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

Élément introductif — Élément central — Élément complémentaire

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ISO/TS 20175 was prepared by Technical Committee ISO/TC 112, Vacuum technology, Subcommittee SC , .

This second/third/... edition cancels and replaces the first/second/... edition (), [clause(s) / subclause(s) / table(s) / figure(s) / annex(es)] of which [has / have] been technically revised.
Introduction

Quadrupole mass spectrometers (QMS) are nowadays used not only in vacuum technology for leak detection and residual gas analysis in vacuum but also in the process industry as an instrument to provide quantitative analysis in processes and to control processes like physical and chemical vapour deposition, etch processes, etc. 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 QMS, 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 Technical Specification to establish such conditions.

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

In continuation of efforts of TC112 during the 1990’s this Technical Specification provides standardized calibration procedures for QMS 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 Technical Specification describes procedures to characterize quadrupole mass spectrometers with an ion source of electron impact ionization and which are designed for the measurement of atomic mass-to-charge ratios \( m/z < 300 \). QMS with other ion sources as chemical ionization, photo-ionization, field ionization sources etc. and for the measurements of higher \( m/z \), which are mainly used to specify organic materials, are out of scope for this standard.

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 Technical Specification 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 shall select that characterization procedure that best suits his needs. These characterization procedures may also be useful for other applications, but great care has to be taken that the settings are the same and the gas mixture and the total pressures are similar in that application.

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 Technical Specification is not only describing how a quadrupole mass spectrometer can be calibrated by a calibration laboratory or a National Metrological Institute with direct traceability to the 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 Technical Specification, 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 Technical Specification 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 etc. and is very specific to the instrument. Instead, it is assumed for this Technical Specification that a manufacturer’s readjustment procedure which can be carried on-site by a user exists. This procedure should ensure that the quadrupole mass spectrometer is in a well defined condition for the characterization.

It is the intention of this Technical Specification 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 only achieved in the so called "scan mode", but not by the "bar graph" or "trend" mode. For this reason, the "scan mode" should be applied for the application of this Technical Specification, if not specified otherwise.

It is not the idea of this Technical Specification that all the parameters described need to be determined for each quadrupole mass spectrometer. However, if the value of a parameter addressed in this technical Specification is given by a manufacturer or measured by a user (e.g. for an inspection test), it should be determined according to the procedure described in this Technical Specification.
It is assumed in this Technical Specification 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 referenced documents are indispensable for the application 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 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 of ISO 14291 apply. In addition are defined:

3.1 carrier gas
gas that accompanies the gas species of interest

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

NOTE Adapted from ISO 3529-3, section 3.3.5

NOTE 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 number of ions entering a quadrupole filter of a QMS to the number of ions exiting it

3.4 scan time
time needed to scan the mass spectrum in a defined range

3.5 scan speed
speed as time per 1u (Δm/z=1)

3.6 linear response range
partial pressure range over which the non-linearity is within a specified limit (ISO 14291)

For the purpose of this TS the limit is 10% from the mean value.

3.7 leak rate measurement
a quantitative measurement of a tracer gas through a leak
3.8 leak rate monitoring

Continuous monitoring of one or several selected gas species in a vacuum system in order to detect a change caused by a leak.

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

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

3.9 interference effect

Difference of sensitivity of a specified gas species as pure gas or as present in a gas mixture.

NOTE This is usually but not exclusively observed at pressures higher than $10^{-4}$ Pa.

3.10 interference gas

Another gas species added to a primary pure gas that may cause a difference of sensitivity of the QMS for the primary gas species.

3.11 interference gas mixture

Mixture of several gas species added to a primary pure gas that may cause a difference of sensitivity of the QMS for the primary gas species.

