40h	NA	Both devices was dismantled and leaved for 1 week at atmospheric pressure in the laboratory.	p <3×10 ⁻⁷ Pa QMS wh: >23h
# 2	Sep 28-27, 2012	Sept 26, 2012	Sept 3-4, 2012	Nov 26-27, 2012	Aug 23 -27, 2012	Aug 30, 2012	Nov 28 - Dec 3, 2012
	QMS wh: >70h p <5×10 ⁻⁷ Pa (EXG) only N ₂ and He used	Different measurements mainly in residual gas of unbaked vacuum system carried out. QMS working hours: >800 h. SEM wh: 200h. Working pressure in the range from 5×10 ⁻⁷ Pa to 1×10 ⁻⁴ Pa. QMS accidentally partly vented (p < 100 Pa, emission automatically switched off)	Different measurements with He and H ₂ carried out. QMS wh. 145h	Vacuum QMS wh: 40h	NA	QMS1 was dismantled for 2 weeks and QMS2 for 1 week, leaved in the box in laboratory at atmospheric pressure	p <5×10 ⁻⁷ Pa QMS wh: at least 12h chamber to atm. once before
# 3	Dec 24-28, 2012	Jan 10, 2013	Jan 9-8, 2013	Feb 13-14, 2013	Aug 28, 2012	Dec 5, 2012	March 11-15, 2013
	ULV changed QMS wh: >65h p <5×10 ⁻⁷ Pa (EXG) only N ₂ , He and	System vented, position of SRG changed to avoid direct facing to ion gauge. QMS baked at 120°C for 48 h.QMS wh: >1500	Different measurements with He, Ar, N ₂ , SF ₆ carried out. QMS wh.80h.	Vacuum QMS wh: 24h	NA	Before and after the 4th measurement, the experiments with leaks and different gases were performed	p <5×10 ⁻⁷ Pa QMS wh: at least 12h chamber to atm. once

	Ar used System to atm. several times	h. SEM working hours: 20 h working pressure in the range from 5×10^{-7} Pa to 1×10^{-4} Pa	Vented with air. 150 °C 30h			(Ar, H ₂ , SF ₆ , He and N ₂)	before
# 4	Apr 25 -29, 2013	March 26, 2013	Apr 10-9, 2013	May 24-23, 2013	Dec 18 -21, 2012	March 11, 2013	May 6 - 7, 2013
	QMS wh: >96h $p < 5 \times 10^{-7}$ Pa (EXG) only N ₂ , He and CO ₂ used vented to atm. EXG faces to QMS SRG changed	Different measurements with H ₂ , He, N ₂ , mainly with Faraday detector. Working pressure in the range from 5×10^{-7} Pa to 5×10^{-4} Pa. SEM detector only used at $p < 5 \times 10^{-6}$ Pa. QMS working hours: >2000 h SEM wh: 50h	Measurements with He, Ar, N ₂ carried out. Vented with air. 24 h 100°C. 10h 150 °C. QMS cal $p < 3 \times 10^{-7}$ Pa QMS wh 70h	Vacuum QMS wh: 24h	at least 1 week under vacuum QMS working hours at least 2 days	Several measurements with the CO ₂ leaks were performed for the calibration purpose	$p < 5 \times 10^{-7}$ Pa QMS wh: at least 12h chamber to atm. once before
# 5	July 29 -26, 2013	June 21, 2013	Aug 2 -26 July 2013	Sep 24-25, 2013	May 27-29, 2013	June 7, 2013	June 25-26, 2013
	QMS wh: >75h $p < 5 \times 10^{-7}$ Pa (EXG) only N ₂ and He used vented to atm. ULV changed Pumps off during 2,5 months then pres. 0,2 Torr	Different measurements with Ar, N ₂ , CO, CO ₂ ; O ₂ , mainly with Faraday detector. Working pressure in the range from 5×10^{-7} Pa to 5×10^{-4} Pa. SEM detector only used at $p < 5 \times 10^{-6}$ Pa. QMS wh: >1600 h SEM wh: 100 h	due to a pump failure vented with air one filament destroyed baked out for 24 hours at a 100°C. $p < 3 \times 10^{-7}$ Pa QMS working hours: > 320 h	Vacuum QMS wh: 24h	at least 1 week under vacuum QMS working hours at least 2 days	Both QMS remained in vacuum or protective pure nitrogen atmosphere	$p < 5 \times 10^{-7}$ Pa QMS wh: at least 12h chamber to atm. once before
# 6	Nov 14 -20, 2013	Sep 26, 2013	Jan 21-20, 2014	Dec 19-18, 2013	Oct 29 -Nov 6, 2013	Sep 6, 2013	Sep 2-3, 2013
	QMS wh: >72h $p < 5 \times 10^{-7}$ Pa (EXG) only N ₂ and He used	Different measurements mainly with H ₂ , He, N ₂ , Ar and H ₂ O with Faraday detector. Working pressure in the range from 5×10^{-7} Pa to 5×10^{-4} Pa. SEM detector not used at all QMS wh: 800 h	System evacuated all the time QMS wh: > 240 h SRG and ion gauge recalibrated	NA	at least 1 week under vacuum QMS working hours at least 2 days	QMS properties study was performed (10/2013) using Ar, CO ₂ , H ₂ , He and N ₂	$p < 5 \times 10^{-7}$ Pa QMS wh: at least 12h chamber to atm. once before
# 7	Jan 8 -23, 2014	Dec 12-12, 2013	April 4, 2014	NA	Feb 3-5, 2014	Dec 11, 2013	Dec 5-4, 2013
	System vented to atm. System modified. QMS and SRG on upper chamber EXG no faces to QMS QMS wh: >72h $p < 5 \times 10^{-7}$ Pa (EXG) only N ₂ , He and Ar used	Different measurements mainly in N ₂ , Ar and H ₂ O with Faraday detector. Working pressure in the range from 5×10^{-7} Pa to 5×10^{-4} Pa. Exposure to Dodecane for 6 h. SEM detector not used at all. SEM wh: 10 h	NA	NA	6 weeks under vacuum QMS wh. at least 2 days	QMS 6 was left for 2 weeks at atmospheric pressure in the laboratory	March 21, 2014 Filament 1 broke down
# 8	Mar.31 -Apr 3, 2014	Mar 18, 2014	NA	NA	May 15-20, 2014	March 18, 2014	NA

