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Surface chemical analysis — Glow discharge mass spectrometry (GD-MS) — Introduction to use

Analyse chimique des surfaces — Spectrométrie de masse à décharge luminescente (GD-MS) — Introduction à l'utilisation

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Foreword

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ISO/TS 15338 was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 8, *Glow discharge spectrometry*, based on Australian Standard AS 3685:1998.

Surface chemical analysis — Glow discharge mass spectrometry (GD-MS) — Introduction to use

1 Scope

This Technical Specification gives guidelines for the operation of glow discharge mass spectrometry (GD-MS) instruments and recommendations for the use of GD-MS. It is intended to be read in conjunction with the instrument manufacturers' manuals and recommendations.

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 18115, *Surface chemical analysis — Vocabulary*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 18115 and the following apply.

3.1
accuracy of measurement
closeness of the agreement between a result and the accepted reference value

3.2
elemental intensity
amount of ion current recorded for a particular element

3.3
pin cell
sample cell used for the analysis of wire and rod samples

3.4
precision of measurements
closeness of the agreement between independent test results obtained under stipulated conditions, normally reported as a standard deviation

3.5
pin, rod and wire samples
samples with cylindrical or square cross-section of nominal length typically 20 mm and not normally exceeding 10 mm across

3.6
transmission
ratio of the number of ions reaching the detector relative to the number of ions entering the mass analyser

4 Safety

4.1 Use of high-voltage power supply and connection of the instrument

Electrical connection should comply with the regulations in force. Particular care should be taken to ensure that connection of the instrument to ground is correct, and the efficiency of the ground connection should be checked.

4.2 Use and storage of compressed-gas cylinders

The compressed-gas cylinders should be regularly tested by the appropriate authorities. Cylinders should not be stored or used inside the laboratory. Rather, they should be located outside the laboratory in a place that is well ventilated, away from direct heat, and accessible to service and safety personnel. The cylinders should be provided with suitable pressure-reducing valves. If more than one cylinder is to be used or stored in close proximity, it is advisable to indicate in some way which cylinder or cylinders are currently in use.

4.3 Handling of cryogenic materials

Vessels containing cryogenic materials should be located so as to minimize the risk to personnel. Areas where cryogenic liquids are stored and used should be ventilated to prevent the accumulation of gas or vapour which could evaporate from the liquid. It is good practice to keep areas where cryogenic liquids are used very clean. All transfer operations should be in accordance with statutory requirements. When a cryogenic liquid is being transferred from one vessel to another, precautions should be taken to minimize any spills and splashing. The requirements of the relevant regulatory authorities should also be met.

5 Principle

In a glow discharge source, electrical power is supplied between the sample (cathode) and the anode by a power supply typically operated in direct current (dc) at 0,5 kV to 2 kV and 1 mA to 300 mA. Argon (or another inert gas such as neon, krypton or helium) is introduced into the discharge cell. The pressure inside the discharge cell is typically a few hundred pascals (Pa). A potential difference is applied between the cathode and the anode and a glow discharge (plasma) is established. Sample material (single atoms and/or clusters) which is sputtered by ions and neutrals diffuses into the plasma.

Ions formed in the glow discharge are extracted from the ion source and pass into a mass analyser. The mass analyser is used to transmit ions of given mass-to-charge ratio to the detector(s). The ions reaching the detector(s) are measured as ion current or counted by a counting system. This information is stored in a computer system. Elemental mass fractions are typically calculated by the instrument software using the ion currents of isotopes, by normalizing the signal to the signal of a matrix element and subsequently comparing the normalized signals with those arising from the corresponding elements in calibration samples.

6 Materials

6.1 Deionized water, 18 MΩ·cm or better.

6.2 Argon gas, or other plasma support gases, of purity better than 99,999 9 % or in accordance with the recommendations of the instrument manufacturer.

6.3 Liquid nitrogen, for cryogenic cooling of the discharge cell.

6.4 Compressed gas, to operate pneumatic valves.

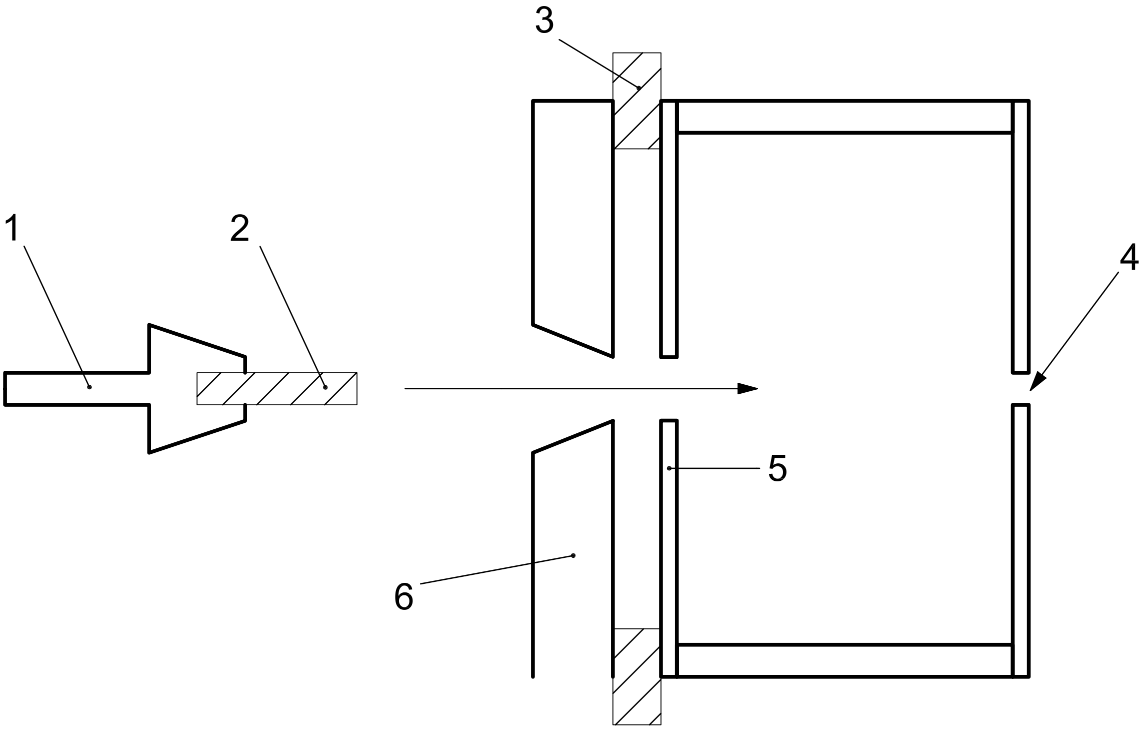
7 Apparatus

7.1 Ion source

7.1.1 General

A glow discharge ion source consists of a glow discharge cell and a power supply. In some designs, the ion source will also contain a series of focusing plates, external to the cell, whose function is to extract ions from the cell and focus these ions into the mass spectrometer.

Typically the body of the discharge cell is connected to the anode output of the power supply. The sample serves in the glow discharge cell as a cathode and is connected to the cathode output of the power supply. Discharge cells have been designed to accommodate samples in the geometries recommended in 8.3, and examples of discharge cells are illustrated with the appropriate sample holders in Figures 1 and 2.



