

Australian Standard™

**Recommended practice for inductively
coupled plasma-mass spectrometry
(ICP-MS)**

Part 1: Principles and techniques



This Australian Standard was prepared by Committee CH-016, Spectroscopy. It was approved on behalf of the Council of Standards Australia on 7 July 2005. This Standard was published on 9 September 2005.

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Australian Standard™

Recommended practice for inductively coupled plasma-mass spectrometry (ICP-MS)

Part 1: Principles and techniques

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PREFACE

This Standard was prepared by the Standards Australia Committee CH-016, Spectroscopy.

The objective of this Standard is to describe principles, techniques and operating procedures involved in the setting up and operation of inductively coupled plasma mass spectrometry for chemical analysis. The recommendations in this Standard are intended to apply to Australian standard methods for inductively coupled plasma-mass spectrometry.

This Standard is part of a series as follows:

AS

4873 Recommended practice for inductively coupled plasma-mass spectrometry (ICP-MS)

4873.1 Part 1: Principles and techniques

4873.2 Part 2: Quantitative determinations

The term ‘informative’ has been used in this Standard to define the application of the appendix to which it applies. An ‘informative’ appendix is only for information and guidance.

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STANDARDS AUSTRALIA

Australian Standard

Recommended practice for inductively coupled plasma-mass spectrometry (ICP-MS)

Part 1: Principles and techniques

SECTION 1 SCOPE AND GENERAL

1.1 SCOPE

This Standard sets out recommendations and operating procedures in the application of inductively coupled plasma-mass spectrometry (ICP-MS) to chemical analysis. This Standard refers principally to quadrupole based instruments, but some clauses are applicable to other types of ICP-MS instruments such as magnetic sector and time-of-flight mass spectrometers.

This Standard should be read in conjunction with the instrument manufacturer's recommendations and AS 3641.1.

NOTE: An overview of possible spectral interferences is given in Appendix A.

1.2 REFERENCED DOCUMENTS*

The documents below are referred to in this Standard:

AS

- | | |
|--------|---|
| 1940 | The storage and handling of flammable and combustible liquids |
| 2772 | Radiofrequency radiation |
| 2772.2 | Part 2: Principles and methods of measurement—300 kHz to 100 GHz |
| 2850 | Chemical analysis—Interlaboratory test programs—For determining precision of analytical method(s)—Guide to the planning and conduct |
| 2929 | Test methods—Guide to the format, style and content |
| 3641 | Recommended practice for atomic emission spectrometric analysis |
| 3641.1 | Part 1: Principles and technique |
| 3641.2 | Part 2: Inductively coupled plasma excitation |

AS/NZS

- | | |
|--------|---|
| 2243 | Safety in laboratories |
| 2243.2 | Part 2: Chemical aspects |
| 2243.5 | Part 5: Non-ionizing radiations—Electromagnetic, sound and ultrasound |

ISO

- | | |
|----------|--|
| Guide 30 | Terms and definitions used in connection with reference materials |
| Guide 32 | Calibration in analytical chemistry and use of certified reference materials |
| 3696 | Water for analytical laboratory use—Specification and test methods |

* Additional documents are listed in Appendix B for information only.

- ISO
5725 Accuracy (trueness and precision) of measurement methods and results
5725-2 Part 2: Basic method for determination of repeatability and reproducibility of a standard measurement method
- BS
5703 Guide to data analysis and quality control using cusum techniques (series)

1.3 DEFINITIONS

For the purpose of this Standard, the following definitions apply.

NOTE: A glossary of terms is given in Appendix C to provide additional guidance and explanation of terms used in the fields covered by the AS 4873 series.

1.3.1 Accuracy

The closeness of agreement between a test result and the true or accepted reference value. (AS 2850).

1.3.2 Analyte

The element whose concentration or quantity is to be determined.

1.3.3 Blank reagent solution

A solution for monitoring reagent impurities prepared by adding to the solvent the same amount of reagents (without the sample) as added to the test sample.

1.3.4 Blank sample solution

Prepared in the same way and using the same reagents as the test sample solution but leaving out the test portion or by taking a quantity of water as large as the test portion. This solution is then included in the preparation procedure.

1.3.5 Blank calibration solution

Prepared in the same way as the calibration solution but without adding the analyte.

1.3.6 Calibration solution

A solution used to calibrate the instrument, prepared either from a stock solution(s) or from a Certified Reference Material. (See ISO Guides 30 and 32.)

1.3.7 Check calibration solution

A solution of similar composition as one of the calibration solutions, but prepared with different stock solutions from a different source.

NOTE: These solutions may also be used as linearity verification solutions (see Clause 1.3.15 and Table 3).

1.3.8 Concentration (*C*)

Quantity of a substance in a defined volume or mass.

Concentration may be expressed in milligrams per litre (mg/L) or milligrams per kilogram (mg/kg). Where concentration is very low, the mass may be expressed as micrograms, nanograms, or similar units as appropriate.

1.3.9 Determination

The process of quantifying analyte(s) in the test sample solution up to and including measurement and calculation.

1.3.10 Interference check solutions

The solutions used to determine the *f* factor. (See Clause 3.2.3 and Table 1.)

1.3.11 Instrument detection limit (*IDL*)

The smallest concentration that can be detected with a defined statistical probability using a clean instrument and a clean solution, e.g. dilute nitric acid (Clause 4.5).

1.3.12 Isobaric interference

Isobaric interferences are spectral overlap interferences due to isotopes of other elements which have the same nominal mass as the analyte isotope. These interferences may be corrected by use of elemental interference equations. (See Section 3.)

1.3.13 Laboratory sample

The sample sent to the laboratory for analysis.

1.3.14 Linearity

A straight line relationship between the mean result of measurement and the quantity of the analyte.

1.3.15 Linearity verification solution

A solution with exactly the same concentration of the matrix components as the calibration solutions, but having an analyte concentration half that of the (highest) calibration solution (Clause 5.7).

NOTE: Refer to Clause 1.3.7 and Table 3.

1.3.16 Mass discrimination effects

Different response for the same number of ions of different masses.

1.3.17 Mean result

The mean value of n results.

1.3.18 Method detection limit (*MDL*)

The smallest concentration of analyte that can be detected with an analytical method with a defined statistical probability for defined maximum matrix element concentrations (Clause 5.9.2).