4 Symbols and abbreviated terms

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Designation</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{eff}$</td>
<td>Effective conductance of a duct</td>
<td>m³/s or L/s</td>
</tr>
<tr>
<td>$f$</td>
<td>Fragmentation factor</td>
<td>1</td>
</tr>
<tr>
<td>$m$</td>
<td>Molecular mass in atomic mass units</td>
<td>u</td>
</tr>
<tr>
<td>$M$</td>
<td>Molecular mass</td>
<td>kg</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure or partial pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$p_0$</td>
<td>Residual pressure or residual partial pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$r_x$</td>
<td>Relative sensitivity for a specified gas species “x” divided by sensitivity $S_{N2}$ for nitrogen</td>
<td>1</td>
</tr>
<tr>
<td>$I$</td>
<td>Ion current at partial pressure $p$</td>
<td>A</td>
</tr>
<tr>
<td>$I_0$</td>
<td>Ion current at residual pressure $p_0$</td>
<td>A</td>
</tr>
<tr>
<td>$MDC$</td>
<td>Minimum detectable concentration</td>
<td>1</td>
</tr>
<tr>
<td>$MDPP$</td>
<td>Minimum detectable partial pressure</td>
<td>Pa</td>
</tr>
<tr>
<td>$q_v$</td>
<td>Volume intake of vacuum pump</td>
<td>m³/s or L/s</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
<td>J mol⁻¹ K⁻¹</td>
</tr>
<tr>
<td>$S$</td>
<td>Sensitivity (coefficient)</td>
<td>A/Pa</td>
</tr>
<tr>
<td>$S_{N2}$</td>
<td>Sensitivity for nitrogen</td>
<td>A/Pa</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
<td>K</td>
</tr>
<tr>
<td>$T_P$</td>
<td>Transmission probability</td>
<td>1</td>
</tr>
<tr>
<td>$z$</td>
<td>The ionization state of a molecule</td>
<td>1</td>
</tr>
<tr>
<td>$\Delta m$</td>
<td>Mass resolution as defined in ISO 14291</td>
<td>u</td>
</tr>
<tr>
<td>CEM</td>
<td>Continuous dynode electron multiplier</td>
<td></td>
</tr>
</tbody>
</table>
5 Parameters needed or recommended to be characterized for the different applications

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

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

5.1 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

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

d) Minimum detectable concentration for helium in nitrogen (nitrogen partial pressure at around 10% of the maximum operational pressure or around $10^{-3}$ Pa)
e) Mass resolution at $m/z = 4$ and optionally also $m/z = 28$

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

5.2 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)

5.3 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 system it is recommended:

a) Linear response range for nitrogen, oxygen, and argon

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)

For other systems it is recommended:

a) Sensitivity for the gas to be monitored as air constituent (nitrogen, oxygen, or argon), in the major residual gas constituent at its maximum operational pressure (nitrogen equivalent) between partial pressure of $10^{-7}$ Pa and maximum operational pressure (nitrogen equivalent)

b) Relative sensitivity factors for the monitoring gas as a result of measurement a)

c) Fragmentation pattern for the monitoring gas as a result of measurement a)

d) Minimum detectable concentration for the monitoring gas in the major gas constituent

5.4 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 partial pressure for water vapour

g) 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 When the residual gas is water vapour, no need to characterize the interference effect.
5.5 Residual gas analysis

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

b) Sensitivity for hydrogen, methane, nitrogen, carbon dioxide, argon, and krypton at a total pressure of $10^{-5}$ Pa (nitrogen equivalent) in a mixture of 30% hydrogen, 10% methane, 30% nitrogen, 20% carbon dioxide, 5% argon and 5% krypton

c) Fragmentation pattern for methane, nitrogen, carbon monoxide (optionally), carbon dioxide, argon and krypton in pure gas, preferably at $10^{-5}$ Pa.