Key

1 sample holder

2 sample

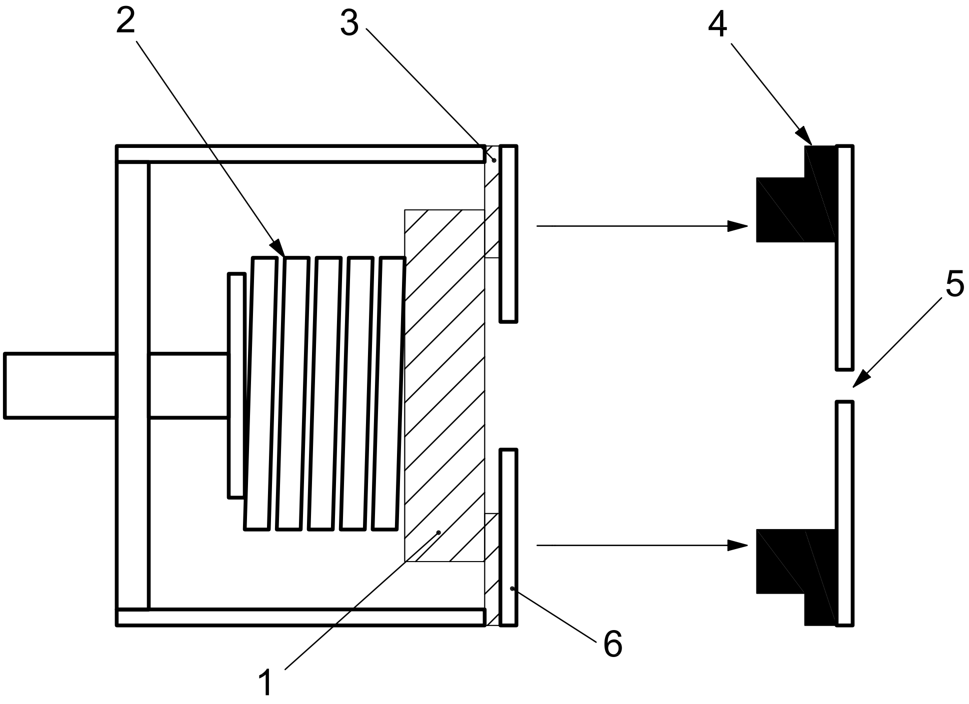
3 insulator

4 ion exit slit

5 anode plate

6 cathode plate

Figure 1 — Example of a cell used for the analysis of pin samples



Key

1 sample cathode
2 spring
3 insulator
4 cell body
5 ion exit slit
6 anode plate

Figure 2 — Example of a cell used for the analysis of flat samples

7.1.2 Source parameters

The source parameters are as follows:

a) Electrical

- potential difference between anode and cathode;
- current;
- power.

b) Geometrical

- dimension of sample exposed to plasma;
- anode-to-sample distance;
- cathode dimension;
- mask dimension, where appropriate.

c) Gas type and pressure.

d) Cell temperature.

e) Type of sample.

7.1.3 Operational modes

The direct-current source may be operated in different modes, including:

a) constant current with potential difference adjusted by adjusting the plasma gas pressure;

b) constant potential difference with current adjusted by adjusting the plasma gas pressure;

c) constant current with plasma gas pressure adjusted by adjusting the potential difference.

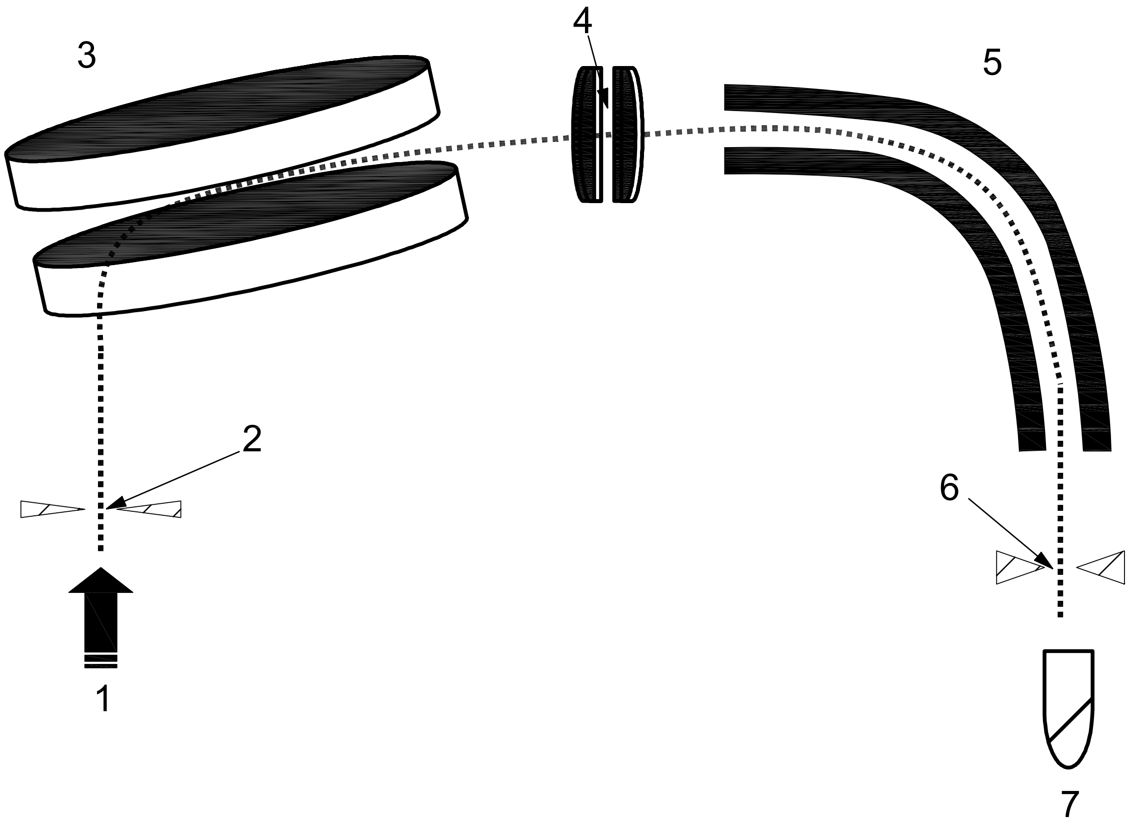
The discharge pressure may be regulated using a mass flow controller, needle valve or knife edge valve. For some types of GD-MS instrument, the high accelerating voltages encountered require a capillary in the gas line to prevent electrical breakdown through the gas line. Radio-frequency-powered GD sources are also being developed for GD-MS.

7.2 Mass analyser

There are two types of mass analyser commonly used for glow discharge mass spectrometry: double-focussing magnetic-sector instruments and quadrupole instruments. Other types, like time-of-flight instruments, are also becoming more common.

a) **Sector mass spectrometer**: This type of instrument (see Figure 3) typically utilizes an electromagnet and an electrostatic analyser (ESA). The magnet achieves mass separation and, as the magnetic field is increased, ions with greater mass-to-charge ratio are transmitted. The ESA acts as an energy filter and transmits only those ions with the appropriate energies.

   This arrangement permits high-transmission and high-resolution operation, giving accurate mass information advantageous with complex sample matrices where there is an increased possibility of interferences. A resolving power of 4 000 is sufficient to overcome most common interferences.