1.3.19 Net intensity (*I*)

The intensity obtained after all corrections have been applied. This may include corrections for dead time, blank, isobaric and polyatomic interferences.

1.3.20 Net intensity ratio (*IR*)

The net intensity of an analyte divided by the net intensity of a reference element (internal standard) in the same solution. (See Clause 3.3.5.2.)

1.3.21 Outer flow

The gas flow between the outer tube and the intermediate tube of a plasma torch.

1.3.22 Polyatomic interferences

Polyatomic interferences are spectral overlap interferences due to molecular ions, which have the same nominal mass as the analyte isotope. These interferences may be corrected by the use of measurements of other ions or other solutions. (See Clause 3.2.2.)

1.3.23 Practical quantitation limit (*PQL*)

Defined by multiplying the MDL by a specified factor, typically 3 (Clause 5.9.2).

1.3.24 Precision

The closeness of agreement between independent test results obtained under prescribed conditions (Clause 5.9.3) and AS 2850.

1.3.25 Pure chemical

A chemical with the highest available purity and known stoichiometry and isotopic abundance. The content of analyte and contaminants should be known with an established degree of certainty.

1.3.26 Raw intensity (I_{raw})

The uncorrected intensity in counts per second (cps) or any other arbitrary units, related to ion current, which is not corrected by the use of measurements of other ions or of other solutions.

1.3.27 Repeatability (r)

The value to which the absolute difference between two single test results obtained with the same method on identical test material, under repeatability conditions may be expected to be less than or equal within a specified probability.

NOTE: See ISO 5725-2.

1.3.28 Repeatability conditions

Conditions where test results are obtained with the same operator, same apparatus, same laboratory and minimum practical time consistent with separated tests.

1.3.29 Reproducibility (R)

The value to which the absolute difference between two single test results obtained with the same method on identical material under reproducibility conditions may be expected to be less than or equal within a specified probability.

NOTE: See ISO 5725-2.

1.3.30 Reproducibility conditions

Conditions where test results are obtained with the same method on identical test material obtained by different operators either in the same or in different laboratories. When the same laboratory is involved, the results should be obtained on different days.

1.3.31 Reproducibility limit

The value to which the absolute difference between two single test results obtained under reproducibility conditions may be expected to be less than or equal within specified probability (generally taken as 0.95).

1.3.32 Reproducibility standard deviation

The standard deviation of test results obtained under reproducibility conditions.

1.3.33 Result

The result of a measurement calculated as concentration (C).

1.3.34 Sensitivity (S)

The ratio of the change in the net intensity (ΔI) to the corresponding change in the concentration of the analyte (ΔC):

$$S = \frac{\Delta I}{\Delta C}$$

1.3.35 Stock solution

A solution with accurately known analyte concentration(s), prepared from pure chemicals. Stock solutions are reference materials within the meaning of ISO Guide 30.

1.3.36 Test portion

A quantity of material taken from the test sample for analysis.

1.3.37 Test sample

Made from the laboratory sample (e.g. by grinding, homogenizing etc.).

1.3.38 Test sample solution

A solution prepared from the test portion on which measurements are carried out.

1.3.39 Uncertainty of measurement

A parameter, associated with the result of a measurement, that characterizes the dispersion of the values that could reasonably be attributed to the analyte.

1.3.40 Unified atomic mass unit (u)

One 'u', the unified atomic unit, is defined as equal to 1/12 the mass of one atom of the most abundant form of carbon, the ¹²C isotope. 1 'u' is equivalent to 1 atomic mass unit (amu) or 1 dalton (Da).

NOTE: The amu and dalton units are not officially approved, despite their common use.

1.4 PRINCIPLE

In the present context, a plasma is a stream of partially ionized gas present at the end of a torch. The plasma is sustained by a radiofrequency (RF) field created by an induction coil around the end of the torch.

The sample is introduced into the plasma as an aerosol. Once in contact with the plasma, the aerosol is desolvated, the residual particles are vaporized. The resulting molecules are then dissociated into atoms, some of which are then ionized. The fraction of atoms ionized depends on the temperature, the electron density and the ionization energy of the element. Plasma is then extracted through an interface/ion lens region to the mass spectrometer where the ions are separated by their respective mass-to-charge ratios (m/z). The number of ions detected in a given time is proportional to the concentration of the analyte. Only a small fraction of analyte atoms in the original sample reaches the detector as ions.

1.5 SAFETY PRECAUTIONS

1.5.1 General

The general safety precautions listed in AS/NZS 2243.2, AS/NZS 2243.5 and AS 1940 should be followed to minimize safety hazards.

1.5.2 Ultraviolet radiation

The ICP generates dangerously high levels of ultraviolet radiation. Most ICP instruments are provided with a safety interlocking system which prevents operation of the plasma when the ultraviolet-absorbing shield is not in position. It is essential that the interlock not be overridden.

1.5.3 Exhaust extraction system

It is strongly recommended that an efficient mechanical ventilation system be installed to exhaust toxic fumes and ozone issuing from the torch. It should be resistant to heat and corrosion. The positioning and capacity of the exhaust system should be in accordance with the manufacturer's specification. Incorrect extraction of the exhaust can cause plasma instability. It is also recommended that the exhaust from the RF generator be vented away from the instrument

1.5.4 Radiofrequency leakage

WARNING: RADIOFREQUENCY RADIATION CAN HEAT BIOLOGICAL TISSUE. INJURY MAY OCCUR IF THE INTENSITY OF THE RADIATION IS SUFFICIENTLY HIGH.

For safety reasons, it is recommended that the ICP torch compartment be checked for radiofrequency (RF) radiation leakage by a recognized testing authority. Radiofrequency leakage tests should be performed when considered necessary. They should be carried out on commissioning the instrument and when a modification to the torch compartment has been carried out. Recommended exposure limits to non-ionizing radiation are given in AS/NZS 2243.5 and methods of measurement are given in AS 2772.2.

SECTION 2 INSTRUMENTATION

2.1 GENERAL

An inductively coupled plasma mass spectrometer (ICP-MS) is shown schematically in Figure 1.