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

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

5.6 Outgassing rate measurement

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

b) Effective pumping speed for nitrogen and optionally for hydrogen and water vapour (see 7.10).

c) Sensitivity for hydrogen, methane, nitrogen, carbon dioxide, argon, and krypton at a total pressure of $10^{-5}$ Pa (nitrogen equivalent) in a mixture of 30% hydrogen, 10% methane, 30% nitrogen, 20% carbon dioxide, 5% argon and 5% krypton.

d) Fragmentation pattern for methane, nitrogen, carbon monoxide (optionally), carbon dioxide, argon and krypton in pure gas, preferably at $10^{-5}$ Pa.

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

6 Vacuum systems to characterize QMS

Most of the characterizations and calibrations described in Section 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 6.1, the systems for gas mixtures in 6.2. 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 Sections 6.1.3 and 6.2.2, 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 must 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. Also, the position of any reference QMS or vacuum gauge and the QMS to be investigated shall not be in the flow direction between gas inlet and exit to the pump.

Temperature of the vacuum systems shall be (23±7)°C.
6.1 Vacuum system for characterization with single gas

6.1.1 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 and 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 to choose a pertinent National Metrological Institute or an accredited calibration laboratory based on ISO 17025.

6.1.2 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 must be considered for the volume of the calibration chamber according to the requirement a) in Section 6.1 of ISO 3567. The stationary equilibrium method (method "b" in Section 7.1.5 of ISO 3567:2012 has to be applied. As described in ISO 3567:2012 the reference gauges must be traceable to the SI. For the purpose of this TS, a hot cathode ionization gauge is recommended as reference gauge. The stability of the calibration parameter of the hot cathode ionization gauge may be checked by a spinning rotor gauge. This may be also used as reference gauge at pressures > 10^{-4} Pa. Capacitance diaphragm gauges can be used at pressures > 10 mPa in addition.

NOTE The reading of non-heated capacitance diaphragm gauges is not gas sensitive, while heated ones reveal a gas dependent reading with a deviation of less than 4% due to thermal transpiration effect in the range from 0.1 Pa up to 100 Pa.

NOTE The accommodation factor of a spinning rotor gauge varies with gas species within about 5% from the one determined for nitrogen. In addition, the controller has to be set for the right gas species.

NOTE The sensitivity of a hot cathode ionization gauge varies with gas species. The according gas correction factors need to be applied. These can be taken from text books or manufacturers specifications. For uncertainties see Section 8.

6.1.3 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 \( q_{pV,i} \) of a single gas species \( i \), the effective pumping speed \( C_{eff,i} \) can be determined by

\[
C_{eff,i} = \frac{q_{pV,i}}{P_i}, \tag{1}
\]

where \( P_i \) is the pressure indicated by the gauge for a pure gas with molecular mass \( M_i \).

Since the measurements are performed in the high vacuum regime, if the effective pumping speed \( C_{eff,i} \) for one gas species \( i \) with molecular mass \( M_i \) is known, it can be calculated for any other gas species \( j \) according to

\[
C_{eff,j} = C_{eff,i} \sqrt{\frac{M_i}{M_j}} \tag{2}
\]
provided that \( C_{\text{eff}} \) is not determined by the pumping speed of the vacuum pump which may be gas species dependent. If temperature at use \( T' \) of the conductance differs by more than 1K than \( T \) when the conductance was calibrated, it should also be corrected for by:

\[
C'_{\text{eff}} = C_{\text{eff}} \sqrt{\frac{T'}{T}}
\]  

(3)

**Note:** For the purpose of this TS, \( C_{\text{eff}} \) can be considered as independent of the volume intake (pumping speed) \( q_V \) of the vacuum pump, when \( C_{\text{eff}}/q_V < 10 \).

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 [2] 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 as for \( C_{\text{eff},i} \) above.

The pressure \( p_i \) for species is calculated from

\[
p_i = \frac{q_{pV,i}}{C_{\text{eff},i}}
\]  

(4)

### 6.2 Vacuum system for characterization with gas mixtures

#### 6.2.1 Continuous expansion system (orifice flow system)

These calibration systems have to 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 must be used.