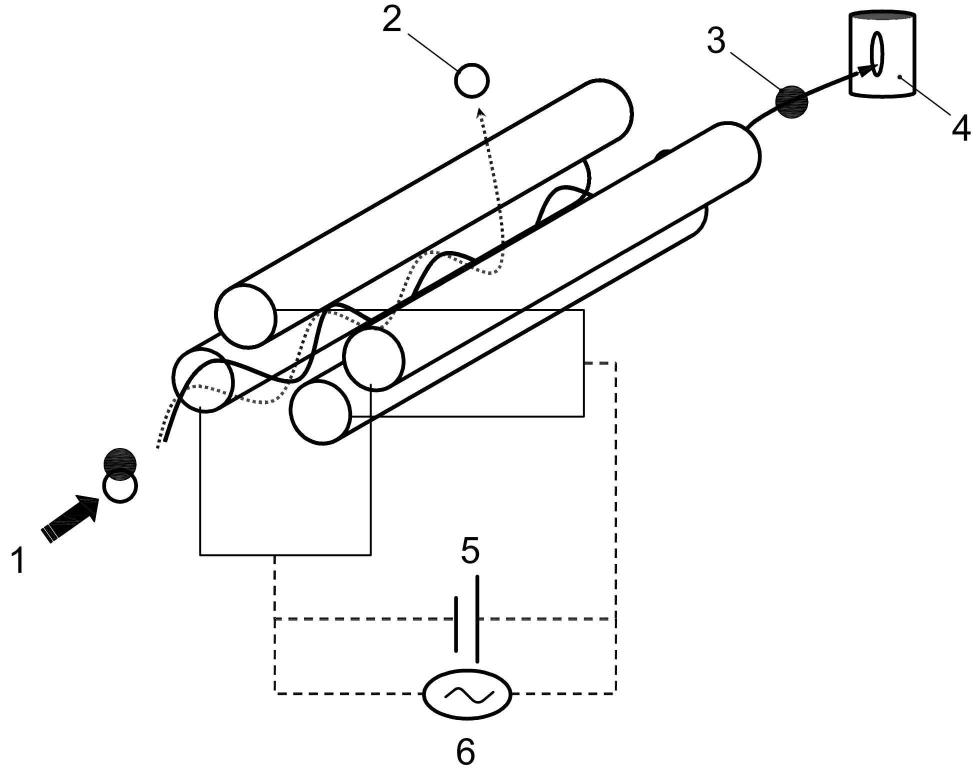
Key

1 ion beam
2 source slit
3 magnet
4 intermediate slit
5 ESA
6 detector slit
7 detector

Figure 3 — Schematic diagram of a magnetic-sector mass analyser

b) **Quadrupole**: This type of mass spectrometer consists of four parallel rods whose centres form the corners of a square and whose diagonally opposite poles are connected (see Figure 4). The voltage applied to the rods is a superposition of a static potential and a sinusoidal radio-frequency potential. The motion of an ion in the x and y directions is described by the Mathieu equation, the solutions of which show that ions in a particular m/z (mass-to-charge ratio) range can be transmitted along the quadrupole axis.

Whilst a quadrupole instrument does not have the high resolution of a magnetic-sector instrument (the resolving power at mass-to-charge ratio 100 is usually less than 200), it has a much faster scanning speed, is compact and is able to achieve low detection limits if interferences are kept low.



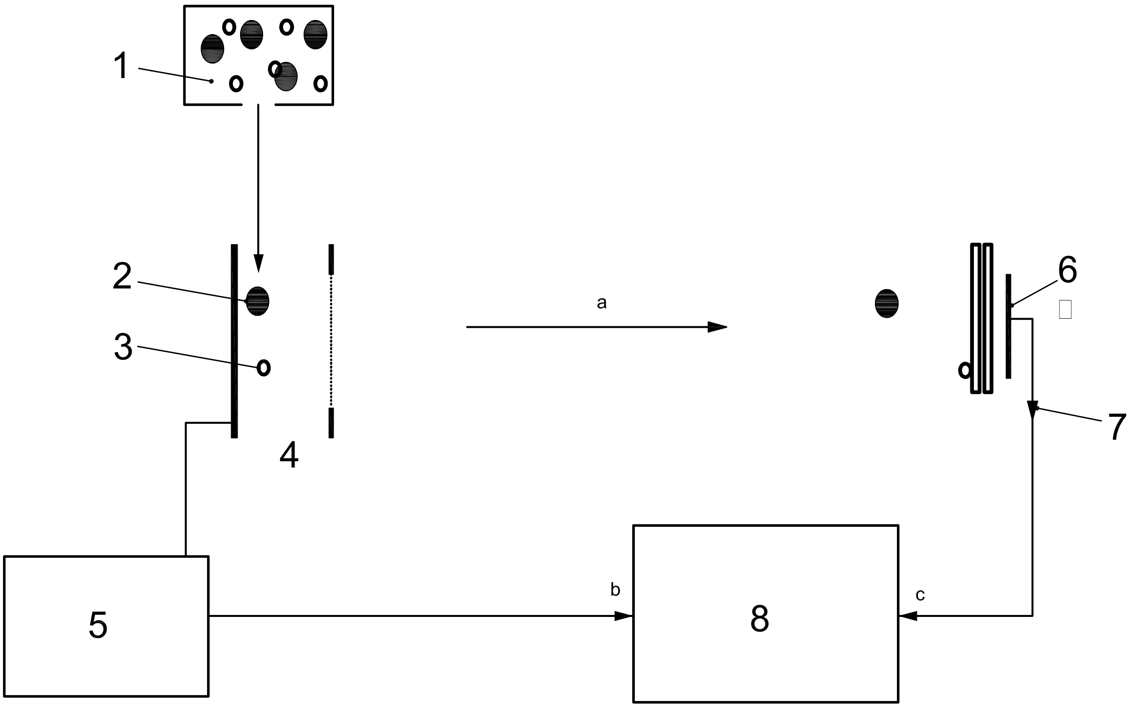
Key

1 from ion source
2 non-resonant ion
3 resonant ion
4 detector
5 d.c.
6 a.c.

Figure 4 — Schematic diagram of a quadrupole mass analyser

c) **TOF (time-of-flight) mass spectrometer**: In this type of mass spectrometer, an ensemble of ions is accelerated by an electric field and then allowed to drift a certain distance before impinging on an ion detector (see Figure 5). In the accelerating field, all ions receive the same kinetic energy, which can be equated to $\frac{1}{2}mv^2$. Therefore, ions with a lower m/z (mass-to-charge ratio) will have a higher velocity and will arrive at the detector earlier than ions with a higher m/z. By measuring the arrival time of ions, the m/z of those ions can be determined.

Whilst quadrupole instruments and sector instruments are m/z filters, TOF instruments do not have to scan in order to record a mass spectrum and therefore have the potential for a higher-duty cycle. TOF instruments intrinsically have a large mass range and good mass accuracy. They also have reasonably good resolving power, allowing them to overcome some interferences.



Key

1	ion source	5	high-voltage pulser (starts the ions)
2	high-mass particle	6	detector (generates stop signal)
3	low-mass particle	7	signal
4	extractor	8	data-acquisition system (records time of flight)

[a] Drift.

[b] One start signal.

[c] Multiple stop signals.

Figure 5 — Schematic diagram of a time-of-flight mass analyser

NOTE Other types of mass spectrometer (e.g. ion trap mass spectrometers) are being adapted for use with glow discharge ion sources.

7.3 Detector system

As a consequence of the wide mass fraction range measured using GD-MS, usually two detectors are required and/or needed, as follows:

a) Ion signals from matrix and major trace elements present at mass fractions typically above 0,1 % are measured using a coarse detector such as a Faraday plate or an electron multiplier, operating in the analogue mode. These detectors simply measure the current generated by the ion beam striking the detector.

b) Ion signals from trace elements present at mass fractions typically below 0,1 % are measured using ion-counting techniques. Examples of ion-counting detectors are the Daly detector and the Channeltron1), multi-channel plate and venetian-blind electron multipliers.

NOTE Any differences in the response of the detectors are reflected in the instrument calibration.

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1) Channeltron® is the trade name of a product supplied by Burle. This information is given for the convenience of users of this Technical Specification and does not constitute an endorsement by ISO of this product.

7.4 Vacuum system

A glow discharge ion source operates at a pressure of approximately 100 Pa, but optimum mass spectrometer performance, in terms of transmission, resolution and abundance sensitivity, requires a pressure in the mass analyser of less than 1×10^{-4} Pa. To achieve such a vacuum level, differential pumping is required. This means that both the ion source housing and the mass analyser are pumped independently.

There are diverse designs:

a) Diode geometry type source

The resulting pressure outside the cell in the ion source is typically 1×10^{-2} Pa under normal operating conditions. In addition, the test sample is usually introduced via a sample interlock, which is evacuated to typically 1 Pa using a rotary pump or other suitable primary vacuum pump. This maintains the integrity of the vacuum inside the source housing and minimizes contamination by atmospheric gases.

