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Vacuum technology — Vacuum gauges — Characterization of quadrupole mass spectrometers for partial pressure measurement

Technique du vide — Manomètres à vide — Description des spectromètres de masse quadripolaires pour mesurage de la pression partielle

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Foreword

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The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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This document was prepared by Technical Committee ISO/TC 112, *Vacuum technology*.

Introduction

Quadrupole mass spectrometers (QMSs) are nowadays used not only in vacuum technology for leak detection and residual gas analysis but also in the process industry as an instrument to provide quantitative analysis in processes and to control processes such as physical and chemical vapour deposition, and etch processes. They are also used for quantitative outgassing rate measurements which are important to characterize vacuum components for critical applications like in the EUV lithography, semiconductor industry or medical instruments.

Total pressure, composition of the gas mixture, settings and the operational history of QMSs, to name a few, have a significant influence on the measured signal, its uncertainty and interpretation. For this reason, it is not possible to calibrate QMS for all its possible applications. Instead, it has either to be calibrated for the special conditions at use or for a standardized condition. It is the purpose of this document to establish such conditions.

There is also a need for standardization in order to enable the users of QMSs to compare the devices of different manufactures and to use the QMS properly.

This document provides standardized calibration procedures for QMSs for some important applications. These have been selected from the results of a survey of the international project EMRP (European Metrological Research Programme) IND12 which was conducted in 2013. This survey included manufacturers, distributors and users of quadrupole mass spectrometers.

Vacuum technology — Vacuum gauges — Characterization of quadrupole mass spectrometers for partial pressure measurement

1 Scope

This document describes procedures to characterize quadrupole mass spectrometers (QMSs) with an ion source of electron impact ionization and which are designed for the measurement of atomic mass-to-charge ratios $m/z < 300$.

This document is not applicable to QMSs with other ion sources, such as chemical ionization, photo-ionization or field ionization sources and for the measurements of higher m/z, which are mainly used to specify organic materials.

It is well known from published investigations on the metrological characteristics of quadrupole mass spectrometers that their indications of partial pressures depend significantly on the settings of the instrument, the total pressure, and the composition of the gas mixture. For this reason, it is not possible to calibrate a quadrupole mass spectrometer for all possible kinds of use. The characterization procedures described in this document cover the applications of continuous leak monitoring of a vacuum system, leak rate measurement with tracer gas, residual gas analysis and outgassing rate measurements. The user can select that characterization procedure that best suits his or her needs. These characterization procedures can also be useful for other applications.

It is also well known that the stability of several parameters of quadrupole mass spectrometers, in particular sensitivity, are rather poor. Therefore, when a parameter has been calibrated, it needs frequent recalibration when accuracy is required. For practical reasons this can only be accomplished by *in situ* calibrations. To this end, this document not only describes how a quadrupole mass spectrometer can be calibrated by a calibration laboratory or a National Metrological Institute with direct traceability to the System International (SI), but also how calibrated parameters can be frequently checked and maintained *in situ*.

By their physical principle, quadrupole mass spectrometers need high vacuum within the instrument. By reducing dimensions or by special ion sources combined with differential pumping the operational range can be extended to higher pressures, up to atmospheric pressure. This document, however, does not include quadrupole mass spectrometers with differential pumping technology. Therefore, it does not cover pressures exceeding 1 Pa on the inlet flange of the quadrupole mass spectrometer.

This document does not describe how the initial adjustment of a quadrupole mass spectrometer by the manufacturer or by a service given order by the manufacturer should be made. The purpose of such an initial adjustment is mainly to provide a correct m/z scale, constant mass resolution or constant transmission, and is very specific to the instrument. Instead, it is assumed for this document that a manufacturer's readjustment procedure exists which can be carried on-site by a user. This procedure is intended to ensure that the quadrupole mass spectrometer is in a well-defined condition for the characterization.

It is the intention of this document that the user gets the best possible metrological quality from his quadrupole mass spectrometer. From investigations it is known that in most cases this can be achieved in the so called "scan mode". The bar graph may also be of an adequate quality depending on the software used for evaluation of the data taken by the quadrupole mass spectrometer. The trend mode, however, often involves the additional uncertainty that a shift of the peak value position on the mass scale causes a shift in ion current. For this reason, the scan mode is preferable for most of the measurement procedures of this document.

It is not the intent of this document that all the parameters described be determined for each quadrupole mass spectrometer. However, it is intended that the value of a parameter addressed in this document be determined according to the procedure described in this document if it is given or measured (e.g. for an inspection test).

It is assumed for this document that the applicant is familiar with both the operation of quadrupole mass spectrometers and high and ultra-high vacuum technology.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3567:2011, *Vacuum technology — Vacuum gauges — Calibration by direct comparison with a reference gauge*

ISO 14291, *Vacuum technology — Vacuum gauges — Definitions and specifications for quadrupole mass spectrometer*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 14291 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

3.1
matrix gas
gas or gas mixture that makes the major contribution to the total pressure

3.2
equivalent nitrogen pressure
pressure of nitrogen which would produce the same gauge reading as the pressure of gas acting on a vacuum gauge

[SOURCE: ISO 3529-3:2014, 2.3.5, modified.]

Note 1 to entry: Nitrogen equivalent depends on the type of gauge, since the relative sensitivity factor is different for different types. For this reason, the term should be used with the type of vacuum gauge.

3.3
transmission probability
ratio of ion current of a certain mass-to-charge ratio exiting a quadrupole filter of a QMS to the current of ions of the same mass-to-charge ratio entering it

3.4
scan speed
speed as u ($\Delta m/z$=1) per time with a defined number of signal points per u ($\Delta m/z$=1)

3.5
linear response range
partial pressure range over which the non-linearity is within a specified limit

Note 1 to entry: For the purpose of this document the limit is ± 10 % from the mean value.

Note 2 to entry: The linear response range can also depend on the conversion of the output current signal to a digital value. Sometimes a single digital bit does not quantise the same amount of current at the lower and upper end of the range.

[SOURCE: ISO 14291:2012, 2.2.18, modified – Notes to entry have been added.]

3.6

leak rate measurement

quantitative measurement of a tracer gas through a leak

3.7

leak rate monitoring

continuous monitoring of one or several selected gas species with respect to the normal background in a vacuum system in order to detect a change caused by a leak

EXAMPLE 1 In an accelerator tube, argon is monitored to detect a leak from air.

