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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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Foreword

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

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This document was prepared by Technical Committee ISO/TC 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.

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.

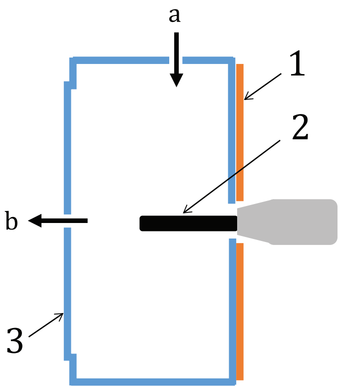
These neutrals diffuse into the plasma where they are subsequently ionised within the equipotential area of the plasma and can then be extracted to a mass spectrometer for analysis. Both magnetic sector and time of flight spectrometers are available.

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

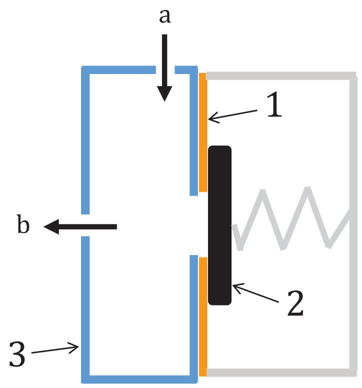
1	insulator
2	sample (cathode)
3	anode (GD cell)
a	Gas inlet (0,3 sccm to 0,6 sccm)
b	To mass spectrometer

Figure 1 — Low flow source pin geometry

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

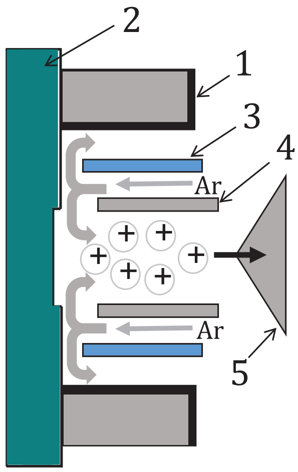
1 insulator
2 sample (cathode)
3 anode (GD cell)
[a] Gas inlet (0,2 sccm to 0,4 sccm)
[b] To mass spectrometer

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 µs, 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}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 $^{40}Ar_2^+$ 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 3×10^{-13} A, equivalent to 2×10^6 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.

6 Routine operations

6.1 Cleaning the system

As with all vacuum systems, cleanliness is extremely important. Any components that fit within the vacuum system should only be handled when wearing gloves. Powder free gloves are preferred otherwise a residue of chemical such as silicon can be left behind.

Some systems have the internal source parts made from tantalum as this is effectively mono-isotopic with an odd number mass that produces less background interferences and can be thoroughly cleaned with acids. The source parts need to be cleaned regularly to remove sputter deposited coating that can produce instability, and if different matrices are analysed these depositions can cause memory effects. In the case of tantalum parts, they should be cleaned mechanically by scrubbing with an abrasive sponge-like material then soaked in an acid suitable to dissolve the matrix material. For particularly difficult matrices a strong acid such as aqua regia (1:3, HNO_3:HCl) with a small percentage (~2 %) HF can be used. The acid wash should then be followed with several washes with deionised water and finally with methanol.

Stainless steel components should be treated more carefully than the tantalum items, but as they are not usually in direct contact with the ion beam a mechanical wash followed by soaking briefly in 50 % HNO_3 and a rinse in deionised water then methanol is normally sufficient.

Any ceramic components should not be cleaned with liquids as they tend to be absorbent, a simple mechanical scrub should suffice.

In order to reduce down time as a result of cleaning source components, it is possible to keep a batch of such parts so that they can be exchanged when necessary and cleaned while the system continues to run.

6.2 Support gas handling

In the low flow versions of GD-MS the purity of the plasma support gas is more critical than in the fast flow systems, so the handling of the entire gas system is critical. Manufacturers will generally supply instructions on the best way to install new bottles and handle the system during both use and idle period.

When installing a new bottle, the valve on the top of the bottle should be left closed and the regulator (normally two stage) fixed in position. All the regulator valves should be fully opened and then the gas bottle valve opened, allowing the pure gas to escape to atmosphere. When the gas has been flowing for around 5 s then the valve at the output of the regulator should be closed. The regulator can then be attached to the gas inlet line which should then be pumped by a rotary or oil free pump back to the valve. Once evacuated the rotary pump should be isolated and the regulator output valve opened and the regulator intermediate valve adjusted to give the correct pressure (around 0,2 MPa is typical). The regulator output valve should then be closed, the system evacuated and then pressurised a second time to flush all the pipework.

If the gas inlet is fitted with a gas cleaning stage, a “getter pump” then the manufacture’s recommendations for using this should be followed.