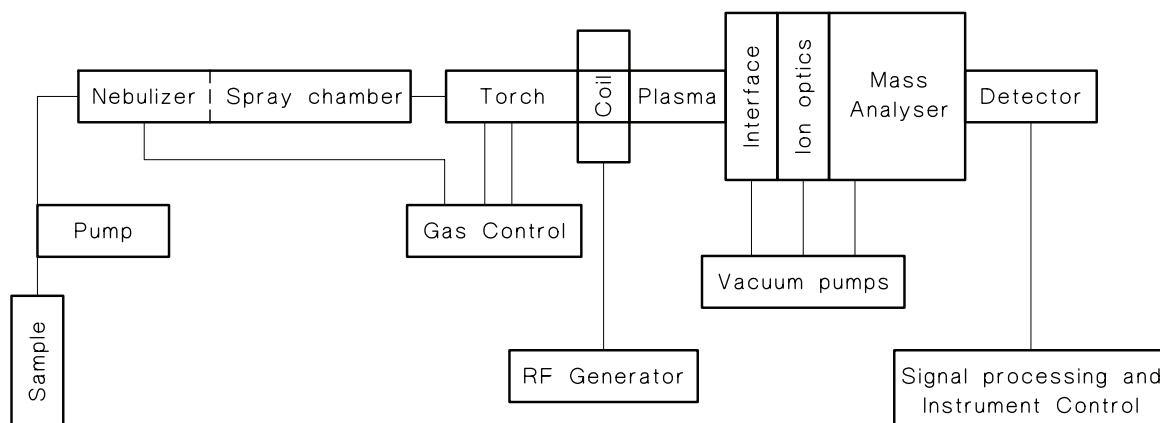


FIGURE 1 SCHEMATIC BLOCK DIAGRAM OF AN ICP-MS

2.2 SAMPLE INTRODUCTION

2.2.1 General

A solution to be measured is introduced into the plasma as an aerosol of liquid droplets suspended in a gas. The solution is taken into a nebulizer, normally with the aid of a pump. The nebulizer then converts the solution into an aerosol. This aerosol enters a spray chamber where large drops are removed as the aerosol collides with the walls or other parts of the chamber. The condensed drops drain away as waste liquid. The remaining small droplets are then transported out of the spray chamber by the gas. They are then carried through the injector tube of the torch (Clause 2.3) and into the plasma.

The sample introduction system should be constructed and operated in such a way that:

- Each aerosol droplet is as small as possible.
- The mass of aerosol transported to the plasma in each successive increment of time is as constant as possible.
- The droplet size distribution and the added mass of the aerosol in each successive increment of time is, as far as possible, independent of the solution to be measured (matrix effect, see Clause 3.3).
- The time taken for the aerosol delivery rate to stabilize, after presentation of a solution, is as short as possible.
- The components of the system are not corroded or contaminated by the solution (for example, hydrofluoric acid, organic solvents, etc). The use of glass and quartz is not appropriate if hydrofluoric acid is to be nebulized.

The various components of the sample introduction system are discussed in Clause 2.2.2 to 2.2.5 in relation to the above recommendations.

2.2.2 Sample pump

The use of a pump to feed the solution to the nebulizer is not necessary with some nebulizers (Clause 2.2.3). The use of a pump ensures that the rate of supply of the solution to the nebulizer is less dependent on the composition of the solution and on hydrostatic effects.

A peristaltic pump should be designed in such a way that it minimizes surges in the supply of solution.

The pressure on the pump tubing should be set according to the instrument manufacturer's instructions. When the pump is not in use, the pressure bars should be released and the tubing loosened from the rollers. The pump tubing is selected for its compatibility with the solution to be nebulized and should be regularly checked for degradation and replaced whenever necessary.

2.2.3 Nebulizer

A number of types of nebulizers may be used for specific applications. Nebulizers such as the concentric and the cross-flow can be self-aspirating. These nebulizers can be used without a pump. Some common nebulizers are as follows:

(a) *Cross-flow*

The cross-flow nebulizer consists of two capillary tubes mounted at a right angle, one being used for the supply of the solution and the other for the supply of the gas. Depending on the distance between the openings of the capillary tubes and their diameter, the nebulizer can be self-aspirating. With larger diameters, the chance of blockages occurring is smaller, but a pump would have to be used to supply the solution.

(b) *V-groove*

In the V-groove nebulizer, the solution flows through a vertical V-groove to a small hole through which argon gas emerges at high velocity. The solution is nebulized by the high speed gas at the outflow opening. The V-groove nebulizer was developed for solutions with high total dissolved solids (TDS) or with fairly large suspended particles.

(c) *Concentric*

The concentric nebulizer consists of two concentric tubes, the outer one being narrowed at the end. The solution flows through the central tube and the gas (Clause 2.4) flows through the tube around it. This creates a region of high gas velocity and reduces pressure around the tip of the central tube and fragments the flowing solution into small droplets (aerosol). This nebulizer performs best with solutions having a low content of dissolved matter. There are also models that are less sensitive to blockages caused by dissolved matter in the solution to be nebulized.

(d) *Micro concentric*

For the nebulizers described above, the efficiency is only a few percent. The efficiency increases when the solution introduction rate is decreased. Micro-concentric nebulizers (MCN) operate at solution flow rates of 10 to 100 $\mu\text{L}/\text{min}$ and efficiencies may approach 100%. These micro-nebulizers often show a very good precision (low relative standard deviation of the measurement) and can also be combined with a membrane desolvator (see Clause 3.2.2(a)).

(e) *Ultrasonic*

In the ultrasonic nebulizer, the solution is pumped through a tube from which it flows over a transducer plate that vibrates at an ultrasonic frequency. The amount of aerosol introduced into the plasma is 10% to 20% of the quantity of the solution entering the nebulizer. The efficiency of other commonly used nebulizers, such as cross flow, v-groove, etc. is of the order of 3%. The aerosol from an ultrasonic nebulizer has to be dried (desolvated) before being introduced into the plasma, otherwise the plasma might extinguish. The aerosol is transported to the plasma by a flow of gas that transports the aerosol from the spray chamber to the injector tube of the plasma torch (inner gas see Figure 2). Compared to other nebulizers, the ultrasonic nebulizer is more susceptible to matrix effects, has a diminished tolerance to high TDS and may require longer rinsing times.

2.2.4 Spray chamber

In the spray chamber, the larger drops of the aerosol are drained away as waste liquid. The outlet for waste liquid has to maintain the pressure in the chamber above atmospheric pressure. The waste liquid is removed either through a drain having a hydrostatic seal or by pumping. Waste liquid should be removed uniformly to avoid pressure variations in the chamber that might contribute to poor precision.