Alternatively, the source can be isolated from the mass analyser via an interlock and/or another device to protect the mass analyser while the test sample is being changed.

b) Grimm type source

The resulting pressure outside the cell is usually in the same range as that inside the cell, which is typically around 100 Pa under normal operating conditions. The test sample is introduced at atmospheric pressure and, after closing the cover around the sample holder, the entire region is pumped to typically 1 Pa using a scroll pump or another suitable primary vacuum pump. During the sample exchange there is a continuous flow of discharge gas through the cell and cover to prevent atmospheric gases from entering the source.

The source is isolated from the mass analyser via a slide valve to maintain the vacuum of the mass analyser while the test sample is being changed.

7.5 Data acquisition and control

The data-acquisition system should be capable of the following:

a) selection of analytes to be determined and isotopes to be monitored;

b) monitoring of key instrument parameters (see 9.8);

c) data acquisition, analysis and storage;

d) data processing;

e) report generation;

f) archiving of data.

8 Samples and sample preparation

8.1 General

The following guidelines should be followed for general sample preparation:

a) use inert materials, e.g. polytetrafluorethylene (PTFE) or polypropylene beakers, when etching samples;

b) use non-contaminating materials for all equipment in contact with the sample;

c) use high-purity acids and solvents.

8.2 Sample type

Glow discharge mass spectrometry is suitable for the trace and ultra-trace elemental analysis of metals, alloys, semiconductors and non-conductors and for depth-profiling applications.

Samples should preferably be in the form of solid material, for example wires, rods, pins, sheets, coupons, irregular pieces, chunks, flat wafers, targets or powders.

NOTE There are also potential applications for GD-MS in the analysis of liquid residues and organic samples.

8.3 Sample geometry

Various instrument manufacturers have developed sample holders for specific sample geometries, e.g. pin/rod/wire samples typically 20 mm in length and up to 10 mm across. For flat samples, the sputtered area is usually 4 mm to 10 mm in diameter. The maximum size of the sample is restricted by the size of the sample holder. Smaller sample sizes are achievable, but not normally recommended because of the resulting reduction in the signal. The thickness of flat samples is not critical and is restricted only by the sample holder design.

8.4 Sample preparation for bulk analysis

8.4.1 General

The objective of sample preparation is to provide a clean representative test sample of the sample under investigation.

All test samples should be of the same nominal size as the calibration or reference sample.

For flat samples, a gas-tight surface is required to seal against the sample holder to maintain the proper argon pressure inside the discharge cell.

8.4.2 Metals, alloys and semiconductors

Samples may be formed into the required geometry by many methods, e.g. casting, rolling, drawing, cutting, machining or etching.

Surface finishing may involve machining, polishing, etching, solvent cleaning or drying.

8.4.3 Powders

Powders may be either conducting or non-conducting and should be treated as follows:

a) Conducting powders should be compacted using a die compaction press into an appropriate geometry in accordance with 8.3.

b) Non-conducting powders are commonly mixed with a conducting medium. This mixture should then be treated as a conducting powder.

The conducting medium should provide a stable discharge whilst providing sufficient signal to perform a meaningful analysis. In addition, a medium should be chosen that minimizes interferences with the analyte(s) to be determined.

8.4.4 Non-conducting samples

For analysis with a direct current source, a secondary cathode (a metal mask containing an aperture) is placed on the surface of the non-conducting sample such that the mask is maintained at the cathode potential.

The secondary cathode should provide a stable discharge whilst providing a sufficient signal to perform a meaningful analysis. In addition, the material of which the secondary cathode is made should be chosen to minimize interferences with the analyte(s) to be determined.

8.5 Sample preparation for depth profiling

Surface preparation may not be necessary or desired. If preparation is carried out, care should be taken not to contaminate the surface or remove surface material of interest.

9 Measurement procedures

9.1 System precautions

9.1.1 General

For general operation of the system, refer to the manufacturers' manuals and recommendations.

The following general precautions should be observed while operating the system:

a) It is good practice to wear a pair of powder-free gloves when handling vacuum components, including all parts of the discharge cell and extraction optics. Vacuum components should be kept in a dust- and moisture-free environment, such as a desiccator cabinet.

b) No specific personal protection equipment is required during normal operation. However, the operator should be aware of any potential hazards associated with specific samples. For example, there is a possibility of toxic materials accumulating in traps, pumps and other reservoirs within the instrument.

9.1.2 Interferences

Interference may occur when two ions (possibly molecular fragments or species) have the same or a similar mass-to-charge ratio. The significance of this interference will vary depending upon the type of mass spectrometer. Where these interferences occur, they cannot be generally resolved using a quadrupole instrument, but in most cases they can be resolved using a magnetic-sector instrument. The most appropriate isotopes, free of interferences and with the highest abundances possible, should be chosen. This will vary between matrices.

As a general guide, for a metal, M, in a discharge atmosphere of argon, Ar, ionization processes produce a stable spectrum consisting mainly of singly charged atomic ions, M^+ and Ar^+, with some dimer ions, M_2^+ and Ar_2^+, present. Multiply charged argon ions, Ar^{2+} and Ar^{3+}, and the like are evident. M^{2+} ions are more significant for metals with a low second-ionization potential. Combinations of metal and argon species, such as MAr^+ and MAr_2^+, are seen but, in general, the more complex the species, the less significant it is. Gaseous impurities, such as nitrogen, oxygen, hydrocarbons and water, lead to the production of interferences such as CO^+, CO_2^+, H_3O^+, ArC^+, ArO^+, $ArCO^+$, ArH^+, MO^+ and MH^+. Cryogenic cooling of the glow discharge cell or the use of a fast-flow ion source reduces these gaseous impurities.

9.2 Selection of discharge parameters and isotopes

9.2.1 Unfamiliar materials

When analysing a material not previously analysed, the operating parameters appropriate to the test sample should be established. The procedure should be as follows:

a) Establish the discharge parameters using conditions recommended by the instrument manufacturer, where available. In general, the lower the melting point of the sample, the lower the applied power should be.

   When gallium or other low melting materials are suspected, use cryogenic cooling to prevent melting.

   NOTE 1 Some materials, such as insulators, may crack as a result of thermal shock.

   NOTE 2 Compacted powder samples may be fragile.

b) Evaluate the potential interferences for each analyte. This may involve the analysis of more than one isotope to ascertain the most appropriate isotope to be used for analysis.

9.2.2 Familiar materials

Once the appropriate discharge conditions and isotopes have been specified, all check measurements and test samples should be tested under identical conditions.

The operational mode should be selected, and the pressure adjusted accordingly to give the desired current and potential, or the potential adjusted accordingly to give the desired current and pressure.

9.3 Presputtering

Presputtering is a form of sample preparation that occurs *in situ* in the discharge itself. Once the test sample has been introduced and the discharge initiated, a delay should occur before the analysis of the test sample takes place. This delay enables any surface contaminants to be sputtered from the test sample and ensures that representative bulk analysis is performed. The time taken for presputtering may be dependent upon any or all of the following:

a) the chemical and mechanical sample preparation prior to analysis;

b) the material being analysed;

c) the types of analyte;

d) the required sensitivity of the analysis.

As for optimum discharge conditions, once presputtering conditions have been determined for a given matrix, they should be kept constant.

NOTE Presputtering is not performed for depth profile analysis where the surface of the sample is relevant to the analysis.

9.4 Optimizing the ion current

Once the discharge conditions have been established, the ion current should be optimized to ensure that the intensities of the ions are acceptable according to the manufacturer’s recommendations and/or the scope of the analysis. This is achieved by changing the potentials on the lenses until the required signal is obtained using a matrix isotope. This signal will vary from matrix to matrix.

9.5 Analytical set-up

The purpose of the analytical set-up is to define the way the mass spectrometer is to be scanned or the data acquired. The following parameters are important:

a) Selection of the isotopes of interest of the relevant analytes.