During normal operation, the source will be exposed to atmosphere regularly so that maintenance work and cleaning of source components can be carried out. It is good vacuum practice to vent the source to a dry gas, either dry nitrogen or low grade argon, rather than exposing it directly to atmosphere.

Again referring to the low flow system with pure support gas, care shall be taken when exposing the source to atmosphere. The support gas should be left flowing at all times that the source is not under vacuum to keep flushing the line. If the gas is turned off then atmospheric contamination can get into the line and can adversely affect results for some time afterwards. Systems that have a very narrow bore capillary insulator to isolate the gas inlet from the acceleration voltage present on the anode to which the gas line is connected are particularly susceptible to this problem and the adverse effects can be seen for some time. While this does not totally eliminate contamination of the line, it greatly reduces any adverse effect.

It is also recommended that a small flow of gas is continually present in all systems during maintenance work, including the fast flow system, as this helps the overall cleanliness and avoids moisture contamination.

7 Calibration

7.1 Mass calibration

In the case of the magnetic sector mass spectrometers it is necessary to calibrate the mass against magnetic field so that the software knows where to find a peak. There is always a software function to do this and it is necessary to acquire data for a known sample and then identify several peaks manually. It is necessary to use peaks across the entire mass range and relatively evenly spread, with more peaks towards the low mass end, as this is where system non-linearity is most evident. On some older systems only the Faraday can be used for this calibration due to a software limitation, and in this case it is necessary to ensure that elements with high concentrations across the whole mass range are included.

For the most limited systems, with Faraday acquisition only, the lowest mass that can be seen on the Faraday cup from the discharge gas is generally 13,3 u from the triply ionised ^{40}Ar isotope. It is possible to find sample with high level of lithium, beryllium or boron, but they shall also contain a high mass. Alternatively, and common practice on some low flow instruments, is to run the sample with no LN_2 cooling, and handle the sample with unprotected fingers before it is loaded. This is normally bad practice, but for the infrequent mass calibration it can be useful as a peak is generally seen at 3 u, created from a hydrogen trimer.

At the high mass end, gold is a good choice as it is mono-isotopic at 197 u, and in a non-cooled system will often produce an AuAr molecule at 237 u.

The software in most systems will indicate the success of the calibration by indicating the difference between the calculated mass for the field at which it was found and the mass that has been identified as being true. Errors should be low across the entire mass range, typically less than 10 millimass units (0,010 u), or peaks may be missed or misidentified during analysis.

In most magnetic sector systems there is a localised recalibration possible, in this case using smaller peaks that are found on the counting detectors as well as those only seen on the Faraday. This process should be performed on production samples and at least once a day, more often if experience shows it to be necessary. Typically, the one isotope of the matrix is used, and a group of peaks associated with the discharge gas, molecules and multi-ionised species, and tantalum can also be found.

When this localised calibration adjustment is performed, the offsets necessary to compensate for mass change will be displayed. If there is a progressive change in the calibration, small drift over a long time, but always in the same direction, then the correction may become too large to be implemented, and a full calibration will be necessary. The manufacturer's documentation should be referred to in order to define such restrictions.

For the TOF-MS systems the mass is calibrated as a function of time. The whole spectrum is collected in a few tens of microseconds, and this is repeated many times. For each sample it is necessary to identify two or more known peaks in the first acquired spectrum, and from these the relationship between mass and time is accurately calculated and applied to all subsequent data.

7.2 Detector calibration

If the mass spectrometer is equipped with two or more detectors then a basic cross calibration is needed to determine their relative efficiency. There are different ways to achieve this.

For the first method, it is necessary to find a stable signal which is low enough to be measured on the multiplier, yet at the same time sufficiently high to be measured on the Faraday. When a sample is running under normal conditions, the total matrix current would be around 10^{-9} A, four orders of magnitude too much. If the discharge conditions are reduced and the beam defocused enough to achieve a signal that is low enough, then the discharge could be unstable, and an accurate measurement very difficult to achieve. It is good practice to find a specific sample for this measurement only, and a very good example would be a tungsten-titanium alloy. It is possible to find such an alloy where the titanium is only a few percent of the total alloy, and thus only a few percent of the total matrix current. In addition, titanium has five isotopes and the isotope at 50 u is only 5,4 % of the total titanium, another very significant reduction in signal.

In the second method, an element with two or more isotopes of very different natural abundances is used. For example, Tantalum has isotopes at 180 u and 181 u, with abundances 0,012 % and 99,988 % respectively. There will be software to measure both isotopes, the smaller on the ion counting, the larger on the Faraday, and then calculate the correction factor needed to give the correct isotope ration. This then yields the ion counting efficiency as in the first method.