Continuous expansion systems as described in Section 6.1.2 are used for this purpose. They are extended either by:

- **a)** several flowmeters in fundamental method

The partial pressures are determined from equation (3).

or

- **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 latter 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
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.

### 6.2.2 In-situ calibration system for gas mixture

The method described in 6.1.3 can be extended to several gas species by having available several gas inlets as described above in Section 6.2.1. The partial pressures are determined from equation (4) or (5).

### 7 Characterization and calibration procedures

#### 7.1 General

For all following procedures it is necessary that the QMS has somehow been adjusted. After the adjustment, the parameters must 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 QMS 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
- 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 like emission current etc., it should be done so. 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. Depending on the quantity to be measured, however, e.g. the minimum detectable pressure of an instrument equipped with SEM, the use of the electron multiplier is required.
In addition, the QMS must be warmed up before the measurements (for warm-up time see manual). A warm-up time of 2 hours is usually sufficient.

### 7.2 Mass resolution

Vacuum system according to 6.1 is sufficient.

The mass resolution \( \Delta m \) 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 \( T_p \) through the quadrupole filter is roughly a constant: \( (m/\Delta m) \cdot T_p = \text{const.} \). Normally the settings are such that \( \Delta m \) is constant throughout the mass range of the QMS. For this reason, it is sufficient to determine \( \Delta m \) at a specific \( m/z \). This standard recommends helium at \( m/z = 4 \). If it is important to know how the mass resolution \( \Delta m \) may vary, two values of \( m/z \) are recommended. This Technical Specification recommends helium at \( m/z = 4 \) and argon near \( m/z = 40 \). 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 of \( (m/z)_j - 1 \) to \( (m/z)_j + 1 \) ten times as background spectrum
4. Expose the QMS to a partial pressure of \((5 \pm 2) \times 10^{-5}\) 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 of \( (m/z)_j - 1 \) to \( (m/z)_j + 1 \) ten 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 \( \Delta m \).

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 is sufficient.

### 7.3 Minimum detectable partial pressure (MDPP)

Vacuum system according to 6.1 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 may not allow to determine the noise around the \( m/z \) of the selected gas species. It would be desirable to prevent the arrival of any ion from reaching the detector, but this option is usually not available.

The procedure to determine the MDPP of helium is the following:

1. Select the detector and the settings of the QMS
2. Determine the sensitivity \( S \) for helium (see Section 7.5) at one partial pressure value in the range between \( 10^{-6} \) Pa and \( 10^{-5} \) 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 \( \sigma_i \) of these values
4. The MDPP is given by the following equation: \( \text{MDPP}_j = \frac{3 \sigma_i}{S_j} \) where \( j \) is the gas species, here helium.
The procedure to determine the MDPP of gas species $j$ with $m/z < 50$ (except helium) is the following:

1. Select the detector and the settings of the QMS
2. Determine the sensitivity $S$ for gas species $j$ (see Section 7.5) at one partial pressure value in the range between $10^{-9}$ Pa and $10^{-5}$ 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 $\sigma_1$ 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 $\sigma_2$ of these values
5. Calculate the mean $\sigma_j = (\sigma_1 + \sigma_2)/2$
6. The MDPP is given by the following equation: $MDPP_j = \frac{3\sigma_j}{S_j}$ where $j$ is the gas species.

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

1. Select the detector and the settings of the QMS
2. Determine the sensitivity $S$ for gas species $j$ (see Section 7.5) at one partial pressure value in the range between $10^{-9}$ Pa and $10^{-5}$ Pa
3. 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 $\sigma_1$ of these values. In the unusual case that there is a signal at $m/z = 62$, select the nearest $m/z$ without signal.
4. The MDPP is given by the following equation: $MDPP_j = \frac{3\sigma_j}{S_j}$ where $j$ is the gas species.

### 7.4 Minimum detectable concentration (MDC)

Vacuum system according to 6.2 is needed.