*Additional notes for Participant-6: Between the measurements (40% time), the QMS remained in the calibration chamber filled with the pure nitrogen 5.0 at atmospheric pressure. Several blackouts appeared during the operation of the QMS, but in these cases the QMS are automatically switched off and remains off in vacuum. Primary pump is isolated by the self-acting valve, no atmosphere or other contaminants are introduced in the vacuum chamber.

3. Measurements and results

3.1. Sensitivity stability measurements

Initial sensitivities of tested instruments for faraday detector are given in **table 4**.

Table 4 Initial sensitivities of tested QMSs at 5×10^{-6} Pa, 5×10^{-5} Pa and 5×10^{-4} Pa for Faraday detector

	<i>S (A/Pa)</i>								
	He (m/z=4)	N ₂ (m/z=14)	N ₂ (m/z=28)	He (m/z=4)	N ₂ (m/z=14)	N ₂ (m/z=28)	He (m/z=4)	N ₂ (m/z=14)	N ₂ (m/z=28)
Instrument	5×10^{-6} Pa			5×10^{-5} Pa			5×10^{-4} Pa		
QMS1	9.448E-07	1.822E-07	1.455E-06	9.338E-07	1.747E-07	1.504E-06	8.748E-07	1.620E-07	1.456E-06
QMS2	5.498E-07	1.278E-07	6.812E-07	5.569E-07	1.207E-07	6.431E-07	5.571E-07	1.214E-07	6.684E-07
QMS3	4.637E-08	2.323E-08	2.549E-07	3.824E-08	2.726E-08	2.822E-07	4.432E-08	2.833E-08	2.957E-07
QMS4	9.286E-07	2.133E-07	2.234E-06	9.569E-07	2.054E-07	2.260E-06	9.568E-07	1.881E-07	2.126E-06
QMS5	6.505E-08	4.756E-08	8.729E-07	1.159E-07	5.190E-08	9.285E-07	1.164E-07	5.304E-08	9.125E-07
QMS6-1	5.094E-07	2.095E-07	2.501E-06	6.010E-07	1.739E-07	2.359E-06	1.196E-06	1.310E-07	1.930E-06
QMS6-2	1.953E-06	3.152E-07	3.541E-06	2.118E-06	2.600E-07	3.643E-06	2.596E-06	1.353E-07	2.549E-06
QMS7-1	2.825E-06	2.610E-07	2.500E-06	2.532E-06	1.693E-07	2.159E-06	2.326E-06	8.152E-08	1.517E-06
QMS7-2	2.509E-06	3.648E-07	3.115E-06	2.418E-06	2.676E-07	3.268E-06	2.378E-06	1.130E-07	1.932E-06
QMS8	1.843E-07	3.383E-08	4.801E-07	1.768E-07	2.732E-08	4.570E-07	2.016E-07	2.345E-08	3.457E-07