EXAMPLE 2 In a fusion reactor, water peaks are monitored to detect a leak from the cooling system.

3.8

fragmentation pattern

pattern (i.e. kinds and relative amounts) of ions produced by a given pure gas in a given mass spectrometer under given conditions

Note 1 to entry: This definition does include the isotopic and isomeric distribution of the species.

[SOURCE: ISO 14291:2012, modified – Notes to entry replaced.]

3.9

interference effect ratio

ratio S_i' / S_i where

S_i' is the sensitivity of a specified gas species i of partial pressure p_i present in an interference gas or interference gas mixture;

S_i is the sensitivity at the same value of p_i when only species i is present.

3.10

interference gas

gas species added to a pure gas that may cause an interference effect

3.11

interference gas mixture

mixture of several gas species added to a pure gas that may cause an interference effect

3.12

dynamic range

ratio of the largest signal to the smallest signal within a spectrum

Note 1 to entry: The difference between minimum detectable concentration (C_{MDC}) as defined in ISO 14291 and dynamic range is that for the C_{MDC} it is acceptable to optimize the signal to noise ratio for the minor constituent, while this is not possible for the dynamic range.

4 Symbols and abbreviated terms

Symbol	Designation	Unit
C_{eff}	effective conductance of a duct, effective pumping speed	m^3/s or L/s
R_{dyn}	dynamic range	1
f	fragmentation factor	1

Symbol	Designation	Unit
I	ion current at partial pressure p	A
I_0	ion current at residual pressure p_0	A
m	molecular mass in atomic mass units	u
M	molecular mass	kg
c_{MDC}	minimum detectable concentration	1
p_{MDPP}	minimum detectable partial pressure	Pa
p	pressure or partial pressure	Pa
p_0	residual pressure or residual partial pressure	Pa
r_{x}	relative sensitivity for a specified gas species “x” divided by sensitivity S_{N2} for nitrogen	1
$q_{V,i}$	volume flow rate of species i into a vacuum pump (pumping speed)	$\mathrm{m^3/s}$ or L/s
R	universal gas constant	$\mathrm{J\ mol^{-1}\ K^{-1}}$
S	sensitivity (coefficient)	A/Pa
SI	System International	
S_{N2}	sensitivity for nitrogen	A/Pa
T	temperature	K
T_{P}	transmission probability	1
z	the ionization state of a molecule	1
Δm	mass resolution as defined in ISO 14291	u
CEM	continuous dynode electron multiplier	
MCP	micro-channel plate	
QMS	quadrupole mass spectrometer	
SEM	secondary electron multiplier	

NOTE The symbol m characterizes the mass of a molecule in u, while m/z characterizes at which position the molecule with mass m appears on the mass scale indicated by the QMS. This is proportional to the mass-to-charge ratio and therefore also to m/z.

5 Parameters for which characterization is required or recommended for the different applications

5.1 General

ISO 14291 requires a certain number of parameters to be stated by a manufacturer for general characterization. This is covered in 5.1. It is also recommended that the general characterization is applied as characterization of an individual QMS and its performance monitored over its lifetime. It is recommended that the parameters described in the following sections are determined to improve accuracy and reliability of the QMS for the specific application mentioned in the section title.

The extent of such characterizations has to be adapted to the application and can usually not be accomplished by a manufacturer for economical reasons.

5.2 General characterization of the QMS

It is required by ISO 14291 that the following parameters are given by the manufacturer for a general characterization:

a) linear response range for pure nitrogen;

b) sensitivity for pure nitrogen in the linear response range as a result of measurement a);

c) minimum detectable partial pressure for helium and nitrogen;

d) dynamic range.

It is recommended that, in addition, the following parameters are given as part of the specification of the QMS:

e) minimum detectable concentration for helium in nitrogen (nitrogen partial pressure at around 10 % of the maximum operational pressure or around 10^{-3} Pa, whatever is lower);

f) mass resolution at $m/z = 4$ and optionally also $m/z = 28$ and 136(Xenon).

NOTE The upper limit of linear response range of conventional QMSs is typically below 10^{-4} Pa except for QMSs designed for pressures higher than 10^{-2} Pa.

5.3 Leak rate measurement and leak rate monitoring (helium leak)

a) linear response range for pure helium;

b) sensitivity for pure helium in the linear response range as a result of measurement a);

c) interference effect of helium within the linear response range for pure helium by introducing nitrogen of partial pressure of 10^{-3} Pa or the typical operational pressure in the application;

d) linear response range for helium in nitrogen as a result of measurement c);

e) minimum detectable partial pressure for helium;

f) minimum detectable concentration for helium in nitrogen (nitrogen partial pressure around 10^{-3} Pa);

g) dynamic range.

5.4 Leak rate monitoring (air leak)

This type of characterization depends on the specific need of application. In particular, it is important whether a clean UHV system as a high energy accelerator or a system at high vacuum with many constituents (e.g. fusion or plasma reactor) is monitored.

For a clean UHV system it is recommended that the following is measured:

a) linear response range for nitrogen, oxygen, and argon, each as pure gas;

b) sensitivity for nitrogen, oxygen and argon in linear response range as a result of measurement a);

c) fragmentation pattern for nitrogen and oxygen as a result of measurement a);

d) relative sensitivity factors for oxygen and argon as a result of measurement a);

e) dynamic range.

For other systems with background in the high vacuum range with a major gas constituent *m* (e.g. argon), it is recommended that the following is measured:

1) sensitivity for the gas to be monitored as air constituent (nitrogen, oxygen, or argon, whichever applies), in the major gas constituent *m* at its maximum operational pressure (equivalent nitrogen pressure) between partial pressure of 10^{-7} Pa and maximum operational pressure (equivalent nitrogen pressure);
2) relative sensitivity factors for the monitoring gas as a result of measurement a);
3) fragmentation pattern for the monitoring gas as a result of measurement a);
4) minimum detectable concentration for the monitoring gas in the major gas constituent;
5) dynamic range.