   Normally, the most abundant isotope for any given element should be chosen. There are instances, however, where interferences may result in the choice of a less abundant isotope. Subclause 9.1.2 gives an indication of likely interferences that should be considered when selecting isotopes. For analysers with full scanning capabilities, such as TOFs and quadrupoles, isotope selection can be made after the measurement as part of the data analysis.

b) Definition of the data file(s) to be used for holding data for the actual test sample(s).

c) Selection of the calibration to suit the analysis (set of relative sensitivity factors, calibration samples, etc.).

d) Definition of other instrumental aspects of the data acquisition, such as:

   — integration time;

   — calibration file;

   — operator identifier.

9.6 Data analysis

Data analysis is performed with a computer. Appropriate algorithms are used to select the peaks of interest. When a given peak has an unresolved interference, it may be helpful to select the peak manually. Instrument manufacturers often provide information in software or in print that can help with these procedures.

The calculation of elemental mass fractions normally proceeds as follows:

a) The detector system of the instrument measures the ion current reaching the appropriate detector for each isotope (including the matrix) as specified in the analytical set-up. A correction depending on the ion detection system used is made for the integration time and/or ion transfer efficiency.

b) The ion currents are corrected for the abundance of each particular isotope recorded to give an elemental ion current.

c) The ratio of each individual elemental ion current to that for the matrix element (single-element matrix) or for all matrix elements (multi-element matrix) is measured. This is called the ion beam ratio (IBR) and constitutes the mass fraction of each element relative to the matrix element. The IBR already represents quantitative data.

d) More accurate quantitative data are obtained using a library of RSFs stored in the instrument software. This is useful for particular element/matrix combinations where matrix-matched standards are not available.

e) Very accurate quantitative data can be obtained through prior analysis of matrix-matched standards (see 9.9). The IBR data for each element is simply multiplied by the respective RSF derived from the analysis of the matrix-matched standard samples.

9.7 Depth profile analysis

During operation, the glow discharge continually sputters atoms from the surface of the test sample. Sputtering rates will vary depending on the source design, the discharge parameters and the material under analysis.

By taking a large number of consecutive replicate readings, it is possible to determine the sample composition as a function of the analysis time. Plotting elemental mass fractions as a function of analysis time then enables a depth profile to be generated. With knowledge of the erosion rate (or the combination of the sputtering rate, the sputtered surface area and the density of the sputtered material, from which the erosion rate may be calculated), it then becomes possible to plot elemental mass fractions as a function of depth.

9.8 Instrument performance

Instrument performance checks consist of a series of tests on various instrumental parameters which reflect the fundamental aspects of performance. The specific checks and specifications will be dependent upon the mass spectrometer used and are normally determined by the instrument manufacturer to demonstrate the instrument performance upon installation. These tests may indicate if there is a problem present and should be carried out regularly after the commissioning period to reduce the chance of degradation in instrument performance.

General checks that should be performed are as follows:

a) **Detector cross-calibration** (if more then one detector is used): Detector cross-calibration is important to provide accurate determination of trace elements.

b) **Mass calibration**: Mass calibration is important to avoid unnecessarily large interferences or selection of an incorrect isotope.

c) **Pressure monitoring**: Ion source and analyser pressures should be monitored to prevent degradation of the vacuum in the ion source, which may cause increased spectral interferences due to elevated gas backgrounds.

d) **Measurement of resolution**: This is important to prevent excessive interferences.

9.9 Analysis

9.9.1 General

Glow discharge mass spectrometry has a wide range of applications. It allows trace element analysis of all metal and non-metal elements. Its use is relatively simple, and it easily lends itself to a series of tests.

However, in order to maintain all the qualities of sensitivity and accuracy for this technique, the test sample on which the measurement is carried out has to be well-suited to the particular instrument.

Glow discharge mass spectrometric methods should take into account the following:

a) the mass fraction ranges suitable for determining the elements being studied;

b) interferences due to the nature of the sample and of the plasma gas;

c) the required sensitivity of measurement;

d) the similarity of sample geometry between calibration samples and test samples;

e) the availability of appropriate calibration samples.

This Technical Specification is written as a single GD-MS determination and may be used in that form. Performing GD-MS determinations in duplicate can allow additional information to be derived and can give improved accuracy.

9.9.2 Measurement using RSFs

For a given GD-MS instrument, the RSFs for all elements in the periodic table usually fall within approximately one order of magnitude, making quantitative GD-MS analysis possible without the use of calibration samples for calibration.

The mass fraction of element X in a single-element matrix sample can be described as follows:

$$w_{X/M} = \mathrm{RSF}_{X/M} \times \mathrm{IBR}_{X/M} \tag{1}$$

where

$w_{X/M}$ is the mass fraction of element X in matrix element M;

$\mathrm{RSF}_{X/M}$ is the RSF value for element X in matrix element M;

$\mathrm{IBR}_{X/M}$ is the ion beam ratio for element X in matrix element M.

Typically, there are two ways to express RSFs. In the case of a single-element matrix, the RSF of the matrix element is usually set to unity (i.e. $\mathrm{RSF}_{X/M} = 1$). However, the RSF of a non-matrix element (usually Fe) may alternatively be set to unity (i.e. $\mathrm{RSF}_{\mathrm{Fe}/M} = 1$). The second method provides an easy way to compare RSFs of given elements across various matrices.

GD-MS instrument manufacturers often provide sets of RSF values, usually referred to simply as RSF_X values, with $\mathrm{RSF}_{\mathrm{Fe}} = 1$. In principle, such values can be used for any matrix. Table 1 and Figure 6 show an example of RSF_X values for each element X.

Using this convention, the mass fraction of element X in a single-element matrix sample can be described as follows:

$$w_X = \mathrm{RSF}_X \times \mathrm{IBR}_X \tag{2}$$

where

w_X is the mass fraction of element X;

RSF_X is the RSF value for element X;

IBR_X is the ion beam ratio for element X relative to Fe.

The mass fraction of element X in a multi-element matrix sample can be described as follows:

$$w_X = \frac{\mathrm{RSF}_X \times \mathrm{IBR}_X}{\sum_{i=1}^{n} (\mathrm{RSF}_{X_i} \times \mathrm{IBR}_{X_i})} \tag{3}$$

where

w_X is the mass fraction of element X;

RSF_X is the RSF value for element X;

IBR_X is the ion beam ratio for element X relative to Fe;

RSF_{X_i} is the RSF value for the ith element X;