Fig.1 illustrates changes in QMS sensitivity normalized to the initial value. Calibration time intervals are about three months at 5×10^{-6} Pa, 5×10^{-5} Pa and 5×10^{-4} Pa using only Faraday detector for Helium, N₂ (m/z=14), and N₂ (m/z=28). All graphs were plotted to the same scale in order to easily compare.

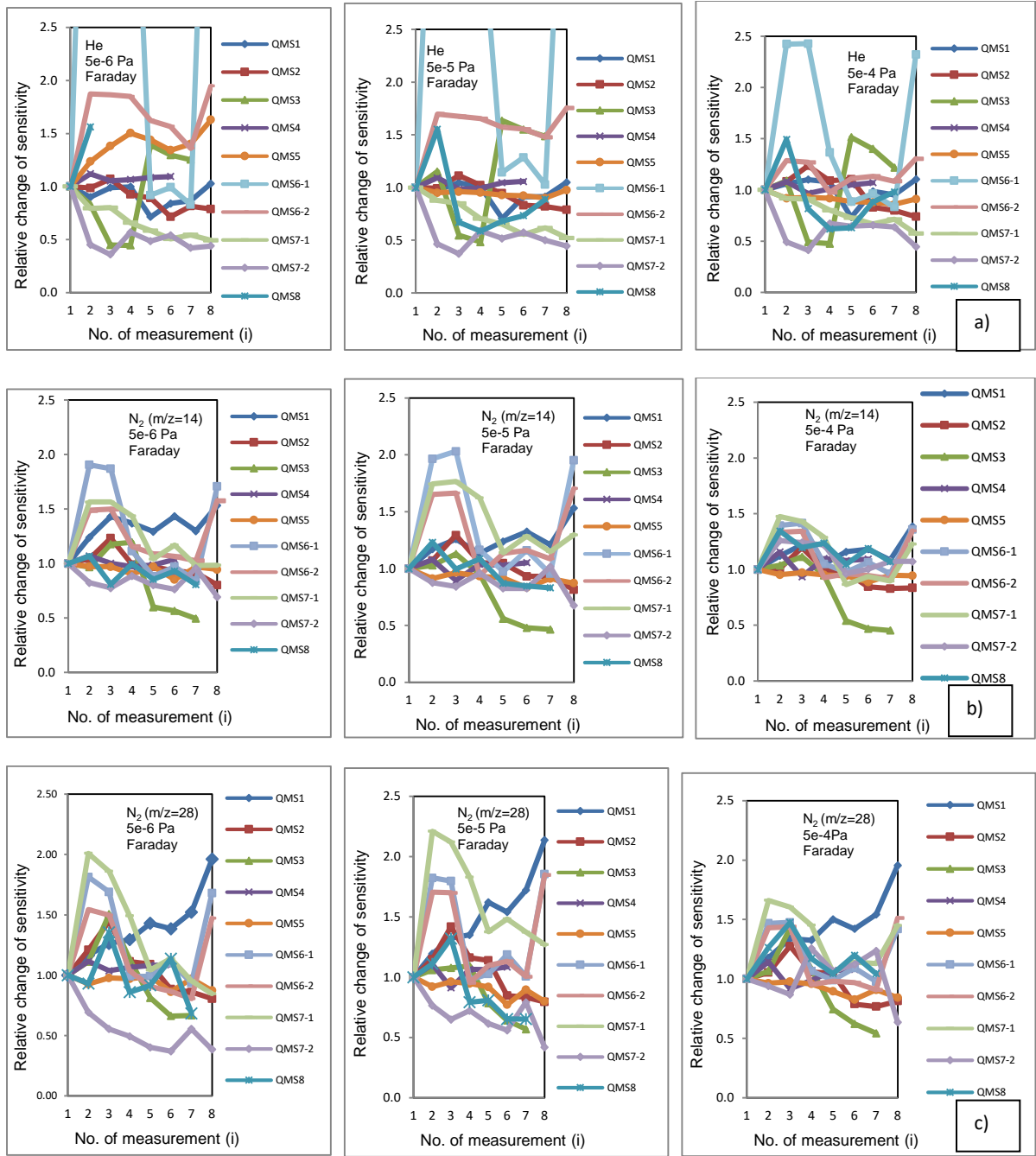


Fig.1 Changes in QMS sensitivity normalized to the initial at 5×10^{-6} Pa, 5×10^{-5} Pa and 5×10^{-4} Pa using only Faraday detector. a) Helium, b) N_2 ($m/z=14$), and c) N_2 ($m/z=28$); time interval between each measurement is about three months.

