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**Surface chemical analysis — Glow  
discharge mass spectrometry —  
Operating procedures**

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

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Published in Switzerland

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## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

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

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see [www.iso.org/patents](http://www.iso.org/patents)).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see [www.iso.org/iso/foreword.html](http://www.iso.org/iso/foreword.html).

This document was prepared by Technical Committee ISO/TC 201, *Surface chemical analysis*, Subcommittee SC 8, *Glow discharge spectroscopy*.

This second edition cancels and replaces the first edition (ISO/TS 15338:2009), which has been technically revised.

The main changes compared to the previous edition are as follows:

- This document is more generic and covers not only the static, cryogenic cooled source, but also the fast flow high power source.
- This document no longer refers to calibration factors specific to one particular instrument type.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at [www.iso.org/members.html](http://www.iso.org/members.html).

# Surface chemical analysis — Glow discharge mass spectrometry — Operating procedures

## 1 Scope

This document gives procedures for the operation and use of glow discharge mass spectrometry (GD-MS). There are several GD-MS systems from different manufacturers in use and this document describes the differences in their operating procedures when appropriate.

NOTE This document is intended to be read in conjunction with the instrument manufacturers' manuals and recommendations.

## 2 Normative references

There are no normative references in this document.

## 3 Terms and definitions

No terms and definitions are listed in this document.

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

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

## 4 Principle

In a glow discharge source, a potential difference is applied between the cathode (the sample to be analysed) and the anode, and a plasma is supported by the introduction of an inert gas, normally argon. This potential difference can be either direct current (DC) or radio frequency (RF), the advantage of RF being that electrically insulating materials can be analysed directly. Inert gas ions and fast neutrals formed within the plasma are attracted to the surface of the sample and their impact results in the production of neutrals by sputtering from surface.

These neutrals diffuse into the plasma where they are subsequently ionised within the equipotential area of the plasma and can then be extracted to a mass spectrometer for analysis. Both magnetic sector and time of flight spectrometers are available.

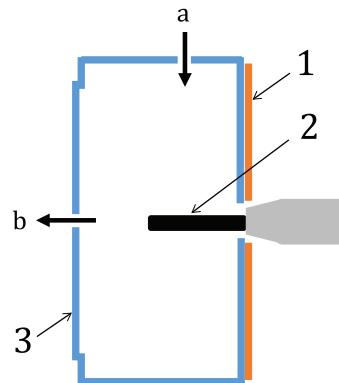
## 5 Apparatus

### 5.1 Ion source

There are two fundamental types of ion source used for the GD-MS, a low flow or "static" source, and a fast flow source. Both types can accept pin samples or samples with a flat surface. A typical pin would be 20 mm long with a diameter of 3 mm, and a typical flat sample would be 20 mm to 40 mm diameter. More details of these dimensions can be found later.

In the low flow source the plasma cell is effectively a sealed unit held within a high vacuum chamber, with a small exit slit or hole to allow the ions to exit the cell and enter the mass spectrometer. The cell body is at anode potential, the acceleration potential of the mass spectrometer, and the sample is held at cathode potential, typically 1 kV below anode potential. In this type of source, the argon flow is typically

one sccm (standard atmosphere cubic centimetres per minute) or less, and the gas used, normally argon, should be of very high purity, six nines five or better. The power of the plasma is relatively low, typically 2 W or 3 W; the potential difference is typically 1 kV and the current 2 mA or 3 mA.



**Key**

- 1 insulator
- 2 sample (cathode)
- 3 anode (GD cell)
- a Gas inlet (0,3 sccm to 0,6 sccm)
- b To mass spectrometer

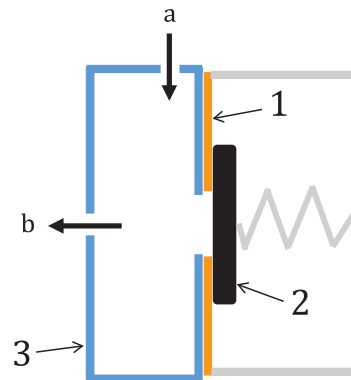
**Figure 1 — Low flow source pin geometry**  
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A schematic diagram of the low flow source in pin geometry is shown in [Figure 1](#). The gas is introduced into the cell through a metal pipe which forms a metal to metal seal with the cell body. On some systems an alternative of a PEEK tube with a ferrule seal to the cell body is used. The pin sample is held in a chuck which sits at cathode potential and the cell body is at anode potential, so the two are separated by an insulating disc. The chuck is actually located against a metal (tantalum) plate which also sits at cathode potential (not shown in the schematic diagram). The whole assembly forms a good gas seal while maintaining good electrical insulation. The only escape for the gas and any ions formed in the plasma is through a small slit or hole at the back of the cell, and this creates a pressure differential between the cell and the surrounding source vacuum chamber. It is normal to measure the pressure outside the cell in a low flow source rather than in the cell itself, the presence of a plasma making the measurement difficult. In this geometry, the potential difference between the anode and cathode “drops” in a small sheath approximately 1mm around the sample, thus leaving the main gas volume in the cell at the same potential. So any ions formed in the “plasma cloud” will not be electrically attracted back to the cathode.