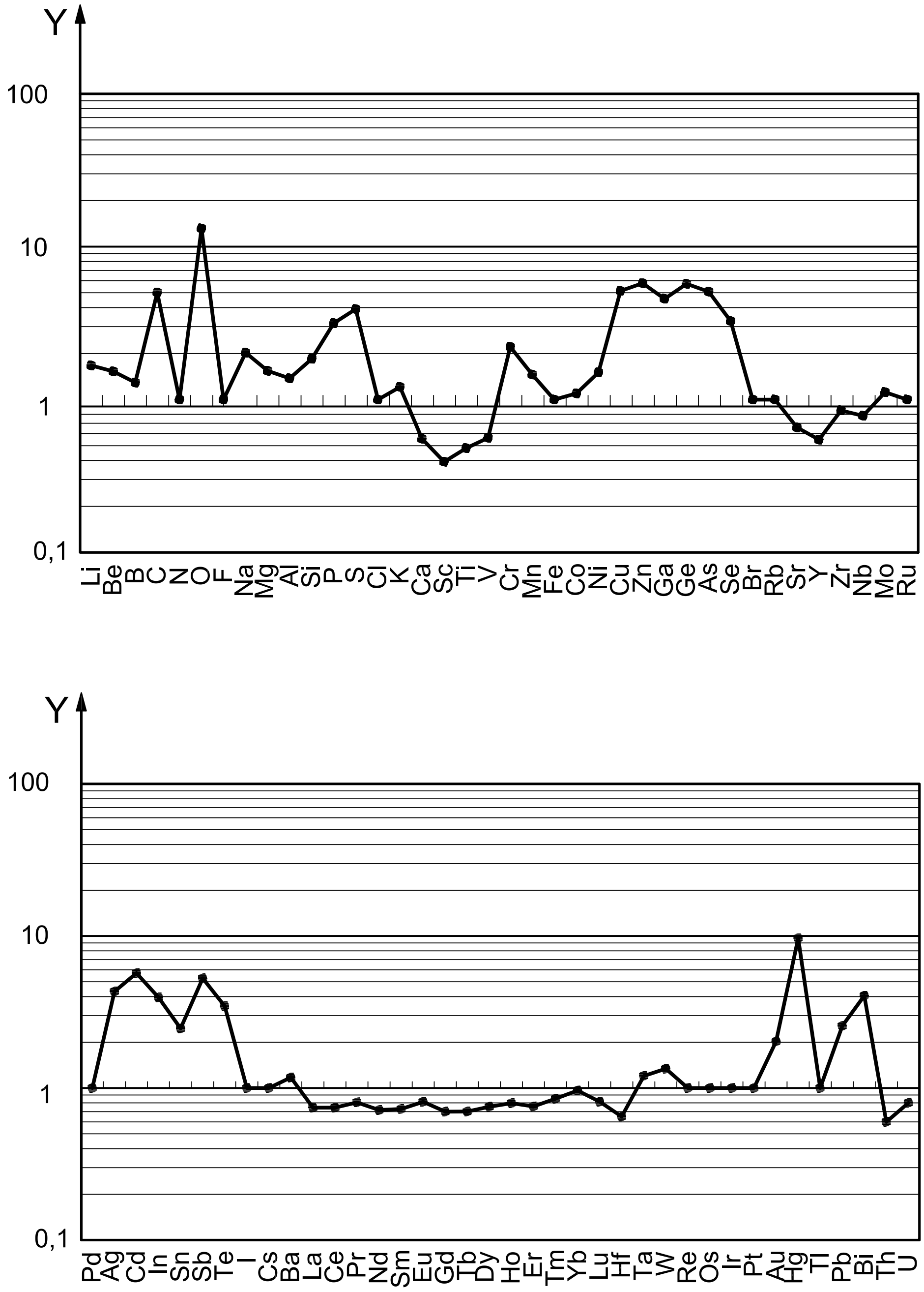
IBR_{X_i} is the ion beam ratio for the ith element X relative to Fe;

n is the number of elements in the matrix.

Table 1 — Example of a set of RSF$_X$ values (standard set for VG9000, RSF$_{\mathrm{Fe}}$ = 1)

Element	RSF$_X$
Li	1,674
Be	1,529
B	1,293
C	5,021
N	1
O	13,162
F	1
Na	2,027
Mg	1,541
Al	1,378
Si	1,846
P	3,159
S	3,903
Cl	1
K	1,208
Ca	0,554
Sc	0,392
Ti	0,481
V	0,562
Cr	2,21
Mn	1,459
Fe	1
Co	1,096
Ni	1,505
Cu	5,144
Zn	5,774
Ga	4,56
Ge	5,72
As	5,075
Se	3,26
Br	1
Rb	1
Sr	0,657
Y	0,546
Zr	0,85
Nb	0,784
Mo	1,119
Ru	1

Element	RSF$_X$
Pd	1
Ag	4,31
Cd	5,705
In	3,95
Sn	2,465
Sb	5,264
Te	3,457
I	1
Cs	1
Ba	1,172
La	0,744
Ce	0,744
Pr	0,806
Nd	0,717
Sm	0,728
Eu	0,81
Gd	0,7
Tb	0,702
Dy	0,754
Ho	0,796
Er	0,756
Tm	0,85
Yb	0,963
Lu	0,813
Hf	0,65
Ta	1,2
W	1,341
Re	1
Os	1
Ir	1
Pt	1
Au	2,024
Hg	9,675
Tl	1
Pb	2,559
Bi	4,048
Th	0,6
U	0,8



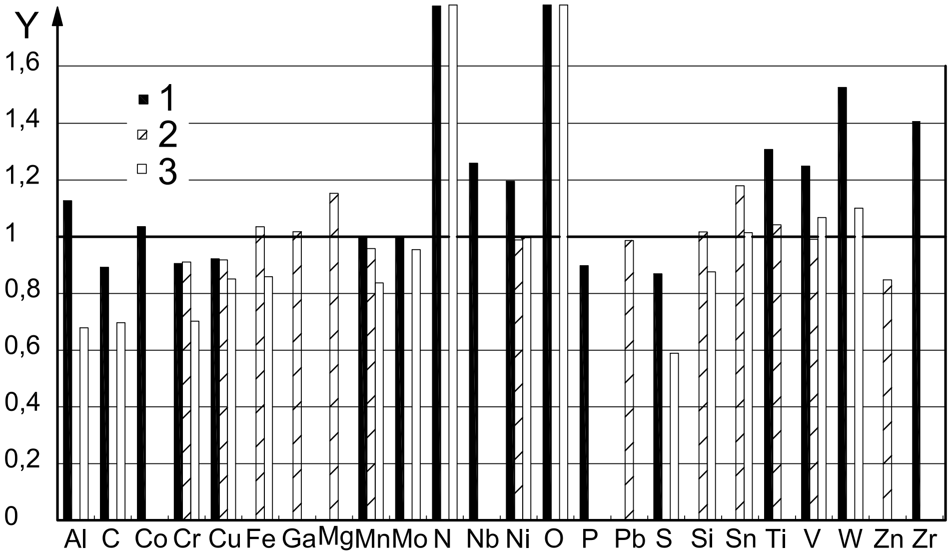
Key

Y RSF$_X$

Figure 6 — Graphical representation of RSF$_X$ **values plotted in order of increasing atomic number**

Employing RSF$_X$ values provided by the manufacturer, uncertainties in the determined values are normally within 50 %, as can be estimated from Figure 7. In this figure, the ratios of RSF$_{X/M\text{-CORR}}$ values (see 9.9.3) to the corresponding manufacturer-provided (VG9000-based) RSF$_X$ values are plotted for a range of elements and for three different matrices — steel, aluminium and titanium. The matrix-corrected RSF values were measured using matrix-matched reference materials, as described in 9.9.4.

NOTE Gaseous elements such as oxygen and nitrogen can exhibit higher levels of uncertainty due to residual atmosphere, chemical preparation, etc.



Key

Y $\text{RSF}_{X/M\text{-CORR}}/\text{RSF}_X$

1 steel

2 aluminium

3 titanium

Figure 7 — Graphical representation of the ratios of $\text{RSF}_{X/M\text{-CORR}}$ values to RSF_X values plotted for a range of elements (in alphabetical order) for three different matrices — steel, aluminium and titanium

9.9.3 Measurement using matrix-corrected RSFs

The best possible accuracy in GD-MS analysis requires the use of calibration samples with a matrix similar to that of the analyte sample (matrix-matched calibration samples) in order to determine the RSFs for the elements of interest in that matrix.

Table 2 gives $\text{RSF}_{X/M\text{-CORR}}$ values for a range of elements in three different matrices (low-alloy steel, aluminium and titanium), along with the corresponding RSF_X values. The mass fraction of element X in a sample can be described as follows:

$$w_X = \text{RSF}_{X/M\text{-CORR}} \times \text{IBR}_X \tag{4}$$

where

w_X is the mass fraction of element X;

$\text{RSF}_{X/M\text{-CORR}}$ is the corrected RSF value for element X in a single-element or multi-element matrix;

IBR_X is the ion beam ratio for element X relative to Fe.