5.5 Leak rate monitoring (water leak)

a) Sensitivity for pure water vapour near 10^{-5} Pa;

b) fragmentation pattern for water vapour as a result of measurement a);

c) interference effect of water vapour at 10^{-5} Pa by introducing nitrogen or the major constituent of the residual gas in the application at 10^{-3} Pa pressure or the operational pressure in the application;

d) linear response range for water vapour in nitrogen or the major constituent of the residual gas as a result of measurement c);

e) fragmentation pattern for water vapour as a result of measurement c);

f) minimum detectable concentration for water vapour in nitrogen or the major constituent of the residual gas (partial pressure preferably near 10^{-3} Pa or the operational pressure in the application).

NOTE 1 When the residual gas is water vapour, there is no need to characterize the interference effect.

NOTE 2 Depending on the surface area, the time to reach equilibrium could be many hours.

5.6 Residual gas analysis

a) Total outgassing rate of the QMS in equivalent nitrogen pressure under residual pressure conditions after a bake-out and optionally outgassing rate for individual gas species of interest;

b) sensitivity for hydrogen, methane, nitrogen and carbon dioxide at a total pressure of 10^{-5} Pa (equivalent nitrogen pressure) in a mixture of 70 % hydrogen, 5 % methane, 20 % nitrogen, 5 % carbon dioxide;

c) fragmentation pattern for methane, nitrogen, carbon dioxide in pure gas, preferably at 10^{-5} Pa;

d) optionally, additional sensitivities for pure gas species to be expected from the chamber may be measured, for example water vapour or dodecane as an easy-to-handle representative of hydrocarbons.

NOTE 1 Interference effect for nitrogen can be determined by comparison of sensitivity in general characterization and measurement b).

The mixture mentioned above shall prevail in the measurement chamber, see Annex A.

If hydrogen is not available in the mixture described above, a separate hydrogen leak may be used to obtain the desired partial pressure, which could also be helpful for safety issues.

NOTE 2 To include water vapour in the gas mixture is desirable, but at the present stage too complicated to be realized.

NOTE 3 The mixture above was selected to be similar to the residual gas composition of a baked system. Further investigations are needed to see if the mixture is also of sufficient significance for an unbaked chamber or sample.

5.7 Outgassing rate measurement

a) Outgassing rate of the QMS in equivalent nitrogen pressure under residual pressure conditions after a bake-out and optionally for individual gas species of interest (see 7.10);

b) effective pumping speed for nitrogen and optionally for hydrogen and water vapour (see 7.11);

c) sensitivity for hydrogen, methane, nitrogen and carbon dioxide at a total pressure of 10^{-5} Pa (equivalent nitrogen pressure) in a mixture of 70 % hydrogen, 5 % methane, 20 % nitrogen, 5 % carbon dioxide;

d) fragmentation pattern for methane, nitrogen, carbon dioxide in pure gas, preferably at 10^{-5} Pa;

e) optionally, additional sensitivities for pure gas species to be expected from the sample may be measured, for example water vapour or dodecane as an easy-to-handle representative of hydrocarbons.

Consider 5.6, NOTEs 1 to 3.

NOTE Interference effect for nitrogen can be determined by comparison of sensitivity in general characterization and measurement b).

The outgassing rate of the instrument is determined by design, the choice of material and the conditioning of the device, but also thermal radiation from the hot filament of the QMS could lead to significant desorption in other places in the chamber, especially if these are contaminated. In this sense, the outgassing caused by the instrument should be determined or repeated *in situ* before measurements of outgassing rate of samples are started.

6 Vacuum systems to characterize QMS

6.1 General

Most of the characterizations and calibrations described in Clause 7 can be performed in a vacuum system where a known pressure of a single pure gas can be established. An important part of the characterizations, however, can only be performed in a system where known partial pressure of at least two gas species can be established. This is due to the interference effect. The single gas systems are described in 6.2, the systems for gas mixtures in 6.3. Such systems can typically be provided by National Metrological Institutes or large research facilities and give the most direct path to the SI.

Due to the instability of some parameters of the QMS, these need repeated determinations *in situ* during use. This equipment for *in situ* calibration, described in 6.2.3 and 6.3.2, is designed for practical use at any place where it is necessary to obtain quantitative results with QMS, but where the effort to achieve this has to be cost-effective.

In all systems, the QMS shall be installed such that there is no direct line of sight to any other ion source, be it from an ionization gauge or another QMS. The position of any reference QMS or vacuum gauge and the QMS to be investigated shall be such that equal gas densities exist at the different locations. This can be accomplished by applying symmetry considerations or by suitably positioning the gas inlet and outlet.

The temperature of the vacuum systems should be 23 °C, but a deviation from this value by 7 K is permitted, if the environmental conditions require this. The QMS to be characterized has to allow this temperature. The temperature variation during the measurements should not exceed 1 K.

6.2 Vacuum system for characterization with single gas

6.2.1 Continuous expansion system (orifice flow system)

Continuous expansion systems are available in National Metrology Institutes or calibration laboratories with high metrological level. The calibration pressure is calculated from the ratio of the injected gas flow rate into the calibration chamber and the conductance of the orifice to the pump. The flow rate is determined by a flow meter such as a constant volume type or a constant pressure type. The conductance is determined from physical first principles. In a modification of the continuous expansion system, the so-called pressure divider systems are used. These rely on the fact that the pressure ratio across a flow restricting element is independent of pressure in molecular flow regime.

When users of QMS ask to characterize their QMS in calibration laboratories, it is recommended that a pertinent National Metrological Institute or an accredited calibration laboratory based on ISO 17025 is chosen.

6.2.2 Calibration system according to ISO 3567:2012

ISO 3567 describes a system for calibration of vacuum gauges by direct comparison with a reference gauge. The usually large volume of a QMS shall be considered for the volume of the calibration chamber according to ISO 3567:2012, 6.1 a). The stationary equilibrium method [ISO 3567:2012, 7.1.5 b)] shall be applied. As described in ISO 3567:2012, the reference gauges shall be traceable to the SI. For the purpose of this document, a hot cathode ionization gauge is recommended as a reference gauge. The stability of the calibration parameter of the hot cathode ionization gauge may be checked by a spinning rotor gauge. This may also be used as a reference gauge at pressures $> 10^{-4}$ Pa. In addition, capacitance diaphragm gauges can be used at pressures $> 10^{-2}$ Pa.