It is standard practice in the low flow source to cool the plasma to near liquid nitrogen temperatures. This has been shown to reduce significantly the formation of molecular species associated with the matrix and plasma support gas combined as dimers or trimers, or with gas backgrounds such as hydrogen, nitrogen and oxygen. Cooling the sample in this way also allows for the measurement of low melting point materials such as gallium and indium, materials that would melt under normal plasma conditions.

Heat transfer between the components of the plasma cell needs to be considered. The whole cell assembly is floated up to the accelerating potential, so the anode will typically be around 6 kV to 8 kV while the sample (cathode) is at approximately 1 kV lower during operation. The design of the heat exchanger, or cooling assembly, means that it will be sitting at ground potential, and so it is connected to the cell insulating disc which is of a larger diameter than the cell body (not shown in [Figure 1](#)). Thus, it is necessary for the insulating disc to have a good coefficient of heat transfer at the same time as being electrically insulating; the material boron nitride is ideal for this and is used in most systems. It is important to consider heat transfer through all junctions, particularly from the cell body and cathode plate through the insulator to the heat exchanger. And in order to make the sample cold, it is

important to use a sample holder, or chuck, that is of a similar diameter to the sample itself. It is possible to maximise the heat transfer if attention is paid to detail, for example, a piece of Indium foil can be cut and shaped to fit between the heat exchanger and the insulator, providing that care is taken to ensure that there can be no electrical leakage.



#### Key

- 1 insulator
- 2 sample (cathode)
- 3 anode (GD cell)
- a Gas inlet (0,2 sccm to 0,4 sccm)
- b To mass spectrometer

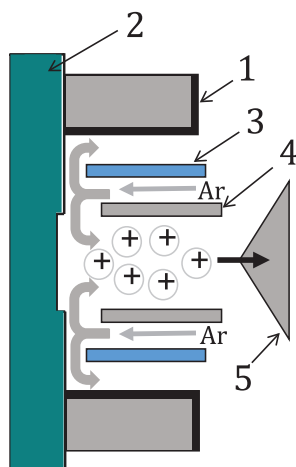
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**Figure 2 — Low flow source flat geometry**

**Figure 2** shows a schematic of the low flow source in flat geometry. The sample, which forms the cathode in the plasma, is pressed against an insulator which in turn is pressed against the cell body which is at anode potential. Again, a good gas seal is formed and the only escape route for the gas and the sputtered particles is through the ion exit slit or hole. The area of the sample exposed to the plasma can be varied by the choice of the insulator used. If a larger area of sample is exposed then a larger ion beam will be produced, but it is possible to use smaller insulators to allow smaller samples to make a gas seal. Or to reduce the area exposed to analysis. Commercial systems will generally have insulators available to allow areas from 2 mm to 20 mm diameter to be exposed, but 10 mm to 15 mm is the normal. The most important need is that the sample surface shall be flat in order to make a good gas seal with the insulating disc.

The gap between the sample (cathode) and the anode has to be small (less than a critical distance, typically 1 mm) to avoid creation of a discharge in the gap. It is often a problem that sputtered material can be deposited on the inner diameter of the insulator, creating a short circuit between anode and cathode. This can be avoided by the use of two insulators with different diameter holes.

**Figure 3** shows the fast flow source. In this geometry the sample (shown here as a flat sample) is pushed against the back of the source and is raised to cathode potential. The discharge gas (normally argon) is injected between a tube at anode potential and a concentric flow tube and is directed towards the sample surface. The flow rate of the argon is in the region of 300 ml/min to 500 ml/min. The same high purity support gas as used in the low flow source is not required, a typical purity would be five nines.



### Key

- 1 insulator
- 2 sample (cathode)
- 3 anode
- 4 flow tube
- 5 cone

**Figure 3 — Fast flow source flat geometry**

The potential difference between anode and cathode is typically 800 V and the current typically 30 mA or 40 mA. Sample atoms that are sputtered from the surface and ionised enter the mass spectrometer through an orifice in the sampling cone as shown in the diagram.

In a fast flow source the signals are largely independent of the sample temperature and Peltier cooling is used to reduce sample overheating. The use of liquid nitrogen cooling is not necessary as the high power of the plasma inhibits the formation of molecular ions. A significant reduction from room temperature is required only for certain high melting point samples.