Fig.1 indicates that the sensitivity of each QMS changed with time and at a different rate relative to its initial measurement. The results demonstrate that, in most of cases, sensitivities of all QMS tend to decrease with time, with some exceptions. Faraday detectors show typical changes of sensitivity in the range between 30 % and 60 % over a three month period, with extreme changes of up to 560 %.

In this study, it is observed that the dispersion in relative change of sensitivity for Faraday between from $\pm 50\%$ to $\pm 30\%$ in pressure range 5×10^{-6} Pa to 5×10^{-4} Pa, by increasing the test pressure and it seems stable during time stability measurements for all gas species, with some exceptions. QMS1 showed slightly different behavior mainly for nitrogen probably because no baking procedure was applied during all measurement sequences. Furthermore, it is necessary to specify that QMS6 and QMS7 were kept in atmospheric conditions prior to rapid increase.

History of usage of the measurements is given in **table 3**. The sensitivity of QMS1 increased as about 100% relative to the initial value for N_2 ($m/z=28$). In QMS1 measurements, baking procedure was not applied to the vacuum system between the measurement runs. According to Blanchard *et al*, the largest changes observed in sensitivity measurements after bakeout and when the QMS was held at large partial pressures less than 1.3×10^{-5} Pa of active gases such as CO and H_2O for extended periods and a positive effect in change of sensitivity was seen by baking [5]. On the other hand, after measurement No.3, QMS2 was baked at 120 °C for 48h. After this application, it can be seen that the sensitivity dropped by 30% from the previous measurements at each pressure value for each mass scale for N_2 . It is likely that baking procedure is the origin of the decrease in sensitivity. No meaningful explanation was found to this contradiction. The pumps of the vacuum system were closed among the measurement runs for QMS1, and then the pressure inside the test chamber was increased up to 133 Pa. Besides, UPS power blackouts resulted in pressure increase in the vacuum chamber with air. It is thought that such effects may have unfavorable effects on QMS1 measurements.

QMS7-1 and QMS7-2 denote the same devices representing the different filament each. At measurement no.2 in **Fig.1**, it is seen that the relative change of sensitivity of QMS7-1 increased up to 120% for N_2 ($m/z=28$). On the contrary, QMS7-2 values tend to decrease up to 30% from the initial measurement for the same mass scale. After measurement no.2, QMS7-1 tends to turn back its initial value within about 30%, while QMS7-2 dropped by 60% from its initial measurement. Similar behavior is observed for N_2 ($m/z=14$). Although it is the same device, a change in different directions has been observed. It is seen that the values of some parameters of QMS7-1 such as focus voltage and field axis potential are lower than that of QMS7-2, which may be attributed this different behavior. Both were appeared to be more

stable in helium measurements and related sensitivities dropped by about 50%. In contrast to the QMS7-1 and QMS7-2, QMS6-1 and QMS6-2 showed the same characteristics at each pressure values for N₂. An extreme increase up to 560% over a three month period at the lowest pressure value for helium was seen for QMS6-1, which is out of the scale in the related figure. Exposure to some kinds of gases such as water, oxygen and fluorine can change the characteristics of the ionizer [6]. Both devices was dismounted and leaved for one week at atmospheric pressure in the laboratory which may be attributed to these rapid changes. This behavioral difference between the devices can be related to the conditions of use and the aging of the filaments.

3.2. Mass scale and mass resolution stability measurements

Initial peak positions are given in **table 5**. The mass scale was reasonably stable and the changes of the peak positions for each devices and gas species were generally less than 0.1 amu with some exceptions (see **Fig.2**). Before measurement no.2 and 3, QMS6 and QMS7 were dismounted and leaved for 1 to 2 weeks at atmospheric pressure in the laboratory. The reason of rapid change in mass scale for QMS7 may be this atmospheric pressure condition. This effect was strongly observed in mostly helium measurements with a change of 0.25amu.