NOTE 1 The reading of non-heated capacitance diaphragm gauges is not gas-sensitive, while heated ones reveal a gas-dependent reading due to thermal transpiration effect in the range 0,1 Pa to 100 Pa.

NOTE 2 The accommodation factor of a spinning rotor gauge varies with gas species within about 5 % from the one determined for nitrogen. Given this, the controller will show the right pressure reading within 5 % provided that the molecular mass has been set to the right gas species.

NOTE 3 The sensitivity of a hot cathode ionization gauge varies with gas species. The respective gas correction factors need to be applied. These can be taken from textbooks or manufacturers' specifications. For uncertainties see Clause 8.

6.2.3 *In situ* calibration system

In this approach, a reference gauge calibrated for the respective gas species i is used to determine the effective pumping speed. In combination with a known gas flow $q_{pV,i,\mathrm{ref}}$ of a single gas species i, the effective pumping speed $C_{\mathrm{eff},i}$ can be determined by Formula (1).

$$C_{\mathrm{eff},i} = \frac{q_{pV,i,\mathrm{ref}}}{p_{i,\mathrm{ref}}} \tag{1}$$

where $p_{i,\mathrm{ref}}$ is the pressure indicated by the gauge for a pure gas with molecular mass M_i. When the pressure is in a range that the flow of gas is of molecular type, which typically is true for $p_i < 10^{-2}$ Pa, it can be assumed that $C_{\mathrm{eff},i}$ is pressure independent. This enables the user to use the determined value of $C_{\mathrm{eff},i}$ even at pressures where no reference gauge is available.

When an orifice or other small conductance element with known geometry is used between chamber and pump system in the *in situ* calibration system, the effective pumping speed $C_{\mathrm{eff},i}$ is calculated from the dimensions.

In the following, known partial pressures will be needed for the calibration of QMS. For this, a known gas flow $q_{pV,i}$ has to be injected into the *in situ* calibration system. This can be accomplished by commercially available mass flow meters, by commercially available standard leaks, or by specially designed leak elements which leak in the desired gas species or gas mixture from a reservoir at known pressure. An example is the SCE element[1], which exhibits molecular flow through it so that the conductance of the SCE element can be calculated for any gas species from the conductance of a known gas species, similar to $C_{\text{eff},i}$ previously. The pressure p_i for species i is calculated from Formula (2).

$$p_i = \frac{q_{pV,i}}{C_{\text{eff},i}} \tag{2}$$

The method to determine $C_{\text{eff},i}$ as described previously is sufficiently accurate. It should be carried out for each species i which is needed for the characterization of the QMS. If the indication of the reference gauge $p_{i,\text{ref}}$ is not available for the desired species i [Formula (1)], $C_{\text{eff},i}$ can be estimated in the following way, if the pumping speed $q_{V,\text{N2}}$ and $q_{V,i}$ are known:

1) measure $C_{\text{eff,N2}}$ for nitrogen;

2) calculate the conductance $C_{\text{tube,N2}}$ of the tubulation leading to the pump using Formula (3);

$$C_{\text{tube, N2}} = \left(\frac{1}{C_{\text{eff, N2}}} - \frac{1}{q_{V,\text{N2}}} \right)^{-1} \tag{3}$$

3) for the species i with relative molecular mass M_i and unknown $C_{\text{eff},i}$ calculate $C_{\text{tube},i}$ according to Formula (4);

$$C_{\text{tube},i} = C_{\text{tube, N2}} \sqrt{\frac{28}{M_i}} \tag{4}$$

4) estimate $C_{\text{eff},i}$ using Formula (5).

$$C_{\text{eff, i}} = \left(\frac{1}{C_{\text{tube},i}} + \frac{1}{q_{V,i}} \right)^{-1} \tag{5}$$

NOTE $q_{V,\text{N2}}$ is usually given by the manufacturer. $q_{V,i}$, if not given by the manufacturer, can be estimated.

6.3 Vacuum system for characterization with gas mixtures

6.3.1 Continuous expansion system (orifice flow system)

These calibration systems shall provide well-defined total pressures of pure gases or well-known partial pressures of at least two gas species in the high and ultra-high vacuum range. For this, no secondary standards for total or partial pressures in the high and ultra-high vacuum shall be used.

Continuous expansion systems as described in 6.2.1 are used for this purpose. They are extended either by:

a) several flowmeters in fundamental method – the partial pressures are determined from Formula (2);

b) reservoirs, one for each species, with a constant and known pressure in front of a calibrated conductance (leak element) into the calibration chamber; or

c) a known gas mixture with constant and known pressure in front of a calibrated conductance.

In the final case, it is important that a known quantitative composition of the mixture is established in the calibration chamber. This can be achieved by molecular flow both in and out of the calibration chamber.

For b) and c) the partial pressures are determined from Formula (6).

$$p_i = \frac{p_{R,i} C_{R,i}(p_{R,i})}{C_{\text{eff},i}} \tag{6}$$

where $p_{R,i}$ is the pressure (respectively partial pressure in case of c) in the reservoir and $C_{R,i}$ conductance of the leak element for species i at this pressure in the reservoir.

6.3.2 *In situ* calibration system for gas mixture

The method described in 6.2.3 can be extended to a gas mixture that is produced by several gas inlets as described above in 6.3.1 or by a single inlet of a gas mixture where the partial flows are known. The system described in 6.3.2 can also be modified as such an *in situ* system for gas mixture. The modification includes the addition of standard leaks or of several gas inlets with known flows. The mixing of gases should happen before they enter the chamber via the regular (single species) gas inlet.

The flow $q_{pV,i}$ from the standard leak converts to partial pressure according to the effective pumping speed $C_{\text{eff},i}$ for species i. $C_{\text{eff},i}$ can be measured according to Formula (1) in 6.2.3 or estimated in the following way, provided that both the pumping speed $q_{V,\text{N2}}$ and $q_{V,i}$ are known from the data sheet of the pump:

1) measure $C_{\text{eff,N2}}$ for nitrogen;

2) calculate the conductance $C_{\text{tube,N2}}$ of the tubulation leading to the pump using Formula (7).

$$C_{\text{tube, N2}} = \left(\frac{1}{C_{\text{eff, N2}}} - \frac{1}{q_{V,\text{N2}}} \right)^{-1} \tag{7}$$

3) for the species i with relative molecular mass M_i and unknown $C_{\text{eff},i}$ calculate $C_{\text{tube},i}$ according to Formula (8).

$$C_{\text{tube},i} = C_{\text{tube, N2}} \sqrt{\frac{28}{M_i}} \tag{8}$$

4) estimate $C_{\text{eff},i}$ using Formula (9).

$$C_{\text{eff, i}} = \left(\frac{1}{C_{\text{tube},i}} + \frac{1}{q_{V,i}} \right)^{-1} \tag{9}$$

The partial pressures are determined from Formula (2).