In all cases described above, the ions are accelerated into the mass analyser by a high potential difference, typically 6 kV to 8 kV. In most cases the source is held at high potential and the analyser at ground, but it is possible to achieve the same potential difference by grounding the source and taking the analyser section to a negative high voltage.

The extracted ions are focussed and steered onto a source defining slit by a series of steering plates and lenses at different potentials. This source defining slit or sampling cone is typically at ground potential and forms the object that the analyser will focus onto the detector. Different sizes of source defining slit are available, in some instruments there is a finite number of alternatives, in others the source defining slit is infinitely adjustable. For high resolution, where interference peaks need to be separated from the peak of interest, a small source defining slit shall be used. But for the analysis of impurities where there is no interference peak, it can be possible to have a large source defining slit to allow more ionised particles to pass through, hence making it possible to detect lower levels of the impurity.

The potential between anode and cathode can either be a steady DC voltage, a radio frequency (RF) voltage, or can be a modulated pulsed voltage. In this last case, the cathode potential is switched rapidly, typically at a frequency of 2 000 Hz with a pulse duration of 50  $\mu$ s, a duty cycle of 10 %. It has been shown that in the case of the fast flow source, this mode of operation can be beneficial for bulk analysis by improving long term stability and precision. It also makes possible depth profiling of layered samples and secondary cathode analysis of insulators.

In the case of the recently developed Time of Flight (TOF) mass spectrometer, the source is similar to the fast flow source and the accelerating potential is always pulsed so that very short bursts of ions are introduced to the analyser section.



## 5.2 Mass analyser

The purpose of the mass analyser is to separate ions of different species by mass. More precisely the separation is by mass charge ratio; an  $^{40}\text{Ar}$  ion with a single charge would be seen at 40 u (atomic mass units), but the same ion with two electrons removed would appear at 20 u. As well as multiple charged species, some molecular species are seen in the spectrum, an example being  $^{40}\text{Ar}_2^+$  which would appear at 80 u.

Some GD-MS instruments work at high resolution and are capable of resolving most interferences from the peak of interest. These systems can also be operated at low resolution if there are no interferences to be resolved, thereby giving a larger signal and more precise measurement or better detection limits.

All mass spectrometers operate under vacuum to ensure that the mean free path without collision is as great as possible, resulting in a cleaner signal at the collector. The analyser section of the instrument should be left under vacuum whenever possible, and for this reason all systems incorporate a valve to isolate the analyser from the source which needs to be exposed to atmosphere frequently.

In those systems which consist of a magnet and ESA (Electrostatic Analyser) the ions are separated in mass by the magnetic field, and any small spread in energy is removed by the ESA. Some systems use a forward style Nier Johnston geometry (ESA then magnet), others use a reverse style (magnet then ESA). A continuous stream of ions will enter the analyser and the masses of interest are measured sequentially. In the case of the TOF, a complete spectrum is acquired for each individual pulse.

## 5.3 Detector system

The magnetic sector GD-MS instruments are designed to measure as large a spread of signal intensities as possible, and there may be more than one type of detector on an instrument.

Very large signals (around  $10^{-9}$  A) can be produced by GD-MS instruments, an ion current equivalent to  $10^{10}$  ions per second. These signals cannot be measured by any ion counting system and so are collected by a Faraday cup and converted to a voltage by a current amplifier. A typical amplifier will produce a signal of 1 V for an ion current of  $10^{-9}$  A. Currents down to  $10^{-14}$  A can be registered by the same amplifier using a digital voltmeter with good resolution.

Below  $3 \times 10^{-13}$  A, equivalent to  $2 \times 10^6$  counts per second, ion counting systems are used. On some instruments this is a Daly system, which consists of a conversion electrode, a scintillator and a photomultiplier tube outside the vacuum. On others it is an electron multiplier mounted inside the vacuum system of the mass analyser. For both of these alternatives the associated electronics will be able to switch the signal between the alternative detectors and will protect the more sensitive multiplier for the incidence of large signals which could cause damage.

On systems which use more than one detector, there will be software to cross calibrate the detectors. Signals of suitable strength are measured both detectors to show the effective efficiency of the multipliers. This can change for many reasons, supply voltage changes or aging being two reasons, and so it is important to monitor it on a regular basis. More details of this calibration and the monitoring are given later.

In time of flight systems, Micro Channel Plates (MCPs) are used to measure the signal as a very fast response is needed. When a pulse of ions is introduced into the analyser, all ions have the same kinetic energy and so different masses travel at different velocities and reach the detector at different times. Data for the whole mass spectrum is acquired and stored for each individual pulse, a full spectrum being acquired in a few tens of microseconds.