In some instruments, there are effectively three collectors; a Faraday and a simultaneous electron multiplier that can be operated in either analogue or pulse counting mode. In these systems, the software will perform a second stage to compare the analogue and pulse counting and define a conversion factor.

Practical measurements have shown that different matrices exhibit different efficiencies, for example titanium shows a significantly higher efficiency than copper when measured on the same instrument. Only one value of efficiency is used for correction of signals measured on the multiplier so there will be errors introduced when the impurity signal for any element not used to calibrate efficiency is ratioed to the signal measured on the Faraday. However, if no relative sensitivity factors (RSF, see later) are used then this error is insignificant; if standard RSF factors are used then the error is still insignificant; but if RSFs measured on a specific instrument are used for absolute accuracy then changing the efficiency measurement will introduce a need for new RSF measurements. Thus it is important for accurate measurements to be consistent when calibrating and always use the same matrix element.

7.3 Routine checks

It is very important to make regular checks that the system calibrations have not drifted.

If the mass calibration has drifted then it is difficult to be certain that the area being scanned would include the mass in question. This is particularly important for the analysis of pure materials, where the impurity of interest may not be present and detection limits are being reported. For this reason, most systems will include a localised mass correction, where several peaks associated with the discharge gas, and therefore always present, can be identified and corrections made for any drift. For lower masses it is simple to verify the calibration, five times ionised argon can be found at nominal 8 u. If six times ionised argon at 6,7 u can be found, then this should be used as well. The lowest mass isotopes measured are normally Lithium at 6 u and 7 u, so these correction peaks will be sufficient, but if hydrogen or helium is to be analysed then it will be necessary to look further.

The highest mass that can be found routinely is often tantalum at 181 u which is normally present in low flow systems from the source components, particularly from the source defining slit. If the matrix to be measured has a high mass, gold at 197 u for example, then this should be included in the localised calibration, as should the matrix combined with argon, $^{197}\mathrm{Au}^{40}\mathrm{Ar}^{+}$ at 237 u in the case of gold. Also matrix single ionized dimmers (MM^{+}) can help in high mass region.

Another basic calibration which can change and gives no indication is the cross calibration between the different detectors. If the efficiency of a multiplier changes but is not recalibrated then it will simply give incorrect answers without warning. Therefore, regular efficiency checks shall be made, either by running a full calibration routine or regularly monitoring an element that is always present and has isotopes that can be measured on different detectors. Argon is an example of this, the peak at 40 u can be measured on the less sensitive detector while the peak at 38 u can be measured on the higher gain. The relative element concentrations, corrected for abundance, may not be in the ratio expected as the efficiency for argon may be different to that for the element used in its definition (see earlier notes) but it should always be consistent. Tantalum is another suitable matrix for checking efficiency as it has two suitable isotopes and will not give memory problems that could be associated with other matrices, as there will always be a background signal from tantalum in the source components.

With systems that routinely run the same matrix it is simple to build a simple test or series of tests that can be run regularly without disrupting the use of the instrument. For example, if the matrix is low mass, say aluminium at 27 u or cobalt at 59 u, then it may be possible to find a standard with very low levels, a few ng/g, of a high mass element such as thorium or uranium. If this is analysed at the beginning of each day and the high mass impurity is found at the right concentration, then it verifies both the mass calibration and the collector calibrations

8 Data acquisition

8.1 Sample preparation

Samples can be run in two basic formats; pin or flat. Most systems offer configurations to run either of these, but with some minor changes to the hardware configuration of the source. Again, cleanliness is very important when preparing samples as the introduction of surface contaminants such as fingerprints can have a detrimental effect on the analysis.

Sample shape consistency is important to the reproducibly of the measurement made. In the case of the pin geometry this is more difficult as a difference in the sample length can make a small but significant difference to the Relative Sensitivity Factors (RSFs) that are used to calculate the true concentration.

Electrically conducting samples can be sputtered directly by a DC plasma, but in the case of non-conducting materials it is necessary to use a different technique. An RF plasma, only available on some instruments, will allow direct sputtering, but if this is not available then another method shall be used. Such methods include mixing with a conducting powder (if sample is also in powder form, using a secondary cathode made from conducting material, or coating the sample with a material such as gallium or indium. This document cannot go into the depth necessary for every matrix type, but can only state that reproducibility and consistency of the sample preparation is the key.

The important point is that for every matrix that is to be analysed, a procedure for the sample preparation should be defined and adhered to whenever possible.