Table 2 — Comparisons of RSF$_{X/M\text{-CORR}}$ values with the original RSF$_X$ values for a range of elements in three different matrices — steel, aluminium and titanium

Element X	RSF$_X$	RSF$_{X/M\text{-CORR}}$ Steel	RSF$_{X/M\text{-CORR}}$ Aluminium	RSF$_{X/M\text{-CORR}}$ Titanium
Al	1,378	1,55		0,94
C	5,021	4,48		3,50
Co	1,096	1,14		
Cr	2,21	2,00	2,01	1,55
Cu	5,114	4,72	4,77	4,35
Fe	1		1,04	0,86
Ga	4,56		4,64	
Mg	1,541		1,78	
Mn	1,459	1,46	1,40	1,22
Mo	1,119	1,12		1,07
N	1	58		125
Nb	0,784	0,99		
Ni	1,505	1,80	1,49	1,50
O	13,162	108		120
P	3,159	2,84		
Pb	2,559		2,52	
S	3,903	3,39		2,30
Si	1,846		1,88	1,62
Sn	2,465		2,91	2,50
Ti	0,481	0,63	0,50	
V	0,562	0,70	0,56	0,60
W	1,341	2,05		1,48
Zn	5,774		4,90	
Zr	0,85	1,20		

NOTE 1 Each RSF$_{X/M\text{-CORR}}$ value in Table 2 was measured by laboratory personnel associated with an expert of ISO/TC 201/SC 8/WG 2 using a VG9000 glow discharge mass spectrometer.

NOTE 2 Several other equivalent descriptions of matrix-corrected RSFs are used by GD-MS practitioners (e.g. matrix-matched RSFs or matrix-specific RSFs).

9.9.4 Measurement using a calibration graph

9.9.4.1 General

As stated in 9.9.2, quantitative GD-MS analyses are possible using RSF_X values (such as those provided by an instrument manufacturer) that are assumed to apply reasonably well to any matrix. Nonetheless, the accuracy of a particular GD-MS analysis can be improved by calibrating specifically for that analysis.

9.9.4.2 Calibration samples

The recommended minimum number of calibration samples is three. The following recommendations are generally valid:

a) Calibration samples should be, if possible, certified reference materials.

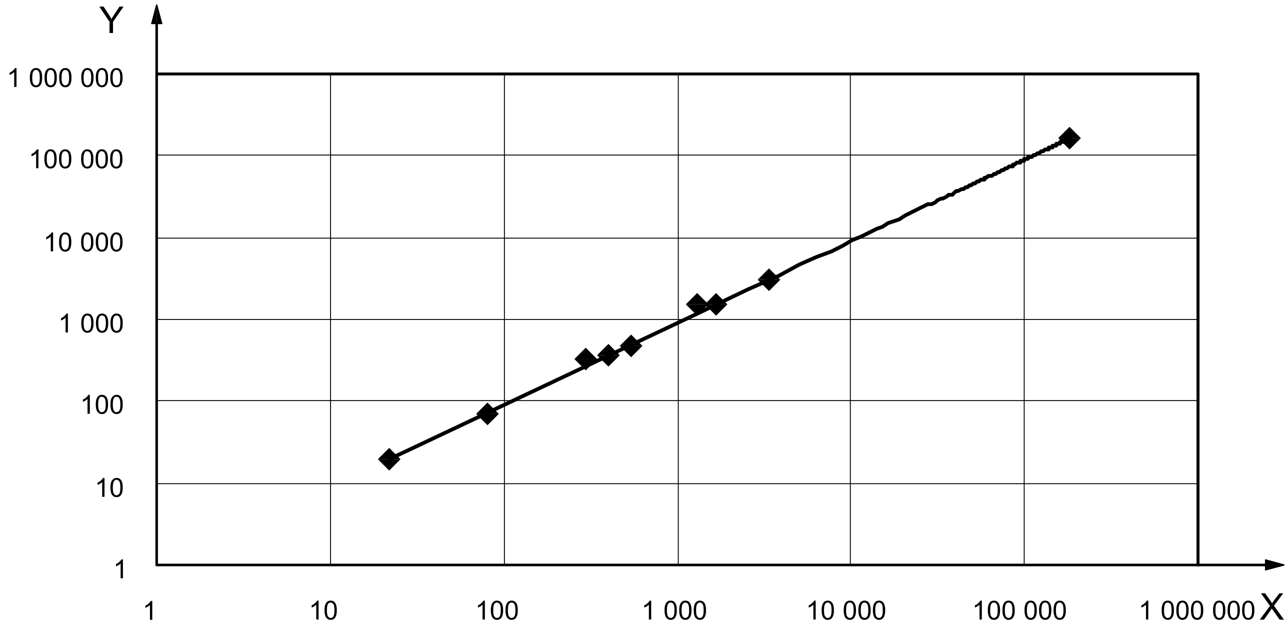
b) The mass fraction of an element of interest in a calibration sample should be determined by recognized methods of chemical analysis.

c) The matrix compositions of the calibration samples and the samples to be analysed should be as similar as possible.

d) The ideal result of calibration is a linear relationship between intensity and mass fraction, but this may be affected by interferences. Such interferences should be investigated during development of the method and measures for their correction should be incorporated.

e) The uncertainties associated with RSFs are determined in part by the uncertainties in the certified mass fractions used to measure them. Because the relative uncertainties of certified mass fractions generally increase with decreasing mass fraction, it is often helpful to measure RSFs using reference materials with a larger analyte mass fraction.

Figure 8 shows an example of an analytical calibration line (certified mass fraction versus IBR) for cobalt in iron-based calibration samples. The slope of the line produces a matrix-matched relative sensitivity factor $\mathrm{RSF}_{X/\mathrm{Fe\text{-}CORR}}$.



$$w_{\mathrm{Co}} = 0{,}895 \times \mathrm{IBR}_{\mathrm{Co}}$$

Key

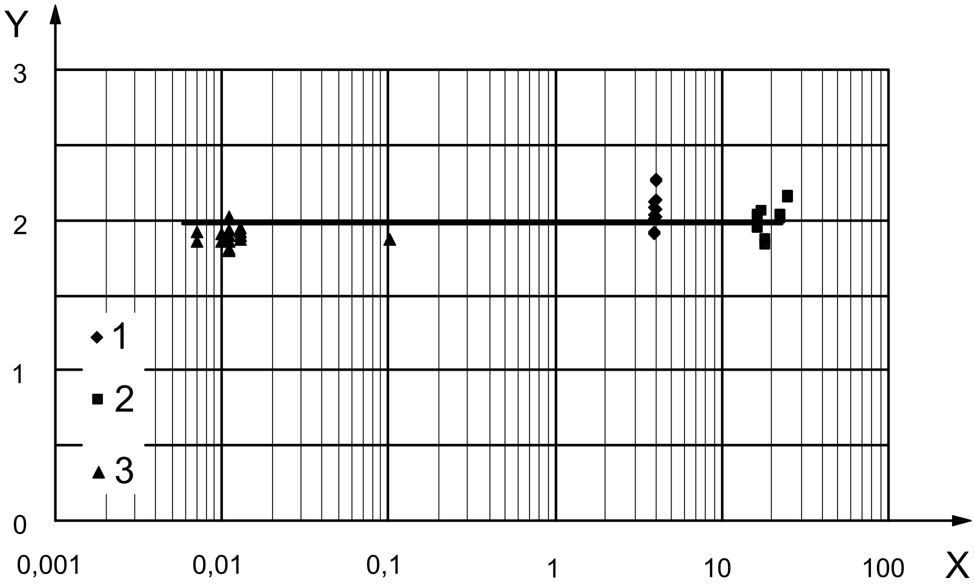
X $\mathrm{IBR}_{\mathrm{Co}}$

Y mass fraction of Co, w_{Co} (µg/g)

Reference material (Fe-based)	NBS 1766	SRM 665	SRM 661	NBS C1285	SRM 663	NBS S 664	SRM 1230 A286	SRM 662	NBS 1250
Certified value of Co (µg/g)	20	70	320	360	480	1 500	1 500	3 000	161 000

Figure 8 — Example of an analytical calibration line (certified Co mass fraction in Fe-based reference materials versus IBR)

NOTE Figure 9 shows an example of a plot of matrix-matched relative sensitivity factor, $\mathrm{RSF}_{X/M\text{-}\mathrm{CORR}}$, values determined from chromium calibration lines derived from iron-based calibration samples. This type of graph is useful for evaluating the independence of the RSF from the analyte mass fraction.