The minimum detectable concentration depends on the gas species to be detected and the carrier gas or carrier gas mixture, 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 Technical Specification recommends to determine the minimum detectable concentration of helium in nitrogen as a general specification of a QMS.

The procedure is the following:

1. Select the detector and the settings of the QMS
2. Expose the QMS to a partial pressure $p_{\text{Nitrogen}}$ 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. Proceed as described in Section 7.2 to detect the MDPP for helium
4. The minimum detectable concentration $MDC$ is given by the following equation: $MDC = \frac{MDPP_{\text{He}}}{p_{\text{Nitrogen}}}$
7.5 Sensitivity

Vacuum system according to 6.1 is sufficient for a single gas, 6.2 is needed, when additional interference gas or mixture has to be added.

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 QMS 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 carrier gas or carrier gas mixture and their partial pressures
3. Measure the complete background spectrum at residual pressure condition of the system in the mass range from 1 to $(m/z)_{k_{\text{max}}}+2$, where $(m/z)_{k_{\text{max}}}$ 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 $m/z \leq 0.1$ and a scan speed of 1 s/u in the mass range 1 up to at least $(m/z)_{k_{\text{max}}}+2$, where $(m/z)_{k_{\text{max}}}$ is the heaviest isotope or isomere that can be expected for gas species $j$
6. If required, add the interference gas or interference gas mixture to the desired partial pressure of species $j$, otherwise proceed with 8
7. Measure the spectrum with a step width of $m/z \leq 0.1$ and a scan speed of 1 s/u in the mass range 1 up to at least $(m/z)_{k_{\text{max}}}+2$, where $(m/z)_{k_{\text{max}}}$ 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 5 and 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 $S_{jk} = \frac{(I_{jk} - I_{0k})}{p_j}$, 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 $(m/z)_k$. The relative change of $S_{jk}$ in the cases of measurement 5 and 7 gives an indication of how much it is influenced by the carrier gas.

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.

NOTE Some QMS do not give a current as signal but a partial pressure or similar. For comparison with other QMS it is recommended to convert this other value 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 2.2.1 in ISO 14291, since only the gas added to the system is considered by $p_j$ 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 $p_j$.
NOTE If the purity of gas \( j \) should be checked, it is recommended for step 3 that the mass spectrum should range up to highest \( m/z \) which may be present in the system (e.g., if a series of pure gases is measured one after the other and it should be checked that the previous gas species is no more present in the system).

### 7.6 Linear response range

Vacuum system according to 6.1 is sufficient for a single gas, 6.2 is needed, when additional interference gas or mixture has to be added as described in 7.5.

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

1. Measure the sensitivity from \( 9 \times 10^{-9} \) Pa or from the minimum operational pressure whichever is greater to \( 9 \times 10^{-3} \) Pa or up to 10% of the maximum operational pressure with two points per decade, preferably at 3 and 9. An extension of the measurement range to lower and higher pressures is possible, but not to pressures higher than maximum operational pressure.

2. The linear response range is the pressure range in which \( S_{j,\text{main}} \) deviates not more than 10% from the mean value in this pressure range. \( k=\text{main} \) denotes the peak of highest intensity (current).

NOTE The measurement of the linear response can be extended to all \( (m/z)_k \) for gas species \( j \). In particular for nitrogen, it may be helpful to use \( (m/z)_k=14 \) to easier distinguish the nitrogen signal from the CO signal. A clear note must be given, if not the main peak is used.

### 7.7 Relative sensitivity factor

Vacuum system according to 6.1 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 Section 7.6. Determine the mean sensitivity \( S_{N_2} \) in this linear response range.

2. Determine the sensitivity and linear response range for gas species \( j \) at its main peak according to Section 7.6. Determine the mean sensitivity \( S_j \) in this linear response range.