Table 5 Initial peak positions of tested QMSs at 5×10^{-5} Pa

Initial peak position 5×10^{-5} Pa			
Instr.	He (4)	N ₂ (m/z=14)	N ₂ (m/z=28)
QMS1	3.948	13.992	28.019
QMS2	3.810	13.872	27.934
QMS3	4.004	13.963	28.016
QMS4	3.970	13.970	27.970
QMS5	4.190	14.000	28.000
QMS6-1	3.988	13.970	27.970
QMS6-2	4.036	13.970	28.000
QMS7-1	3.970	13.976	28.012
QMS7-2	3.970	13.976	27.910
QMS8	4.200	14.120	28.270

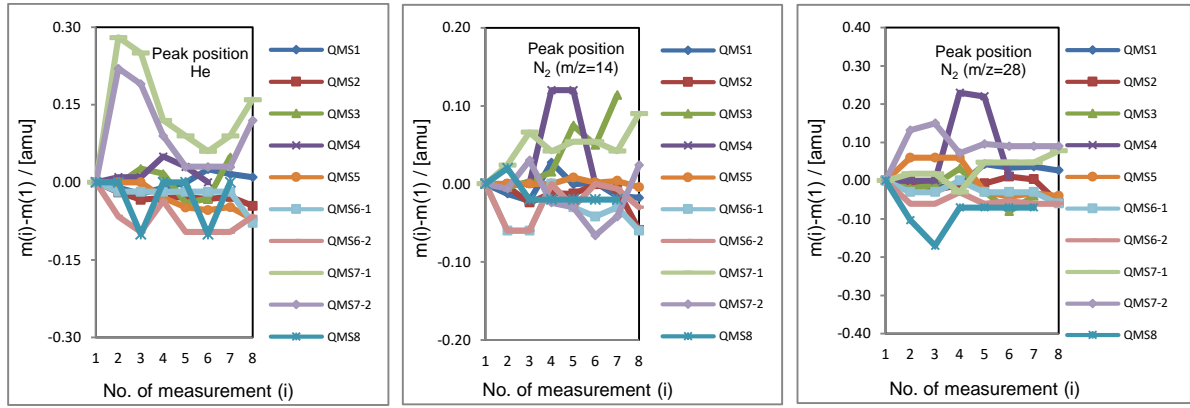


Fig.2. Changes in QMS mass scale normalized to the initial value at 5×10^{-5} Pa for Helium ($m/z=4$), N_2 ($m/z=14$) and N_2 ($m/z=28$); time interval between each measurement is about three months.

Fig.3 indicates the changes in QMS mass resolution normalized to the initial value at 5×10^{-5} Pa for 5%, 10% and 50% of the peak heights for Helium ($m/z=4$) and N_2 ($m/z=28$). Time interval between each measurement is about three months. Initial peak widths at 5%, 10% and 50% of peak height at 5×10^{-5} Pa is given in **table 6**. In **fig.3**, the peak width was reasonably stable and the changes of the peak widths at 5%, 10% and 50% were generally less than 0.1 amu with some exceptions.

Table 6 Initial peak widths of tested QMSs at 5%, 10% and 50% of peak height at 5×10^{-5} Pa

Initial peak width at 5% height				Initial peak width at 10% height				Initial peak width at 50% height			
Instr.	He (4)	N ₂ (14)	N ₂ (28)	Device	He (4)	N ₂ (14)	N ₂ (28)	Device	He (4)	N ₂ (14)	N ₂ (28)
QMS1	1.14	0.98	1.02	QMS1	1.0759	0.9492	0.9613	QMS1	0.7778	0.7087	0.7427
QMS2	1.0230	1.0720	0.9740	QMS2	0.9410	0.9790	0.8970	QMS2	0.6830	0.6960	0.6180
QMS3	0.9300	1.2000	1.0600	QMS3	0.8500	1.1100	0.9800	QMS3	0.6700	0.8700	0.7800
QMS4	0.982	0.876	0.875	QMS4	0.906	0.840	0.835	QMS4	0.664	0.615	0.601
QMS5	0.501	0.645	0.695	QMS5	0.465	0.617	0.663	QMS5	0.387	0.472	0.505
QMS6-1	0.825	0.821	0.814	QMS6-1	0.760	0.770	0.770	QMS6-1	0.445	0.495	0.522
QMS6-2	0.854	0.823	0.826	QMS6-2	0.806	0.774	0.781	QMS6-2	0.587	0.531	0.547
QMS7-1	0.857	0.896	0.899	QMS7-1	0.805	0.832	0.838	QMS7-1	0.576	0.600	0.612
QMS7-2	0.888	0.877	0.888	QMS7-2	0.829	0.820	0.828	QMS7-2	0.609	0.615	0.617
QMS8	0.900	1.370	1.050	QMS8	0.860	0.875	0.955	QMS8	0.440	0.580	0.640