By cooling the spray chamber to 2°C to 5°C, some of the water vapour formed in the nebulization process condenses, reducing the amount of water introduced to the plasma. The formation of some interfering polyatomic ions is thereby reduced (Clause 3.2.2).

2.2.5 Alternative sample introduction systems

A number of alternative sample introduction systems are available for specific applications. Each offers unique capabilities to complement or enhance the performance of ICP-MS systems. The most common are as follows:

(a) *Laser ablation accessory*

This is often employed in geochemistry and several other fields to analyse samples without dissolution. This technique is useful for most solid materials where surface or spatial information is required. The laser can be routinely used with spot size from about 5 to 500 µm. A fine aerosol is formed in a separately positioned laser ablation chamber and is transported by a gas directly to the injector tube of the torch. As the aerosol gas does not contain liquid, less electromagnetic energy is required to achieve the appropriate plasma conditions.

(b) *Electrothermal vaporization (ETV)*

This is useful for removing matrix prior to analysis or where only small sample volumes are available. The sample matrix can be removed during the drying and pyrolysis stages of the heating program after which the analytes are vaporized and transported to the injector tube of the torch by a flow of gas (inner gas, see Figure 2).

(c) *Flow injection*

This provides injection of discrete volumes of solution into the ICP-MS. Although the ICP-MS technique is typically limited to analysis of solutions with less than 0.5% TDS, flow injection allows samples with high TDS to be analysed directly. The sample, typically 500 µL, is injected into a carrier solution stream, minimizing the memory effects of the sample matrix and improving wash-out times.

(d) *Chromatography*

This can be employed to separate the analyte from the matrix or to separate different species of analyte. Ion chromatography has been applied to remove certain matrix ions on-line or alternatively, analyte ions can be removed from an alkali sample matrix, followed by acid elution into the ICP-MS. Liquid chromatography, gas chromatography and capillary electrophoresis have been used for speciation analysis of a range of inorganic and organic forms of various elements.

(e) *Hydride generation*

This allows certain analyte elements to be converted into their gaseous hydrides for separation from the matrix prior to analysis. Sensitivity for these elements can be improved by hydride generation. The technique can avoid the polyatomic interferences that are often present with some of the hydride-forming elements when conventional solution nebulization is used.

(f) *Cold vapour mercury generation*

Metallic mercury has a high vapour pressure at room temperature and this characteristic is utilized to separate the element from the matrix. The method involves processing the sample to produce mercury ions in solution and subsequently reducing these ions to metallic mercury, with chemical reducing agents such as tin(II) chloride or sodium tetrahydroborate (sodium borohydride). An inert gas is bubbled through the solution to drive off mercury vapour (the 'cold vapour') for quantification by various means including ICP-MS.

2.3 TORCH AND PLASMA

The plasma torch consists of three concentric tubes (see Figure 2) and can be either a single unit or an assembly of independent parts. Quartz is commonly used for the tubes. Sometimes the innermost tube (the injector tube) is made of a more inert material, such as aluminium oxide. The torch is adjusted so that the tip of the injector tube is 2 to 5 mm before the induction coil. The aerosol produced in the sample introduction system flows through the injector tube at a rate of approximately 0.5 to 1.5 L/min.

The intermediate gas flows between the injector tube and the intermediate tube with a flow rate in the range of 0 to 3 L/min. The function of the intermediate gas is to increase the separation of the plasma and the ends of the injector and intermediate tubes, thus reducing the temperature at the ends of these tubes. This helps to reduce deposition of dissolved material from the aerosol and also reduces the rate of accumulation of carbon on the ends of these tubes when organic solvents are nebulized.

The outer gas flows between the intermediate and outer tubes with a flow rate of 8 to 20 L/min. The function of the outer gas flow is to maintain the plasma and to cool the outer tube of the torch. The outer gas is commonly known as the plasma gas.

A plasma is a gas in which there is a significant population of ions and free electrons. An inductively coupled plasma is sustained by the interaction of the plasma with a high-frequency electromagnetic field produced by a water cooled or gas cooled induction coil with two to five turns around the top of the torch. The coil is connected to a radiofrequency power supply.

The plasma torch is positioned within the induction coil as shown in Figure 2. The high frequency electric current flowing in the induction coil generates an oscillating electromagnetic field. In the open end of the torch the lines of magnetic force from this field are aligned with the axis of the torch. To start the plasma a high voltage spark is passed through the argon as it enters the torch. Electrons from the spark absorb energy from the electromagnetic field and move in circular paths perpendicular to the axis of the torch. The direction of motion reverses at each half cycle of the RF current in the induction coil.

Accelerated electrons collide with atoms, imparting energy to them and thereby heating the gas. In some of these collisions an electron is released from an atom, forming a singly-charged ion. These released electrons are accelerated by the high frequency electromagnetic fields and collide with other atoms, releasing more electrons. The process continues until the rate of recombination of ions and electrons equals the rate of collisional ionization. This results in the very rapid formation of a steady-state plasma having temperatures that may reach 10 000 K in the region of greatest ionization (see Figure 3).

The plasma is thermally isolated from the quartz tube by the gas flows in the torch. The required flows are produced by introducing the outer gas into the torch in a tangential stream that has to spiral through the narrow gap between the outer and intermediate tubes of the torch. The resulting gas flows keep the plasma stably located near the exit of the torch as shown in Figure 2.

Sample aerosol droplets entering the plasma are desolvated, evaporated and the constituent atoms are ionized.

The torch is located in a separate metal compartment. This compartment is connected to an exhaust system to remove heat and harmful gases. The metal of the compartment protects users and the instrument electronics from the RF radiation, and from the ultra-violet radiation emitted by the plasma. A window of darkened glass to protect the observer's eyes from the intense visible, ultra-violet and infra-red radiation emitted by the plasma allows visual observation of the plasma.

'Cold' or 'cool' plasma conditions, characterized by relatively low plasma power and high inner gas flow rate, may be used to reduce the levels of argon-based ions (Clause 3.2) that interfere with the determination of elements such as potassium, calcium and iron. For cold plasma conditions to be effective, means have to be in place to reduce or eliminate any RF discharge between the plasma and the mass spectrometer interface. Irrespective of the means adopted to overcome RF discharge between the plasma and the mass spectrometer interface, the manufacturer's instructions for establishing cold plasma conditions should be followed.