3. The relative sensitivity factor \( r_j \) is given by 
   \[
   r_j = \frac{S_j}{S_{N_2}}.
   \]

To estimate the uncertainties related to random effects as repeatability of the instrument, at least three independent measurements (pump down 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 3 target pressure points equally distributed over the linear response range.

NOTE The measurement of the relative sensitivity factor \( r_j \) can be extended to all \( (m/z)_k \) for gas species \( j \). In any case, however, the main peak of nitrogen at \( (m/z)=28 \) shall be used as reference. A clear note must be given, if not the main peak of gas species \( j \) is used.

### 7.8 Fragmentation pattern (cracking pattern)

Vacuum system according to 6.1 is sufficient.

The determination of the fragmentation factor is to determine the relative sensitivity factor \( r_{jk} \) for each \( (m/z)_k \) of gas species \( j \). Instead of using \( S_{N_2} \) as reference, use \( S_{j,\text{main}} \) which is the signal for the main peak (see Section 7.5) as such. 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 Section 7.5, points 1 to 8. The fragmentation factor is given by

$$r_{jk} = \frac{(I_{jk} - I_{0jk})}{(I_{j\text{main}} - I_{0j\text{main}})}.$$ 

The conditions of the measurements must be clearly reported.

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

### 7.9 Outgassing rate

Vacuum system according to 6.1 is sufficient.

For many applications, it is sufficient to determine the total outgassing rate of the QMS in nitrogen equivalent. In this case, an ion gauge is sufficient. In special applications, however, e.g. 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 Section 6). The procedure to determine the total outgassing rate is as follows.

**Outgassing rate in nitrogen equivalent:**

1. Pump to residual pressure condition of your system in the desired condition (a bake-out is usually carried out before).
2. Select the settings of the QMS, switch on and let warm-up the QMS for two hours.
3. Record the pressure $p_{QMS}$ indicated by the ionization gauge. It is recommended that this has been calibrated for nitrogen.
4. Switch off the QMS and wait for 15 min.
5. Record the pressure $p_0$ indicated by the ionization gauge.
6. The outgassing rate is determined by $q_{out} = (p_{QMS} - p_0) \cdot C_{eff}$.

**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 warm-up the QMS for two hours.
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 $q_{out,j} = (I_j - I_{0j}) \cdot S_j \cdot C_{eff}$.

**NOTE** 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 should 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.
7.10 Pumping speed

Vacuum system according to 6.1 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 \( C_{\text{eff},j} \) on the chamber has to be known (see Section 6). The chosen partial pressure must be high enough to avoid significant disturbance from outgassing of the QMS. \( 10^{-6} \) 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 warm-up the QMS for two hours
3. Expose the two QMS to \( p_j \) to measure the spectrum in the relevant mass range with QMS 2.
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).
6. The pumping speed for gas species \( j \) (nitrogen and hydrogen) is determined by

\[
C_j = \frac{(I_{2j} - I_{1j})S_j}{p} \cdot C_{\text{eff}}
\]

If the purpose of this characterization is to compare different QMS, it is recommended to choose hydrogen and nitrogen as species and a partial pressure of \( 10^{-6} \) Pa.

8 Measurement uncertainties

The measurement uncertainties during calibrations of the different 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 Uncertainty is given at the time of calibration and does not include stability of the quantity. Instability may be a significant additional uncertainty contribution during later use and needs to be evaluated by repeated measurements and experience.

NOTE 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 MDPP).

The uncertainties depend on the quantity which was determined. In detail, the following uncertainties must be considered:

8.1 Uncertainty of mass resolution

This uncertainty is determined by the uncertainty of the background signal (noise, stability), the standard deviation of \( \Delta m \) 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 is dominating the uncertainty and sufficient to report.
8.2 Uncertainty of 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 can be assumed as 10%. The relative uncertainty of the sensitivity can also be assumed as 10%, so that a total standard uncertainty \( u(\text{MDPP}) \) of 14% is reasonable to report.