Nitrogen can be replaced by any other gas j where $q_{V,i}$ is known from the data sheet of the pump. In this case, the relative molecular mass of nitrogen 28 has to be replaced by M_j in Formula (8).

NOTE 1 $q_{V,\text{N2}}$ is usually given by the manufacturer. $q_{V,i}$, if not given by the manufacturer, can be estimated.

NOTE 2 If a standard leak for a mixture is provided with a reservoir, the composition in the reservoir will change with time when the flow out of it is of molecular type. Due to the higher conductance of light molecules, the portion of light species will be diminished.

7 Characterization and calibration procedures

7.1 General

For all following procedures it is necessary that the QMS has been adjusted. After the adjustment, the parameters shall not be changed.

Some users may have special adjustment procedures, because they have gained a lot of experience with their device and optimized it for their application. If these users require a calibration from someone else, they need to communicate these adjustment procedures so that the QMS can be calibrated with the same adjustments as during use. For less experienced users it is recommended that they use the adjustment procedures recommended by the manufacturer.

All operational parameters that are used during the measurements shall be recorded. Different QMSs may have different parameters that can be changed by the user or that can be recorded. These parameters can include:

- emission current;
- electron energy;
- extraction voltage;
- focus voltage;
- field axis potential (also called ion energy);
- SEM voltage;
- resolution setting;
- any other parameter that can be adjusted by the user.

If the manufacturer recommends performing "calibration" or "tuning" (like mass scale alignment or resolution setting) on a regular base (daily up to yearly) or after changing some parameters such as emission current, this should be done. Also, a re-zeroing of the electrometer may be a part of the (re) adjustment procedure.

In general, for accurate measurements and calibration purposes, the use of a secondary electron multiplier should be avoided whenever possible, since it is known that the amplification of this is unstable due to surface and aging effects. However, depending on the quantity to be measured, for example the minimum detectable pressure of an instrument equipped with SEM, the use of the electron multiplier is required. Whenever a SEM is used and a Faraday cup is available, it is advisable to measure the gain of the SEM.

In addition, the QMS shall be warmed up before the measurements (for warm-up time see manual). A warm-up time of 2 h is usually sufficient.

For some parameters, a bake-out will improve the performance of the QMS. A bake-out is strongly recommended before the measurements of 7.10 and 7.11. The QMS should be conditioned (operation during bake-out, degas, etc.) in the same manner as before its use for outgassing measurement.

7.2 Mass resolution

A vacuum system according to 6.2 is sufficient.

The mass resolution Δm depends mainly on the settings of the quadrupole voltages for the given geometry and RF-frequency of the quadrupole filter. The product of mass resolving power $m/\Delta m$ and transmission probability T_p anticorrelate. Normally the settings are such that Δm is constant throughout the mass range of the QMS. For this reason, it is sufficient to determine Δm at a specific m/z. This document recommends helium at $m/z = 4$. If it is important to know how the mass resolution Δm may vary, two values of m/z are recommended. This document recommends helium at $m/z = 4$ and argon near $m/z = 40$. Other m/z values may be added. The procedure is as follows:

1) pump to residual pressure conditions of your system;

2) select the detector and the settings of the QMS and the desired gas species with $(m/z)_j$;

3) measure the spectrum with a step width of $m/z \leq 0,05$ or the minimum step width if greater than 0,05 and a scan speed of 1 s/u in the range $(m/z)_j - 1$ to $(m/z)_j + 1$ 10 times as background spectrum;

4) expose the QMS to a partial pressure of $(5 \pm 2)\cdot 10^{-5}$ Pa of the desired gas (helium, argon) with $(m/z)_j$;

5) measure the spectrum with a step width of $m/z \leq 0{,}05$ or the minimum step width if greater than 0,05 and a scan speed of 1 s/u in the range $(m/z)_j$-1 to $(m/z)_j$+1 10 times;

6) subtract background and determine for each scan the two values of m/z at 5 % of peak height. An interpolation between points is usually necessary. The positive difference is Δm.

NOTE Sometimes the peak height is not evident from data, because the shape of the peak is not smooth. In this case, an estimate of the peak height can be obtained from a fit procedure.

7.3 Minimum detectable partial pressure (p_{MDPP})

Vacuum system according to 6.2 is sufficient.

The minimum detectable pressure depends on the gas species, since the noise around the m/z of the selected gas species depends on the value of m/z. In addition, for some gas species the residual gas composition might not allow for the determination of the noise around the m/z of the selected gas species. It is desirable to prevent the arrival of any ion from reaching the detector, but this option is usually not available.

The procedure to determine the p_{MDPP} of helium is:

a) select the detector and the settings of the QMS;

b) determine the sensitivity S for helium (see 7.5) at one partial pressure value in the range 10^{-9} Pa to 10^{-5} Pa;

c) measure the noise at $m/z = 5$ with 100 values at residual pressure, each with an integration time of 1 s, and determine the sample standard deviation σ_I of these values;

d) the p_{MDPP} is given by $p_{\mathrm{MDPP}\,j} = \dfrac{3\sigma_I}{S_j}$, where j is the gas species, here helium.

If the QMS does not allow an integration time of 1 s to be set, 100 values within a total time as close as possible to 100 s should be taken.