One week after measurement No. 8, a defect on electronics cooling fan of QMS2 was found. Increased temperature of the electronics probably caused shifts in mass scale and peak widths. After replacement of the fan the mass scale and resolution was checked again and values returned close to the ones at measurement No.7.

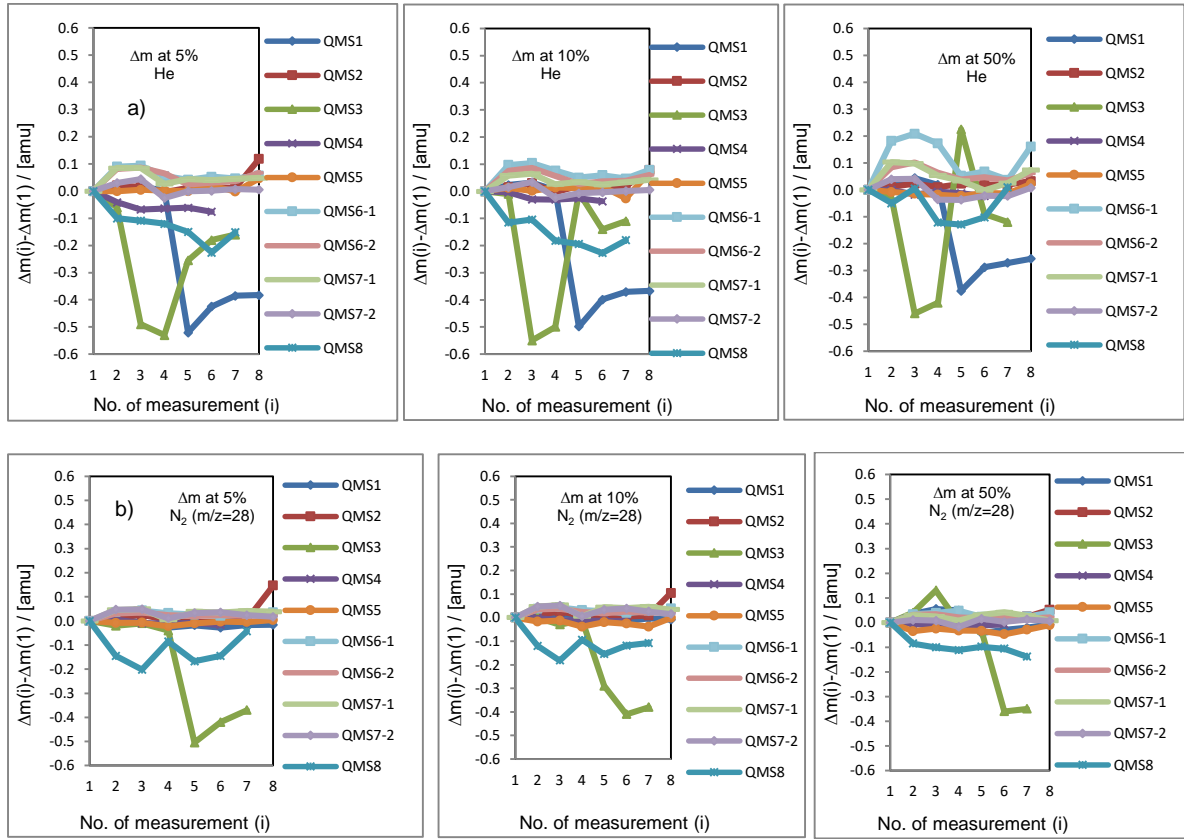


Fig.3. Changes in QMS mass resolution normalized to the initial value at 5×10^{-5} Pa for 5%, 10% and 50% of the peak heights a) Helium ($m/z=4$), b) N_2 ($m/z=28$); time interval between each measurement is about three months.