For flat samples the surface should be as clean (ideally polished) and as flat as possible as it is this surface that forms the gas seal at the back of the cell. Any roughness will allow gas to escape and make it difficult to stabilise and reproduce the plasma conditions. Various anode diameters can be used depending upon the size of the sample. Again, in routine analysis the anode diameter should never be varied as this may change the calibration. For bulk analysis a larger anode diameter will give better matrix signal and show less effect from inclusions. For analysis of small samples or for analysis of a specific area on the surface, a smaller anode diameter can be used, but at the expense of signal intensity.

8.2 Procedure setup

While TOF systems will always acquire data for the whole mass spectrum, magnetic systems will only scan the area around the peaks of interest. If the instrument is set to have a mass resolution of 4 000, which is a typical running mass resolution to separate most interferences, then the peak width is the inverse of this, 250 ppm. This means that there are vast areas of baseline which need to be ignored in order to make the acquisition efficient.

The software controlling the instrument will calculate the magnetic field at which the peak of interest is expected and set the magnet to that field. The mass will then be stepped in very small increments over that peak by stepping the accelerating voltage or stepping the voltage on a deflector plate after the magnet, and peak height readings taken in each channel. The voltage is stepped rather than the magnetic field to ensure that the same number of points are used on each peak, as these will be integrated during the analysis and the ratioed to the matrix peak. If the magnetic field were stepped rather than the voltage, then there would be a different number of channels on low mass peaks than on high mass, due to the non-linear relationship between mass and field (mass is proportional to field squared).

The width of the scan over each peak is defined by the operator by varying the number of steps (channels) and the size of the step. If the mass calibration of the instrument is known to be good then the width can be reduced. However, it can be good practice to have the scan wide enough to include interfering peaks which are known to be close as these can be used to confirm the accuracy of the mass calibration and peak identification.

The main purpose of the procedure for analysis is to define the elements of interest. At least one element shall be defined as the matrix, to which all impurities will be ratio'ed. More than one element can be defined as in the case of alloys, or all elements defined if the aim is to define the composition with respect to the whole. When defining an element, it should be the largest available matrix isotope that is known to be free of interferences to achieve the best possible detection limit. If more than one isotope is chosen to be measured, then it is necessary to define which is the primary. This will be used for calculation of the signal representing the elemental concentration and used in all subsequent calculations. It is useful to include more than one isotope, particularly for samples which are not routinely analysed, as any unexpected interferences will be highlighted by inconsistent element concentrations.

For some materials, especially pure matrices, it can be useful to include several interference peaks at masses spread over the spectrum. The presence of these peaks is dependent upon matrix and discharge support gas (usually Ar), but there will normally be a peak associated with tantalum at 181 u, formed from the material used to construct the source components. Any such peaks should be ignored in the calculations of composition, but they serve as valuable indicators that the mass calibration has not drifted.

8.3 Data acquiring

When the sample is loaded into the cell and the glow discharge started, it should always be left for sufficient time to stabilise. The conditions for running a sample will be dependent on the matrix, and it is not possible to show all the possible variations in this document. A general guide will be given.

For most samples, it is desirable to presputter the surface in order to clean off any surface contamination that will affect the measurements. This will also clean the surface, making the ongoing discharge more stable. Typically, this presputter period will be at a higher power of plasma than the analysis, but again this is matrix dependent. Some matrices, such and nickel alloys, can be presputtered with a high power plasma, thus achieving surface cleaning in a shorter time. But other matrices, for example gallium, need to be treated more gently.

Once the presputter period is complete, data will be acquired following the operator defined procedure described above. Most laboratories will repeat the acquisition two or more times to show consistency of results. With pure matrices, it will often be seen that the low mass elements (below about 60 u) will start at a raised level and will decrease with time. Higher mass elements do not tend to show this behaviour and will stabilise more quickly. So it can be time efficient to split the acquisition procedure into two parts; acquire and analyse data for elements heavier than (for example) 100 u. While this is being done, the lower elements will be reaching their stable levels and can be analysed later.

It is always good practice to make a quick measurement of all elements of interest before the main measurement, as it is always possible for problems to occur with the discharge or with the analyser section of the instrument, and a quick measurement at least provides some data rather than all being lost.

9 Quantification

9.1 Element integral calculation

The measurement of a peak is not a single channel (peak jumping) measurement, at high resolution; it is impossible to guarantee that the top of a peak is found, it will be a series of steps/channels over the peak. At each of these steps a reading of ion current will be taken, either by analogue measurement on the Faraday for larger signals or by counting ions for smaller signals. The channels to represent the peak will be chosen by the software but this can be overridden by the operator if necessary.

In the case of the Faraday, the measurement is already an analogue representation of ion current and the internal software will store a value in Amperes. For ion counting systems (Daly or Electron Multipliers) each channel is a number of counts and this needs to be converted to ion current. Firstly, the number of