The procedure to determine the p_{MDPP} of gas species j with m/z < 50 (except helium) is:

1) select the detector and the settings of the QMS;

2) determine the sensitivity S for gas species j (see 7.5) at one partial pressure value in the range 10^{-9} Pa to 10^{-5} Pa;

3) measure the noise at $m/z = 5$ with 100 values at residual pressure, each with an integration time of 1 s, and determine the sample standard deviation σ_1 of these values;

4) measure the noise at $m/z = 35$ with 100 values, each with an integration time of 1 s, and determine the sample standard deviation σ_2 of these values;

5) calculate the mean $\sigma_I = (\sigma_1 + \sigma_2)/2$;

6) the p_{MDPP} is given by $p_{\mathrm{MDPP}\,j} = \dfrac{3\sigma_I}{S_j}$, where j is the gas species.

The procedure to determine the p_{MDPP} of gas species j with $m/z \geq 50$ is the following:

i) select the detector and the settings of the QMS;

ii) determine the sensitivity S for gas species j (see 7.5) at one partial pressure value in the range 10^{-9} Pa to 10^{-5} Pa;

iii) measure the noise at $m/z = 62$ with 100 values at residual pressure, each with an integration time of 1 s, and determine the sample standard deviation σ_I of these values. In the unusual case that there is a signal at $m/z = 62$, select the nearest m/z without signal;

iv) the p_{MDPP} is given by $p_{\mathrm{MDPP}\,j} = \frac{3\sigma_I}{S_j}$, where j is the gas species.

7.4 Minimum detectable concentration (C_{MDC})

Vacuum system according to 6.3 is needed.

The minimum detectable concentration depends on the gas species to be detected and the matrix gas, since ionization probability, space charge effects and transmission probability both to and through the quadrupole filter play important roles. Due to the importance of helium for leak rate measurement, this document recommends determining the minimum detectable concentration of helium in nitrogen as a general specification of a QMS.

The procedure is:

1) select the detector and the settings of the QMS;

2) expose the QMS to a partial pressure p_{Nitrogen} of nitrogen between $8 \cdot 10^{-4}$ Pa and $2 \cdot 10^{-3}$ Pa (or maximum pressure compatible with SEM or 10 % of the maximum operational pressure), preferably at $1 \cdot 10^{-3}$ Pa;

3) it is recommended that the QMS is adjusted such that the signal-to-noise value for helium is maximized by measuring noise (see Clause 4) and sensitivity (see Clause 5);

4) measure the current noise at $m/z = 5$ with 100 values when the nitrogen pressure of step 2) is still present, each with an integration time of 1 s, and determine the sample standard deviation σ_I of these values;

5) determine the sensitivity S for helium (see 7.6) at one partial pressure value in the range 10^{-9} Pa to 10^{-5} Pa, also when the nitrogen pressure of step 2) is still present;

6) the p_{MDPP} is given by $p_{\mathrm{MDPP}\,j} = \frac{3\sigma_I}{S_j}$, where j is the gas species, here helium;

7) the minimum detectable concentration C_{MDC} is given by $C_{\mathrm{MDC}} = \frac{p_{\mathrm{MDPPHe}}}{p_{\mathrm{Nitrogen}}}$.

7.5 Dynamic range

Vacuum system according to 6.2 is needed.

The procedure is:

1) select the detector and the settings of the QMS;

2) expose the QMS to a partial pressure p_{Nitrogen} which is below saturation level for the main peak of nitrogen;

3) measure the ion current of the main peak of nitrogen;

4) measure the current noise at $m/z = 36$ with 100 values, each with an integration time of 1 s, and determine the sample standard deviation σ_I of these values;

5) the dynamic range is given by $R_{\mathrm{dyn}} = \frac{I_{\mathrm{Nitrogen}}}{3\sigma_I}$;

6) round R_{dyn} to one significant digit.

7.6 Sensitivity and interference effect ratio

Vacuum system according to 6.2 is sufficient for a single gas, 6.3 is needed, when additional interference gas or mixture has to be added for the measurement of interference effect ratio.

The sensitivity S_j for a gas species j at a specified m/z is only defined for the special condition that comprises all the settings of a QMS, the partial pressure of gas species j and the other partial pressures present at the same time and exposed to the ion source of the QMS. Fortunately, the sensitivity is usually constant for a wider partial pressure range independent of other partial pressures, if the partial pressures are low enough. In general, it can be assumed that the sensitivity is constant (within ± 10 %), if the sum of all partial pressures is below 10^{-5} Pa. For many QMSs this is true up to 10^{-4} Pa, but rarely above.

The procedure to determine sensitivity at a specific partial pressure point is as follows:

1) pump to residual pressure condition of your system;

2) select the detector and the settings of the QMS and the desired gas species j and possibly a matrix gas or matrix gas mixture and their partial pressures;

3) measure the complete background spectrum at residual pressure condition of the system in the mass range 1 to $(m/z)_{k\max}$+2, where $(m/z)_{k\max}$ is the heaviest isotope or isomere that can be expected for gas species j;

4) introduce gas species j of the desired partial pressure p_j into the system;

5) measure the spectrum with a step width of $m/z \leq 0{,}1$ or the minimum step if greater than 0,1 and a scan speed of 1 u/s in the mass range 1 up to at least $(m/z)_{k\max}$+2, where $(m/z)_{k\max}$ is the heaviest isotope or isomere that can be expected for gas species j;

6) if required, inject the interference gas or interference gas mixture, otherwise proceed with step 8);

7) measure the spectrum with a step width of $m/z \leq 0{,}1$ or the minimum step if greater than 0.1 and a scan speed of 1 u/s in the mass range 1 up to at least $(m/z)_{k\max}$+2, where $(m/z)_{k\max}$ is the heaviest isotope or isomere that can be expected for gas species j;

8) subtract the background spectrum from the spectrum measured at both step 5) and step 7). The signal peaks at the $(m/z)_k$ that are significantly above the background signal are noted;

9) the sensitivity is calculated according to $S_{jk} = \frac{\left(I_{jk} - I_{0k}\right)}{p_j}$, where I_{jk} is the peak signal of gas species j at $(m/z)_k$ at p_j and I_{0k} is the background signal at $(m/z)_k$. If an interference gas or gas mixture is used, calculate $S'_{jk} = \frac{\left(I'_{jk} - I_{0k}\right)}{p_j}$, where I'_{jk} is the peak signal of gas species j at $(m/z)_k$ at p_j and the interference gas or mixture present, and I_{0k} is the background signal at $(m/z)_k$. The interference effect ratio is given by S'_{jk}/S_{jk}.