8.3 Uncertainty of minimum detectable concentration (MDC)

This uncertainty is determined by the uncertainty of the MDPP (see above) and the uncertainty of the nitrogen pressure. If a calibrated total pressure gauge is used for the measurement of the nitrogen pressure, the uncertainty is typically 5%. Therefore, in this case, if \( u(\text{MDPP})=14\% \), it is \( u(\text{MDC}) = 15\% \).

8.4 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 latter 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 be rarely 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 to use a relative standard uncertainty of 10% for nitrogen and 15% for other common, non absorbing gas species (not vapours, hydrocarbons, etc.).

8.5 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.

8.6 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 be rarely < 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 etc.). If no further analysis is done and the relative standard uncertainty of the result of repeat measurements is below 10%, it is recommended to use a relative standard uncertainty of 15% for common, non absorbing gas species (not vapours, hydrocarbons, etc.). This value considers some correlation of measurements for \( S_{N2} \) and \( S_j \).

8.7 Uncertainty of fragmentation factor

The uncertainty \( u(r_{jk}) \) is determined by the uncertainty of two signal readings \( I_{jk} \) and \( I_{j,\text{main}} \) at a common partial pressure \( p_j \). Therefore, the uncertainty of \( p_j \) does not contribute. The uncertainties of the background levels are included in the standard deviation of the mean of repeat measurements, which therefore gives the total standard uncertainty.

NOTE Any non-linearity in the signal response is inherent to the QMS and no additional uncertainty. For this reason, however, \( r_{jk} \) is specific to the individual QMS and cannot be used in another piece of the same type or in another QMS type without considering additional uncertainty.

NOTE The fragmentation factor may depend on pressure and interference gas.

8.8 Uncertainties of outgassing rate and pumping speed

It can be expected that there is a significant uncertainty that needs to be attributed to these values. A rigorous uncertainty evaluation is difficult, but only needed in special cases. In general, it should be assumed that the relative standard uncertainty of both pumping speed and outgassing rate is characterized by a factor of 2 (-50%, +100%).
8.9 Long-term stability of characteristic parameters of QMS

It is well known [9] that the important parameters of QMS may be subject to large changes with time. Some changes can be correlated to their use (contaminations on electrode surfaces), to changes in adjustments, to aging effects (mainly SEM and filament), to maintenance (change of filament or ionizer), but many changes cannot be explained for clear reasons [15]. It is one of the purposes of this TS to help those users that need reasonable accuracy with QMS to monitor these changes by in-situ calibrations. This will help to assume lower uncertainties due to use and time effects than given below.

The following list gives rough estimates of the relative long-term of the important QMS parameters, when the QMS have been operated under relative clean ultrahigh vacuum conditions (exposure only to humid atmospheric air, and rare gases) and only adjustments recommended by manufacturers carried out.

Sensitivity for nitrogen with Faraday collector:...

SEM gain:...

Mass resolution:...

Fragmentation factor for nitrogen:...

MDPP:...

9 Reporting results

The report or calibration certificate shall be written according to ISO 17025. In particular, the following shall be included in the certification:

— short description of the calibration system including its measurement equipment with its traceability, e.g., when a certified gas mixture, the origin of the same;

— type of QMS, manufacturer and serial number and possible other equipment with it;

— the adjustment procedure that has been applied before, if applicable;

— all settings of the instrument (see introduction to Section 7);

— ambient temperature, including its variation during the calibration; total residual pressure in the calibration chamber before the measurements;

— calibration gas mixture, if applicable;

— the parameter that was measured with reference to this TS.

10 References


[5] AVS Tentative Standards 2.1 "Calibration of Leak detectors of the Mass Spectrometer Type"


[12] STANDARD DEFINITIONS OF TERMS RELATING TO MASS SPECTROMETRY (IUPAC Recommendations 2006)


[15] Long-term investigation of QMS; EMRP IND12 investigation to be published.