Mass resolution effect on QMS's sensitivity measurements were taken using Helium for the other task of the project that is outside the scope of this study between measurement No. 3 and No.4 for QMS1, then measurement No.4 was taken but no significant effect was seen on 4th measurements. Therefore, it is not considered to be a fault resulted from the helium measurements taken for the other task. Again, mass resolution effect on QMS's sensitivity measurements were taken using Nitrogen and CO_2 for the other task of the Project between measurement No. 4 and No.5, and no any helium measurements were performed in this period on the vacuum system. Notwithstanding, a significant decrease around 50% is seen after the measurement No.4 with relevant QMS1 for helium measurements followed by a return of up to 20% in the following measurements (see **Fig.3**). No meaningful explanation for this change has been found.

3.3. SEM Gain stability measurements

Changes in SEM Gain of tested QMSs normalized to the initial value at 5×10^{-5} Pa for Helium ($m/z=4$) and N_2 ($m/z=28$) are given in **Fig.4**. Another source of sensitivity instability can be the gain of SEM detector which dropped gradually over time for most of instruments. In case of helium, drop of -50 % to -80 % was observed for QMS2, QMS3, QMS6-1 and QMS6-2, with typical changes of -30 % over a period of 2 years for other instruments. For one instrument the gain unexpectedly increased by 100 %. Initial SEM gains of tested instruments at 5×10^{-5} Pa are given in **Table 7**.

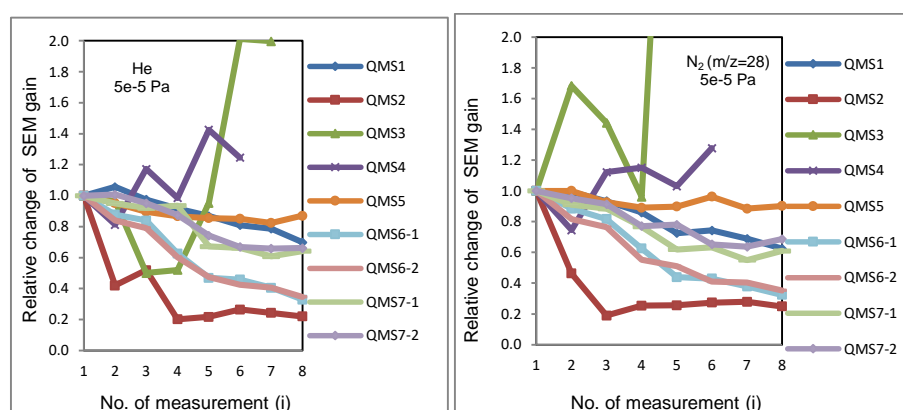


Fig.4. Changes in QMS SEM Gain normalized to the initial value at 5×10^{-5} Pa for Helium ($m/z=4$) (left) and N_2 ($m/z=28$) (right); time interval between each measurement is about three months.

Table 7 Initial SEM gain values of tested QMSs at 5×10^{-5} Pa

Instr.	Initial SEM gain		
	He (4)	N ₂ (14)	N ₂ (28)
QMS1	1277	1161	1212
QMS2	6474	4545	4556
QMS3	104	30	21
QMS4	3082	2243	2203
QMS5	338	174	108
QMS6-1	3426	2868	2979
QMS6-2	3312	2769	2947
QMS7-1	2361	2696	2312
QMS7-2	2246	2556	2201
QMS8	NA	NA	NA

According to participant2's declaration, there was probably a mistake at Helium SEM gain measurement at no.3 for QMS2. Most probably, the high voltage on SEM was not switched

off when the detector was switched to Faraday. They have observed strange results when Faraday detector is used and high voltage is still present on SEM.

Blanchard *et al* investigated long term trend in sensitivity of QMS within 90 days and 65 days, and observed a drop in sensitivity less than 320% and change less than $\pm 15\%$ with and without using SEM, respectively. They pointed out that no significant long term change was observed in the sensitivity when Faraday was used, in contrary to that, slowly decreasing in sensitivity with SEM was observed [5]. Similarly, Basford *et al* emphasized that electron multipliers are unstable since the gain depends on the composition of the active surface. Gain changes with time by alteration the surfaces caused by surface reactions and baking [6]. Similar behavior was observed in this study. While the relative sensitivity of change outputs is more stable in time for Faraday, within given $\pm 50\%$ to $\pm 30\%$ band, for each gas species and pressure points, those seem to slowly decrease in time within the same band in the case of SEM measurements, as highlighted in previous studies [5,6]. Calcatelli *et al* observed less than $\pm 20\%$ sensitivity change without using SEM during the test period of 310 days for Argon [7]. Yoshida *et al* observed maximum $\pm 25\%$ sensitivity change without using SEM during the test period of 757 days for different gases including nitrogen and helium [8].