To estimate the uncertainties related to random effects as background signal scatter and short-term drift as well as repeatability of the instrument, at least three independent measurements (pump down in between) have to be carried out. Seven measurements spread over two different days are recommended.

Some QMS do not give a current as signal but a partial pressure or similar. For comparison with other QMS it is recommended that this other value is converted to a current. If this is not possible, the unit of S shall be explained.

NOTE The definition of sensitivity is in accordance with the definition in ISO 14291, 2.2.1, since only the gas added to the system is considered by pj and therefore we can set $p_0 = 0$, which is the signal at I_{0k}. The difference $(I_{jk} - I_{0k})$ in signal corresponds exactly to the quantity p_j.

The measurement of sensitivity can be extended to all $(m/z)_k$ for gas species j. In particular for nitrogen, it could be helpful to use $(m/z)_k = 14$ to distinguish the nitrogen signal from the CO signal. A clear note shall be given if something other than the main peak is used.

The sensitivity greatly depends on the detector and SEM gain. For this reason, any sensitivity value measured should be stated with the type of detector and SEM gain for the measured species.

If the purity of gas j is checked, it is recommended for step 3) that the mass spectrum ranges up to the highest m/z present in the system (e.g. if it is checked that the previous gas species is no longer present in the system).

If the scan speed of 1 u/s cannot be set, a similar value should be chosen. The scan mode is recommended. Other modes such as bar graph are allowed.

7.7 Linear response range

Vacuum system according to 6.2 is sufficient for a single gas, 6.3 is needed, when additional interference gas or mixture has to be added.

The procedure to determine the linear response range is as follows:

1) Measure the sensitivity for the pure gas from $9{\cdot}10^{-9}$ Pa or from the minimum operational partial pressure of the system, whichever is greater, to $9{\cdot}10^{-3}$ Pa or up to 10 % of the maximum operational pressure. Two points per decade, preferably at mantissa values 3 and 9, are recommended. An extension of the measurement range to lower and higher pressures is possible, but not to pressures higher than maximum operational pressure.

2) If an interference gas or mixture has to be added, repeat the measurement described in 1) with the interference gas or gas mixture present at the desired pressure.

3) The linear response range is the largest pressure range in which the minimum and maximum value of $S_{j,\mathrm{main}}$ deviate not more than 10 % from the mean of the two values in this pressure range. k = main denotes the peak of highest intensity (current).

NOTE The upper limit of linear response range is normally dependent on total pressure.

See 7.6.

7.8 Relative sensitivity factor

Vacuum system according to 6.2 is sufficient.

The procedure to determine the relative sensitivity factor r_j for a gas species j is as follows:

1) Determine the sensitivity and linear response range for nitrogen at its main peak according to 7.7. Determine the mean sensitivity S_{N2} in this linear response range.

2) Determine the sensitivity and linear response range for gas species j at its main peak according to 7.7. Determine the mean sensitivity S_j in this linear response range.

3) The relative sensitivity factor r_j is given by $r_j = \dfrac{S_j}{S_{\mathrm{N2}}}$.

To estimate the uncertainties related to random effects as repeatability of the instrument, at least three independent measurements (pump the gas out in between) have to be carried out for each gas. Seven measurements spread over two different days are recommended. For the repeat measurements it is sufficient to select three target pressure points distributed over the whole linear response range.

The measurement of the relative sensitivity factor r_j can be extended to all $(m/z)_k$ for gas species j. In any case, the main peak of nitrogen at $(m/z) = 28$ shall be used as reference. A clear note has to be given if something other than the main peak of gas species j is used.

7.9 Fragmentation pattern (cracking pattern)

Vacuum system according to 6.2 is sufficient.

To determine the fragmentation factor, the relative sensitivity factor r_{jk} for each $(m/z)_k$ of gas species j has to be measured, similar to the relative sensitivity factor as described in 7.8. However, it is not necessary to generate an accurate partial pressure p_j of gas species j.

Since the fragmentation pattern may depend on it, p_j shall be given with an uncertainty of a factor of 2.

Proceed as described in 7.6, steps 1) to 8). The fragmentation factor is given by $r_{jk} = \frac{\left(I_{jk} - I_{0k}\right)}{\left(I_{j\text{main}} - I_{0\text{main}}\right)}$. I_{jk} is the peak signal of fragment k of species j and $I_{j\text{main}}$ is the main peak of species j.

To estimate the uncertainties related to random effects as repeatability of the instrument, at least three independent measurements (pump the gas out in between) have to be carried out.

NOTE r_{jk} does normally depend on electron energy and pressure.

7.10 Outgassing rate of QMS

Vacuum system according to 6.2 is sufficient.

For many applications, it is sufficient to determine the total outgassing rate of the QMS in equivalent nitrogen pressure. In this case, an ion gauge is sufficient. In special applications, however, for example where outgassing rates have to be measured for UHV applications, it is necessary to determine outgassing rates individually for each gas species j. In this case, another QMS with known S_j has to be attached to the chamber. The effective pumping speed C_eff on the chamber has to be known (see Clause 6). The procedure to determine the total outgassing rate is as follows.

Outgassing rate in equivalent nitrogen pressure:

a) pump to residual pressure condition of your system in the desired condition (a bake-out is usually carried out before);

b) select the settings of the QMS, switch on and let the QMS warm up for 2 h;

c) record the pressure p_QMS indicated by the ionization gauge. It is recommended that this has been calibrated for nitrogen;

d) switch off the QMS and wait for 15 min;

e) record the pressure p_0 indicated by the ionization gauge;

f) the outgassing rate is determined by $q_{out} = \left(p_\text{QMS} - p_0\right) \cdot C_\text{eff}$.

Outgassing rate for gas species j (the outgassing rate of QMS 1 has to be determined by QMS 2):

1) pump to residual pressure condition of your system after a bake-out of at least 24 h at 150 °C;

2) select the settings of the QMS 1, switch on both QMS and let the QMS warm up for 2 h;

3) measure the complete background spectrum at residual pressure condition of the system in the mass range from 1 to at least 100 with QMS 2. Record all relevant peaks I_j;

4) switch off QMS 1 and wait for 15 min;

5) measure the complete background spectrum at residual pressure condition of the system in the mass range from 1 to at least 100 with QMS 2. Record all relevant peaks I_{0j} as above;

6) the outgassing rate for gas species *j* is determined by $q_{out,j} = \frac{\left(I_j - I_{0j}\right)}{S_j} \cdot C_{\text{eff, N2}}$.