Key

X certified value (mass fraction in %)

Y $\mathrm{RSF}_{X/M\text{-CORR}}$

1 high-speed steel

2 stainless steel

3 low-alloy steel

Figure 9 — Example of independence of $\mathrm{RSF}_{X/M\text{-CORR}}$ from analyte mass fraction (Cr in iron-based reference materials)

9.9.4.3 Calibration verification

It is recommended that a control sample be analysed to verify the calibration. The control sample should be a certified reference material or a secondary reference material preferably traceable to nationally recognized standards. The chemical composition of the control sample should be similar to that of the test samples.

This control sample should be analysed after calibration and then at a frequency (for example, daily, weekly or every tenth sample) appropriate to the application and workload of the mass spectrometer. If significant deviation from acceptable results occurs, and no reason can be found, recalibration may be necessary.

9.9.4.4 Acceptance of results

If the results from the instrument show a high degree of variability and no reason can be found, the repeatability of the instrument should be tested using a material of known homogeneity. The sample used should be a control sample or calibration sample. The test should be performed in accordance with the instrument manufacturer’s recommendations.

10 Test report

Where a laboratory issues data in the form of a report (e.g. an assay certificate for a customer), it is recommended that the report contain the following information, unless legal or other requirements make this impossible:

a) the name and contact information of the laboratory which carried out the analysis;

b) a laboratory-unique identification of the report (such as a serial number or laboratory ID) as well as identification of each page of the report and an indication of the total number of pages;

c) identification of the customer for whom the sample was analysed;

d) the date on which the analysis was carried out;

e) identification of the test method used;

f) the detection limit, where appropriate;

g) any unusual observations made during the course of the analysis that may have had an effect on the result;

h) the signature and identification of the person responsible for the analysis;

i) the date the test report was issued.

An example of a test report for bulk analysis is shown in Table 3. Figure 10 shows a typical depth profile result.

Table 3 — Example of a test report for GD-MS analysis of a bulk sample

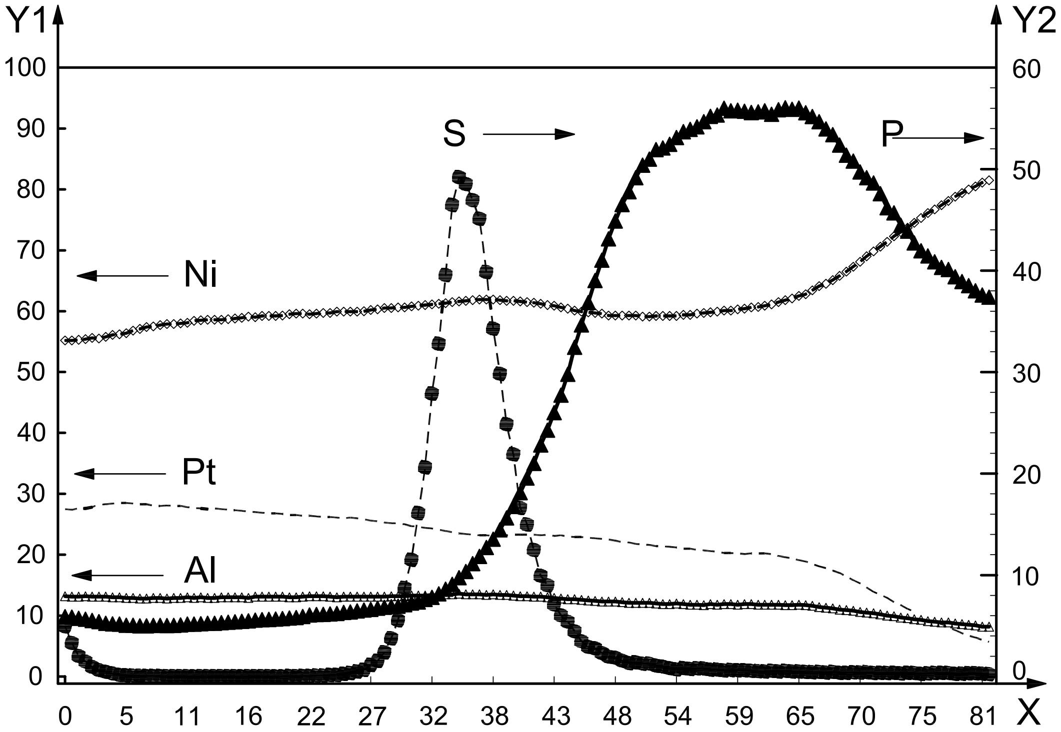
GD-MS
ANALYTICAL REPORT

GDMS Analysis Inc.
206 Snow ball street
12345 Glacer town
Antarctica
Phone 00000001
Fax 00000002
penguin@antarctica.com

Customer	**ABC, Inc.**	*P.O #*	**PO1234**
Date	**January 1, 2010**	*Job #*	**JB-AB645**
Customer ID	**Hf-metal** **Lot # 2345-bottom**	*Sample ID*	**AD10203**

Element	Mass fraction µg/g	Element	Mass fraction µg/g
Li	<0,005	Ag	<0,05
Be	<0,001	Cd	<0,05
B	0,01	In	<0,005
F	<0,05	Sn	<0,05
Na	0,02	Sb	<0,05
Mg	<0,01	Te	<0,05
Al	0,008	I	<0,01
Si	0,16	Cs	<0,001
P	0,07	Ba	<0,005
S	0,97	La	<0,005
Cl	<0,05	Ce	<0,005
K	<0,01	Pr	<0,005
Ca	<0,01	Nd	<0,005
Sc	<0,5	Sm	<0,005
Ti	0,76	Eu	<0,005
V	0,02	Gd	<0,005
Cr	0,02	Tb	<0,005
Mn	<0,005	Dy	<0,005
Fe	0,2	Ho	<0,005
Co	0,03	Er	<0,005
Ni	0,35	Tm	<0,005
Cu	0,07	Yb	<0,005
Zn	0,02	Lu	<0,005
Ga	<0,01	Hf	Matrix
Ge	<0,01	Ta	<1
As	<0,005	W	0,007
Se	<0,05	Re	<0,01
Br	<0,05	Os	<0,05
Rb	<0,005	Ir	<0,1
Sr	<0,05	Pt	<0,1
Y	<0,05	Au	<0,05
Zr	240	Hg	<0,05
Nb	0,06	Tl	<0,01
Mo	0,07	Pb	<0,01
Ru	<0,005	Bi	<0,01
Rh	<0,01	Th	<0,001
Pb	<0,05	U	<0,001

www.gdms- antarctica.com 1 of 1 **Reviewed by ________**



Key

X depth (µm)

Y1 mass fraction in % (for the Ni, Pt and Al profiles)

Y2 mass fraction in mg/g (for the S and P profiles)

Figure 10 — Example of a GD-MS depth profile for an Ni-Pt-Al coating on an Ni super-alloy substrate

Bibliography

[1] ISO 5725-1, *Accuracy (trueness and precision) of measurement methods and results — Part 1: General principles and definitions*

[2] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results — Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

[3] ISO 5725-6, *Accuracy (trueness and precision) of measurement methods and results — Part 6: Use in practice of accuracy values*

[4] AS 3685:1998, *Recommended procedures and principles of glow discharge mass spectrometry (GD-MS)*

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