3.4. MDPP stability measurements

It can be seen in Fig.5 that there are large dispersions in the MDPP during this period of time. MDPP changed by a factor 2 in a period of two years, with some exceptions. One instrument was not used in proper way. Initial MDPP values of tested instruments are given in Table 8.

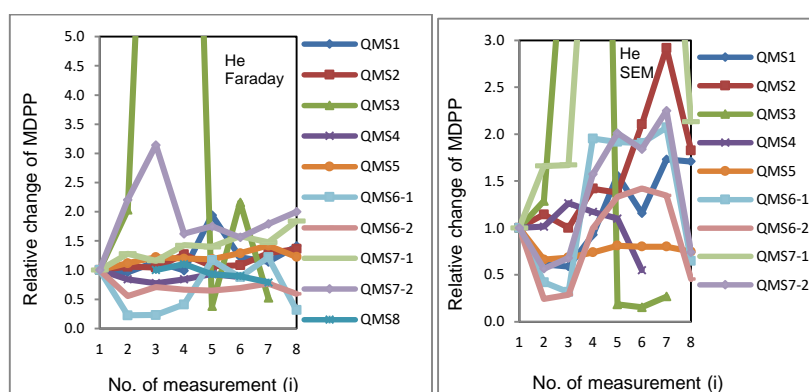


Fig.5. Changes in MDPP normalized to the initial value for Helium ($m/z=4$) for Faraday (left) and SEM (right); time interval between each measurement is about three months.

Table 8 Initial MDPP values of tested QMSs

Initial MDPP		
Instr.	Faraday	SEM
QMS1	1.2E-09	5.2E-11
QMS2	6.8E-09	1.4E-11
QMS3	9.1E-07	1.2E-08
QMS4	4.7E-09	2.3E-12
QMS5	9.2E-08	5.0E-10
QMS6-1	1.9E-09	7.2E-12
QMS6-2	6.6E-10	8.2E-12
QMS7-1	5.9E-10	3.4E-12
QMS7-2	6.4E-10	1.1E-11
QMS8	3.2E-08	NA

Table 9 Changes of sensitivities in two years and maximum single jumps of sensitivities in three months are given for tested QMSs.

Instruments	Change in two years in sensitivity	Maximum single jump in 3 months
QMS1	110%	35%
QMS2	25%	30%
QMS3	60%	120%
QMS4	10%	20%
QMS5	60%	20%
QMS6-1	500%	560%
QMS6-2	90%	80%
QMS7-1	50%	120%
QMS7-2	60%	60%
QMS8	40%	60%

4. Conclusion

A few general observations can be made from the results. In summary, changes of sensitivities in two years and maximum single jumps of sensitivities in three months for tested QMSs are given in **table 9**. According to these results, QMS4 appears to be the most stable instrument in terms of sensitivity measurements.

There have been significantly questions raised including performance of the device which affects the accuracy, how the stability is related to time, gas species and pressure, how the history of usage affects the performance of the device. The QMS users should find the possible reasons of extreme examples observed in this study and examine its assumptions about the characteristics of their device.

Time stability characterization of eight quadrupole mass spectrometers (QMSs) was investigated by seven national metrology institutes in the framework of EMRP IND12 project that was funded by the European Metrology Research Program. A comprehensive study was carried out and a set of appropriate parameters were considered and suggested to characterize QMSs from a metrological point of view: sensitivity, mass scale, mass resolution, secondary electron multiplier (SEM) gain and minimum detectable partial pressure (MDPP).

The obtained results have shown that one of the main parameters which influence the time stability over time is the sensitivity of QMSs for both cases of Faraday. Typical variations between 30% and 60% were registered over a relative short period (three month), confirming that the sensitivity has to be frequently tested to characterize a measurement system involving a QMSs. Sensitivities changed within $\pm 50\%$, with some exceptions. In case of sensitivity measurements, typical changes in three months period less than 60% for 6 instruments and more than 60% for 3 instruments were observed, with extreme up to 560%.

The changes of the peak widths and peak positions were generally less than 0.1 amu. A further relevant parameter to be taken into account resulted by the SEM gain, which tends to decrease over time, with typical changes between 30% and 80% over a period of two years. MDPP changed by a factor 2 in a period of two years, with some exceptions.

Acknowledgements

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