2.4 GAS AND GAS CONTROL

Argon is used as the inner, intermediate and the outer gas. The purity of the argon should comply with the instrument manufacturer's recommendations. Controlled amounts of oxygen may be added to the intermediate gas to avoid carbon build up on the sampling cone when analysing solutions made up in organic solvents. Excessive addition of oxygen may result in degradation of the sampling cone (see Clause 2.6). Mixtures of argon and hydrogen or nitrogen may improve the sensitivity for certain elements and/or reduce the formation of interfering polyatomic ions (Clause 3.2).

The gas flow rates should be stable, particularly the inner gas. Mass-flow controllers, which keep the mass flow rate of a gas constant and almost independent of temperature and initial pressure, may be used.

2.5 GENERATOR

The RF generator delivers an alternating current that sustains the plasma. This current has a frequency of 27 or 40 MHz and a power between 0.6 and 2 kW. Two types of generator are available, crystal controlled and free oscillating.

The two types of generators differ in how they handle the problem of transferring a constant level of RF power into the plasma when the impedance of the plasma changes as different samples are introduced. In a crystal-controlled generator, the frequency of the RF power is kept constant. The power is coupled into the plasma with the aid of an impedance-matching network. This is adjusted automatically so that the power transferred to the plasma remains constant even when the impedance of the plasma changes.

Free-oscillating, also called free running, generators keep the power constant by allowing the frequency of the RF power to change in response to changes in the plasma impedance.

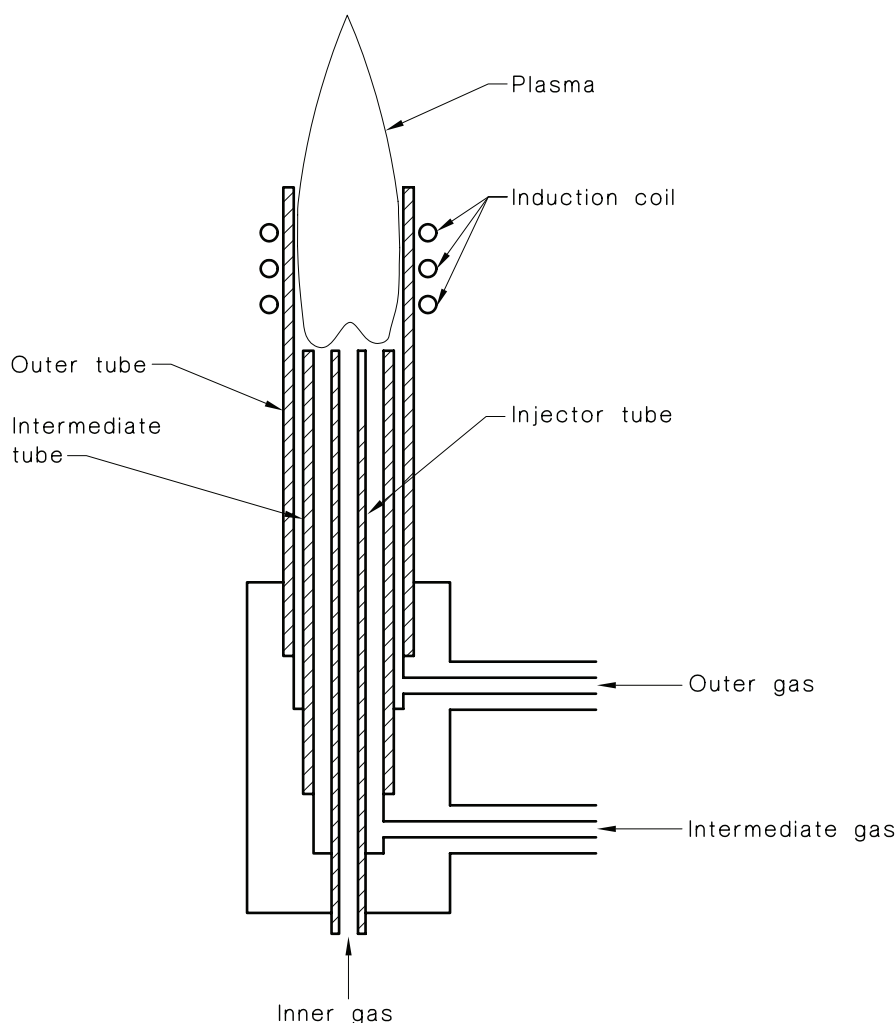


FIGURE 2 THE INDUCTIVELY COUPLED PLASMA TORCH

2.6 TRANSFER OF THE IONS TO THE MASS SPECTROMETER

Ions are transferred from the plasma to the mass spectrometer (Clause 2.7) through the interface. The interface consists of the sampling cone and skimmer cone separated by an evacuated region, called the expansion chamber. During operation, the pressure in the expansion chamber is maintained in the range 10^2 to 10^3 Pa. At the centre of each cone is an orifice with a diameter in the range 0.3 to 1.3 mm, the orifice of the skimmer cone usually being smaller than that of the sampling cone. The cones may be made of nickel, platinum or other appropriate metal.

The plasma is sampled through the orifice of the sampling cone into the expansion chamber, where a supersonic jet is formed. The central part of this jet flows through the orifice of the skimmer cone into the vacuum chamber that houses the ion optics.

Less than 1% of the gas sampled from the plasma is transmitted to the ion optics.

Platinum or platinum-tipped cones are preferred for the determination of nickel at low concentrations and when oxygen is added for oxidation of organic constituents. These cones are more resistant to chemical attack and therefore provide a longer service life.

A deposit of material from the measurement solutions may form around the orifice of each cone and can influence the analysis. See Clauses 3.2.1, 4.2 and 4.6.