This measurement should be carried out in a condition that will deliver lowest possible outgassing rate of the QMS. Since outgassing rates of samples normally will not exceed a certain limit, it is desirable to use the lowest possible outgassing rate of the QMS in order to obtain a worst-case outgassing rate of the sample.

NOTE For hydrogen longer waiting periods than 15 min might be necessary.

7.11 Pumping speed of QMS

Vacuum system according to 6.2 is sufficient.

In some cases of outgassing rate measurement systems, the pressure difference across a relative small conductance is measured. In these cases, the pumping speed of the QMS may lead to a significant underestimation of the outgassing rate. The user shall select gas species *j* and partial pressure p_j for the determination of the pumping speed according to his application. Another QMS with known S_j for this species has to be attached to the chamber. The effective pumping speed $C_{eff,j}$ on the chamber has to be known (see Clause 6). The chosen partial pressure shall be high enough to avoid significant disturbance from outgassing of the QMS. A pressure between 10^{-6} Pa and 10^{-5} Pa is recommended. The procedure to determine pumping speed is as follows.

Pumping speed for gas species *j* (the pumping speed of QMS 1 has to be determined by QMS 2):

1) pump to residual pressure condition of your system after a bake-out of at least 24 h at 150 °C;

2) select the settings of the QMS 1, switch on both QMS and let the QMS warm up for 2 h;

3) expose the two QMS to p_j to measure the spectrum in the relevant mass range with QMS 2. The signal is I_{2j};

4) switch off QMS 1 and wait for 15 min;

5) measure the spectrum with QMS 2 (gas is still injected with the same flow rate). The signal is I_{1j};

6) the pumping speed for gas species *j* (nitrogen and hydrogen) is determined by $C_j = \frac{\left(I_{2j} - I_{1j}\right)}{S_j p_j} \cdot C_{\text{eff},j}$.

If the purpose of this characterization is to compare different QMSs, it is recommended that hydrogen and nitrogen are chosen as species and a partial pressure of 10^{-6} Pa.

8 Measurement uncertainties

8.1 General

The measurement uncertainties during calibrations of the different parameter (quantities) described above are on the one hand difficult to evaluate, because there are many influences. On the other hand the accuracy needed is usually moderate. For this reason, a rough estimate of the measurement uncertainties during calibrations is sufficient.

NOTE 1 Uncertainty is given at the time of calibration and does not include stability of the quantity. Instability might be a significant additional uncertainty contribution during later use and needs to be evaluated by repeated measurements and experience.

NOTE 2 For several of the parameters the uncertainty is not an important information, because the uncertainty is either very small (e.g. for mass resolution) or a rough value is sufficient for the user (e.g. for p_{MDPP}).

The uncertainties depend on the parameter (quantity) which was determined. Consider the uncertainties detailed as follows:

8.2 Uncertainty of mass resolution

This uncertainty is determined by the uncertainty of the background signal (noise, stability), the standard deviation of Δm of the 10 measurements (which again depends on the slope and peak of the curve), and the step width m/z. Normally, the relative standard deviation of the 10 measurements dominates the uncertainty and is sufficient to report. The relative uncertainty is typically less than 2 %.

8.3 Uncertainty of p_{MDPP}

This uncertainty is determined by the uncertainty of the sensitivity and the uncertainty and stability of the noise signal. Since 100 measurements are taken, the relative uncertainty of the noise is rather small. The relative uncertainty of the sensitivity, however, is within a factor of 2 considering the effect of nonlinearity in the range 10^{-9} Pa to 10^{-5} Pa, so that p_{MDPP} is accurate within a factor of 2.

8.4 Uncertainty of minimum detectable concentration (C_{MDC})

This uncertainty is determined by the uncertainty of the p_{MDPP} (see above) and the uncertainty of the nitrogen pressure. The uncertainty of the measurement of the nitrogen pressure is within about 5 %, negligible compared to the uncertainty of the p_{MDPP}. Therefore, C_{MDC} is also accurate within a factor of 2.

8.5 Uncertainty of dynamic range

This value shall be rounded to one significant digit. The measured value will have an uncertainty of less than 50 % when performed according to this document.

8.6 Uncertainty of sensitivity

This uncertainty is determined by the uncertainty of the background signal I_{0k} (noise, stability), the uncertainty of the signal I_{jk} and the uncertainty of the relevant partial pressure p_j. While the last quantity (p_j) cannot be evaluated by repeat measurements, the first two are best evaluated by repeat measurements. The relative standard uncertainty of p_j strongly depends on the calibration system, but will rarely be below 5 %. If no further analysis is done and the relative standard uncertainty of the result of repeat measurements is below 10 %, it is recommended that a relative standard uncertainty of 10 % for nitrogen and 15 % for other common, non-absorbing gas species (such as not vapours or hydrocarbons) is used.

8.7 Uncertainty of linear response range

Although there is a small relative uncertainty for the linear response range, there is no need to give a number, since the linear response range is not a quantity that is used in other model equations.

8.8 Uncertainty of relative sensitivity factor

This uncertainty is determined by the uncertainty of the sensitivity of nitrogen S_{N2} and the sensitivity S_j of the gas species j under observation. The standard uncertainty due to random effects can best be evaluated by repeat measurements. This, however does not include the uncertainty of p_j and p_{N2}, which will rarely be < 5 %. Some of the uncertainty contributions of p_j and p_{N2} may be correlated (e.g. same conductance element or same mass flow controller is used for the two gas species, same reference gauge). If no further analysis is done and the relative standard uncertainty of the result of repeat measurements is below 10 %, it is recommended that a relative standard uncertainty of 15 % for common, non absorbing gas species (such as not vapours or hydrocarbons) is used. This value considers some correlation of measurements for S_{N2} and S_j.

8.9 Uncertainty of fragmentation factor

The uncertainty $u(r_{jk})$ is determined by the uncertainty of two signal readings I_{jk} and $I_{j,\mathrm{main}}$ at a common partial pressure p_j. Therefore, the uncertainty of p_j does not contribute. The uncertainties