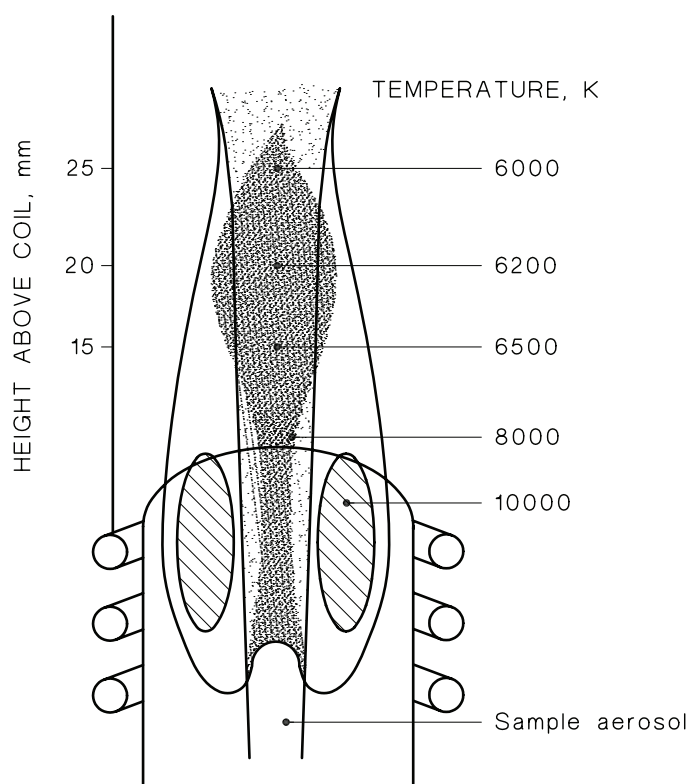


FIGURE 3 SCHEMATIC REPRESENTATION OF AN INDUCTIVELY COUPLED PLASMA

2.7 THE MASS SPECTROMETER

2.7.1 General

The mass spectrometer consists of an ion optics system, an analyser and a detector. In the ion optics system, the ions are extracted from the plasma and transported to the mass analyser in the form of an ion beam with parameters required for the best performance of the particular mass analyser. In the mass analyser the ions are separated according to their mass-to-charge ratio (m/z).

2.7.2 Ion optics system

The ion optics system can consist of one or more components for directing and focussing ions. Electrical potentials on the ion optics components result in the formation of a beam of ions directed towards the entrance of the mass analyser. The unwanted neutral particles are removed by the vacuum pump. (See Clause 4.3.6.)

As well as ions and neutral particles, photons emitted by the plasma enter the ion optics system. Arrangements are made in the design and construction of the mass spectrometer to minimize the number of neutral particles and photons entering the mass analyser. Neutrals or photons hitting the detector would cause an increase in the background noise. Several different arrangements are used in commercial ICP-MS instruments.

2.7.3 Mass analysers

2.7.3.1 General

Several types of mass analysers are used in ICP-MS analysis including quadrupole, magnetic sector and time-of-flight.

2.7.3.2 *Quadrupole ICP-MS*

A quadrupole mass analyser consists of four, round or hyperbolic, parallel metal rods about 20 cm in length to which direct current (DC) and RF potentials are applied. This assembly is housed in a continuously evacuated compartment. The ions are introduced to the central axis, at the beginning of the rods. The ratio of RF to DC is kept constant as the amplitude of the RF is changed. At a specific combination of DC-potential and RF-amplitude, only ions with values of m/z within a specific narrow range have a stable trajectory through the space between the opposite ends of the rods. Ions with lower or higher m/z values hit the rods and are neutralized. Thus the quadrupole acts as a mass filter.

An ICP-MS quadrupole mass analyser resolves at approximately unit mass. The resolution is usually characterized by the peak width at 10% of the peak height. This is typically set at 0.7 u. See also Clause 4.3.4.

An important quality characteristic of a quadrupole mass analyser is the abundance sensitivity.

If a peak is present at $m/z = M$, and no peak is present at $M-1$ or $M+1$, the abundance sensitivity is then defined as the ratio of the net intensity at M to the net intensity at $M-1$ or $M+1$. The abundance sensitivity is an indication of the ability to measure a small peak next to a major peak. Abundance sensitivity values of 10^6 for the $M-1$ mass and 10^8 for $M+1$ mass may be obtained, although values of, respectively 10^4 and 10^6 are more common in routine analysis. Sometimes the abundance sensitivity is presented inversely as the ratio of the net intensity at $M+1$ or $M-1$ to that at M .

2.7.3.3 *Magnetic sector ICP-MS*

One limitation of a quadrupole mass spectrometer is that the resolution is not sufficient to separate ions having the same nominal m/z ratio. This means that interferences can be caused by polyatomic and doubly charged ions (see Clause 3.2).

Many of the interferences experienced in quadrupole systems are avoided by using a high-resolution mass spectrometer with a magnet and an electrostatic analyser (ESA). The ions are accelerated by a potential of 5 to 8 kV and separated by appropriate magnetic and electric fields. Depending on the type of instrument, the ESA is located either in front of or behind the magnet. Ions from the interface are focussed by ion lenses onto a slit in front of the spectrometer and are then focussed by the magnet and ESA onto a second slit in front of the detector. Ions are focussed both with respect to direction of movement and energy at the entrance slit (double focussing). The resolution can be changed by changing the slit widths. This can be performed with continuously adjustable slits or by using slits with fixed widths. The resolution that may be obtained is 10 000 to 30 000, depending on the type of instrument.

Resolution is defined here as the average mass divided by the mass difference of two adjacent peaks of equal height that are separated with a valley between them at 10% of the peak heights (10% valley definition: $m/\Delta m$; m = average mass and Δm = difference of the two masses); Δm is equivalent to the peak width of one peak at 5% of the peak height.

The non-spectral background of mass spectrometers of this type is lower than 0.1 cps. The sensitivity is higher than that found with quadrupole instruments operated at similar resolution. The higher sensitivity is a consequence of the high voltage used to collect and accelerate ions and of the lower pressure in the spectrometer. These gains in sensitivity are lost at higher resolution because of the reduction in ion transmittance. For example, at a resolution of 10 000, where As^+ is separated from ArCl^+ , the ion transmission is reduced to 1% of that found in the low resolution mode and the sensitivity is correspondingly reduced.

Scanning over the full mass range is slower than with a quadrupole instrument because of the slow response of the magnet, although with newer and stronger power supplies, the scan time can be reduced to about 0.2 s. Electrostatic scanning over a limited mass range is fast.

2.7.3.4 *Time-of-flight ICP-MS*

In a time-of-flight (TOF) mass spectrometer all positive ions in a defined section of the ion beam, simultaneously start movement towards the detector when a high voltage acceleration pulse is applied. During the flight to the detector, ions form compact packets according to their mass-to-charge ratio. All ions are registered by the same detector but at different intervals after the application of the acceleration pulse. The usual technique to record a mass-related measurement is to digitize and save values of the output current with very short time steps. Every time step from the beginning of the acceleration pulse relates to a different mass interval. The process repeats after the packet of the heaviest mass ions from the previous cycle has reached the detector.

The ion current values from all cycles are then summed in parallel in time bins. Ion counts can be accumulated in time bins instead of ion current values. The measurement of each mass peak is taken as a sum of the counts in time bins corresponding to each mass interval Δm .

As TOF-MS works in cycles, it is a non-continuous ion sampling technique. The slightly lower sensitivity in count rate per mass compared to quadrupoles is compensated by the effectively simultaneous measurement of all masses. If 10 masses are to be measured, the accumulation of the same number of counts can take approximately the same time as for a quadrupole mass spectrometer.

An advantage of TOF-MS is the effectively simultaneous registration of all isotopes. This helps to negate the effect of plasma density variation, when isotopic ratios are measured and allows rapid multi-element measurements of the short-duration transient signals produced by ETV and laser ablation systems.

2.7.4 The detector

The detection system includes an electron multiplier detector with a first electrode, at a large negative potential, that releases electrons when ions collide with the electrode.

This electrode is sometimes called the ‘conversion dynode’ or ‘cathode’, but more commonly it is simply referred to as the ‘first dynode’. The first dynode is followed by a chain of dynodes in which each electrode is at a less negative potential than the one immediately preceding it. Each dynode releases more than one electron in response to the impact of an electron from the preceding dynode, so that the impact of a single ion on the first dynode results in a pulse of approximately 10^8 electrons from the last one. A fast pre-amplifier/discriminator arrangement processes the output of the electron multiplier to generate a signal proportional to the rate of arrival of ions at the first dynode.

The upper counting rate of this system may be, for example, 2 to 4×10^6 pulses per second (counts per second, cps), and is determined by two factors. Firstly, there is a maximum output current that can be sustained by the detector. The second limiting factor is the response time, or dead time, of the detector electronics, the time during which a new pulse cannot be detected. If the time interval between the arrival at the detector of two ions is shorter than the dead time, the second ion is not detected. Both factors cause a relative decrease in count rate at higher rates. For modern instrumentation the dead time is about 10 to 20 nanoseconds (ns). The ICP-MS software should include a mathematical routine to correct for the loss of linearity caused by the dead time.

A commonly used equation is:

$$N' = \frac{N}{1 - ND} \quad \dots 2.7.4$$

where

N' = corrected count rate

N = observed count rate

D = dead time, in nanoseconds

The inherent noise produced by this type of detector is very low, usually 0.1 counts per second or less and is of minor importance for ICP-MS measurements. In practice, the observed background may be 3 to 30 cps. The higher value is probably caused by energetic neutrals and/or photons that reach the detector despite measures taken to prevent this (see Clause 2.7.2).

Several methods are applied to increase the upper limit of the dynamic range of the measurement. This can be achieved by having fewer ions reach the detector by defocusing the ion beam. Other methods lower the multiplication factor of the detector by decreasing the potential applied to it, or by collecting only a fraction of the electrons generated. When one of the last two methods is applied, the resulting current is measured in an analogue manner. This is called the analogue mode, in contrast to the pulse counting mode. Modern instrumentation can switch automatically to analogue mode when too high a signal is detected. This prevents damage to the detector.

Another recent approach to increasing the dynamic range of a pulse-counting electron multiplier is to vary its sensitivity. When the detected ion intensity reaches a specified level, the voltage applied to one of the dynodes is changed to a pre-selected value that matches sensitivity to the ion intensity.

The lifetime of the detector is finite and depends on usage. The sensitivity of the detector slowly decreases with use and the applied voltage needs to be increased to restore the sensitivity.

Other detectors that are sometimes used in ICP-MS are:

- (a) Electron multipliers having a continuous dynode.
- (b) Daly detectors (electrons released when ions strike a conversion dynode are focused on a fluorescent screen causing it to emit light, which is detected by a photomultiplier).
- (c) For some applications, the ion intensity is high enough that a Faraday cup (a metal electrode without amplification) may be applied.

2.8 SIGNAL PROCESSING AND INSTRUMENT CONTROL

In ICP-MS, measurements are made at discrete points of the mass range. The full mass range from Li to U is divided into several thousand of these points. In a quadrupole ICP-MS, three modes of operation are used:

- (a) *Peak jump mode*

In peak jump mode only selected peaks are measured and the measurement is made at the top of the peak. For example, with 1 point per mass selected, and 10 peaks to be measured, only 10 discrete measurements would be required. The advantage of peak jump mode is the high signal to noise ratio resulting from using all the measurement time to measure only the masses of interest but no extra information is gained and interferences may go unnoticed.

The number of points per mass measured in the peak-jump mode is normally in the range 1 to 3 and this mode gives the highest signal-to-noise ratio. Some time is necessary for the quadrupole to stabilize at the next mass before a new reading is taken. The 'quadrupole settling time' increases the total measurement time above the sum of the measurement times at the individual masses. The high sampling frequency, by providing almost simultaneous measurements of the analyte and the reference element, (see Clause 5.5) reduces the effects of low-frequency noise caused by the nebulizer, spray chamber and plasma resulting in improved precision (lower relative standard deviation) of the intensity ratio.

(b) *Scan mode*

In scan mode, all the points between the starting mass and the end mass are measured. Regions of no interest can be omitted. If the software is selected to measure 20 points per mass and the scan region is 10 mass units wide, that represents 200 discrete measurements. Scan mode acquires information across the entire scan region but the signal to noise ratio is lower because much of the time is spent measuring off-peak masses.

The scan mode can be used to obtain information about isotopic patterns of elements or polyatomic ions for identification purposes. The time for one scan over the full mass range may be below 0.1 s.

(c) *Single ion monitoring mode*

Measurements can also be made at only one mass. This can be useful when transient signals have to be measured (e.g. coupling of a chromatography instrument to ICP-MS).

In magnetic sector ICP-MS, a discrete point is defined by the width of the slits. Time-of-flight ICP-MS registers the complete mass spectrum by default. Normally, the spectrum is accumulated during chosen time periods. The minimal time period corresponds to one cycle of the mass spectrometer.

The integration time is determined by the number of sweeps, dwell time and the number of points measured per mass. The values of these parameters may be set by the user.

SECTION 3 INTERFERENCES BY CONCOMITANTS

3.1 GENERAL

The presence of concomitants in the sample can cause interferences, i.e. systematic errors in the measurement.

Interferences are classified into spectral and non-spectral interferences. Spectral interferences have an additive influence on the analytical measurement when not separated from the mass peak of the analyte. They are caused by isobaric ions or polyatomic ions having the same m/z ratio as the analyte ions. Non-spectral interferences, usually called matrix effects, have enhancement or suppression effects depending on the elements and are due to the composition of the solution to be measured.

3.2 SPECTRAL INTERFERENCES

3.2.1 General

Spectral interferences can be caused by:

- (a) An isotope of another element having the same measured mass as the analyte isotope (isobaric interference), e.g. $^{58}\text{Fe}^+$ (interference) and $^{58}\text{Ni}^+$ (analyte).
- (b) Polyatomic ions, also called molecular ions, originating from the plasma gas (argon), the sample solution (oxygen) or the matrix components (e.g. chloride). Examples are $^{40}\text{Ar}^{35}\text{Cl}^+$ (interference on $^{75}\text{As}^+$) and $^{44}\text{Ca}^{16}\text{O}^+$ (interference on $^{60}\text{Ni}^+$).
- (c) Doubly charged ions such as Ba^{2+} (interference on $^{65}\text{Cu}^+$, $^{66}\text{Zn}^+$, $^{67}\text{Zn}^+$ and $^{68}\text{Zn}^+$).

Polyatomic ions can be formed in the plasma or in the interface region, especially in the cooler boundary layers of the sampling and skimmer cones. Therefore, the condition of the cones can be of importance in the formation of polyatomic ions (Clause 2.6).

Oxide interferences are usually characterized by monitoring the CeO^+/Ce^+ ratio while aspirating a cerium solution. The level of doubly charged ions is usually characterized via $\text{Ce}^{2+}/\text{Ce}^+$ or $\text{Ba}^{2+}/\text{Ba}^+$. These ratios should be as low as possible (typically 3% or lower). The doubly charged ion ratio for Ba is about twice the ratio for Ce, due to the lower second ionization potential (IP2) for Ba (10.0 eV compared to 10.85 eV for Ce). See also Clause 4.4.

3.2.2 Possible remedies for polyatomic ion interference

Possible remedies for reducing polyatomic ion interferences are as follows:

- (a) Decreasing the water load of the plasma, thus reducing oxide interferences. This can be achieved by:
 - (i) Cooling the spray chamber to 2°C–5°C.
 - (ii) Desolvating the aerosol using a condenser and/or a semi-permeable membrane.
 - (iii) Utilizing an alternative sample introduction system (see Clause 2.2.5) e.g. ETV, laser ablation, micro-concentric nebulizer.
- (b) Decreasing the concentration of potentially interfering elements, e.g. by avoiding the use of hydrochloric acid or by the use of a membrane desolvator, which can reduce the level of chloride interferences as the membrane is permeable to hydrochloric acid.

In this case, nitric acid should be used where possible for acidifying the solutions or for sample digestions.

- (c) Optimizing the measurement conditions to maximize the ratio of analyte intensity to the intensity of the interferent. Optimization parameters include plasma power, inner gas flow rate, sample introduction rate, sampling depth (distance between torch and tip of sampling cone), etc. (Clause 5.3).
- (d) Adding gases such as H₂, N₂, CH₄, etc. to the inner gas, intermediate gas, outer gas, or to all gases, giving improvement in specific cases.
- (e) Adding alcohols, e.g. ethanol, to the sample for the reduction of ArCl⁺ interference.
- (f) Using spectral fitting approaches: modelling of the spectrum with inputs such as the isotopic patterns of the analytes and of all relevant interfering species. However, an unambiguous fit may be difficult to obtain in the 50 to 90 mass region due to the possible presence of an excessive number of spectral components. This technique may be useful in other mass regions.
- (g) Using cold plasma conditions (Clause 2.3) for specific situations (see also Clauses 5.3.4 and 5.3.5).
- (h) Using correction equations. See Clause 3.2.3.
- (i) Using a collision cell or a reaction cell.

This approach to reducing polyatomic ion interferences uses a collision or reaction cell with a quadrupole, hexapole or octapole ion guide. The cell is flushed with a reaction or buffer gas. Collisions of plasma ions with molecules of this gas result in change of the composition of the ion beam in a predictable way. Polyatomic ions and ions with high electron affinity may be neutralized and or removed from the ion stream (see Clause 3.2). Gases that have been used include H₂, He, Xe, N₂, O₂, NH₃ and CH₄. These gases differ in their effectiveness, depending on the specific polyatomic ion interferences of interest.

- (j) Using magnetic sector ICP-MS in high resolution mode. (Clause 2.7.3.3).

3.2.3 Correction equations

The use of correction equations is based on the assumption that the number of the molecular (and doubly charged) ions formed is a fixed fraction of the number of parent ions present in the plasma, independent of variations of the sample composition and small variations of the plasma conditions.

For example, tungsten oxide ions (WO⁺) interfere with mercury determination. The number of WO⁺ ions is a fixed fraction of the number of W⁺ ions for a particular set of tuning conditions. After measuring the blank corrected intensity of WO⁺ (at mass 202) and of W⁺ (at mass 186) of a W standard solution (e.g. 100 µg/L), an interference factor f can be calculated from the following equation:

$$f = \frac{WO^+ \text{ net}}{W^+ \text{ net}} \quad \dots 3.2.3(1)$$

For an unknown sample, the WO⁺ interference can be calculated by measuring the ¹⁸⁶W⁺ intensity and multiplying the value by f . To obtain the corrected intensity for ²⁰²Hg⁺, the calculated WO⁺ intensity is subtracted from the gross intensity at mass 202. The following equation applies:

$$I_c(^{202}\text{Hg}^+) = I(^{202}\text{Hg}^+) - f \times I(^{186}\text{W}^+) \quad \dots 3.2.3(2)$$

where

- I = net intensity at the stipulated mass
- I_c = corrected net intensity at the stipulated mass
- f = interference correction factor