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**General rules for high frequency
plasma mass spectrometry**

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Foreword

This translation has been made based on the original Japanese Industrial Standard revised by the Minister of Economy, Trade and Industry through deliberations at the Japanese Industrial Standards Committee as the result of proposal for revision of Japanese Industrial Standard submitted by Japan Analytical Instruments Manufacturers' Association (JAIMA)/Japanese Standards Association (JSA) with the draft being attached, based on the provision of Article 12 Clause 1 of the Industrial Standardization Law applicable to the case of revision by the provision of Article 14.

Consequently **JIS K 0133**:2000 is replaced with this Standard.

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General rules for high frequency plasma mass spectrometry

1 Scope

This Japanese Industrial Standard specifies the general rules for the use of a high frequency plasma mass spectrometer in qualitative and quantitative analyses of the target elements and the isotope ratio measurement.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this Standard. The most recent editions of the standards (including amendments) indicated below shall be applied.

JIS B 9920 *Classification of air cleanliness for cleanrooms*

JIS K 0116 *General rules for atomic emission spectrometry*

JIS K 0211 *Technical terms for analytical chemistry (General part)*

JIS K 0215 *Technical terms for analytical chemistry (analytical instrument part)*

JIS K 0553 *Testing methods for determination of metallic elements in highly purified water*

JIS K 0557 *Water used for industrial water and wastewater analysis*

JIS Z 8402-1 *Accuracy (trueness and precision) of measurement methods and results—Part 1: General principles and definitions*

JIS Z 8402-2 *Accuracy (trueness and precision) of measurement methods and results—Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

3 Terms and definitions

For the purposes of this Standard, the terms and definitions given in **JIS K 0116**, **JIS K 0211**, **JIS K 0215**, **JIS Z 8402-1** and **JIS Z 8402-2** and the following apply.

3.1 high frequency plasma

inductively coupled plasma (ICP), generated by induction of high radio frequency power, and microwave-induced plasma (MIP), generated by induction of high microwave frequency power

3.2 high frequency plasma mass spectrometer

an analyzer of elements and isotopes which measures the number of ions at mass-to-charge ratio (m/z) of target elements by ionizing the target elements in samples with high frequency plasma and injecting the resultant ions into a mass spectrometer

3.3 ionization source

a part which consists of a high frequency plasma of high energy source to ionize the target elements and an electric power supply for high frequency plasma

3.4 interface

a part which consists of a sampling cone, a skimmer cone, etc. that is exhausted differentially in order to sufficiently inject ions generated by high frequency plasma at atmospheric pressure into a mass spectrometer at high vacuum

3.5 mass separator

a part which makes ions go through an electric field and/or a magnetic field in order to separate them according to their mass-to-charge ratio (m/z)

3.6 spectral interference

interference caused by overlapped mass spectrum of atoms or multi-atomic ions whose mass-to-charge ratio (m/z) is close to that of the target elements

3.7 non-spectral interferences

any other interferences than spectral interference, which is encountered in measurement using a high frequency plasma mass spectrometer

3.8 memory effect

overlap between the signals of target elements in present samples and the signals of elements that were contained in previous samples or calibration standards which were remained in a high frequency plasma mass spectrometer or its accessories

3.9 resolution

the capacity of limitation of a mass spectrometer to resolve two adjacent spectral lines

3.10 instrument limit of detection, ILOD

the concentration equivalent to a signal that is equal to three times the standard deviation obtained by a series of ten replicate measurements of a calibration blank

3.11 method limit of detection, MLOD

the concentration equivalent to a signal that is equal to three times the standard deviation obtained by a series of ten replicate measurements of a laboratory reagent blank

3.12 limit of quantification, LOQ

the concentration equivalent to a signal that is equal to 10 times the standard deviation obtained by a series of ten replicate measurements of a laboratory reagent blank

When the analytical value is obtained by subtracting the laboratory reagent blank, it is the concentration equivalent to a signal that is equal to $14.1 (= \sqrt{2} \times 10)$ times the standard deviation

3.13 abundance sensitivity

a ratio of the degree of overlap of mass spectrum against the adjacent mass number to its peak height

3.14 calibration standard

solution containing target elements of known concentration, which is used to draw a working curve

3.15 calibration blank

solution in which concentration of target elements is zero and whose composition is the same as that of calibration standard

3.16 internal standard element

the element to be added to the calibration standard, calibration blank, and test sample solution in the same amount for each, in order to calibrate the non-spectral interference and time-dependent fluctuation of sensitivity of a high frequency plasma mass spectrometer

3.17 quality control

procedure to assure that the analysis is performed correctly according to the specified criteria in order to ensure the reliability of data

3.18 quality control solution

solution containing target elements of known concentration, which is used to confirm the stability and effectiveness of calibration standard, prepared by dilution and/or mixing, and for initial and periodical inspections of performance of instruments

3.19 laboratory reagent blank

signals given by water or matrix not containing target elements

Such water or matrix that has been processed in the same way as samples, including contact with glass tools and instruments used during analysis as well as addition of solvent, reagent, and internal reagent blank. The purpose is to examine whether or not contamination is caused by laboratory environment of target elements or interference elements, reagents and tools.

4 Outline

In high frequency plasma mass spectrometry, liquid samples are nebulized by the nebulizer at the sample injector, transported by carrier gas, and injected into high frequency plasma. Gas samples are directly mixed with carrier gas and injected. Solid samples are either liquefied by acidification and processed in the same way as liquid samples, or crushed into particles by laser ablation etc. and injected into high frequency plasma. The injected samples are heated and dissolved in plasma under atmospheric pressure. Target elements in samples are ionized. After going through the vacuum-exhausted interface, the ionized elements are converged by an ion lens optical system, injected into a mass separator, and separated according to their mass-to-charge ratio (m/z). Then, they enter a detector and are output as an electric signal. The output signals are data-processed in terms of mass spectrum display, preparation of working curve, determination of target elements etc., being displayed on a display apparatus, a printer, etc. as analytical results.

5 Instrument

5.1 Construction of instrument

A high frequency plasma mass spectrometer consists of a sample injector, ionizer, interface, ion lens, mass separator, detector, gas controller, vacuum exhaust, system controller, and a data output unit. Figure 1 shows an example of basic construction of the instrument.

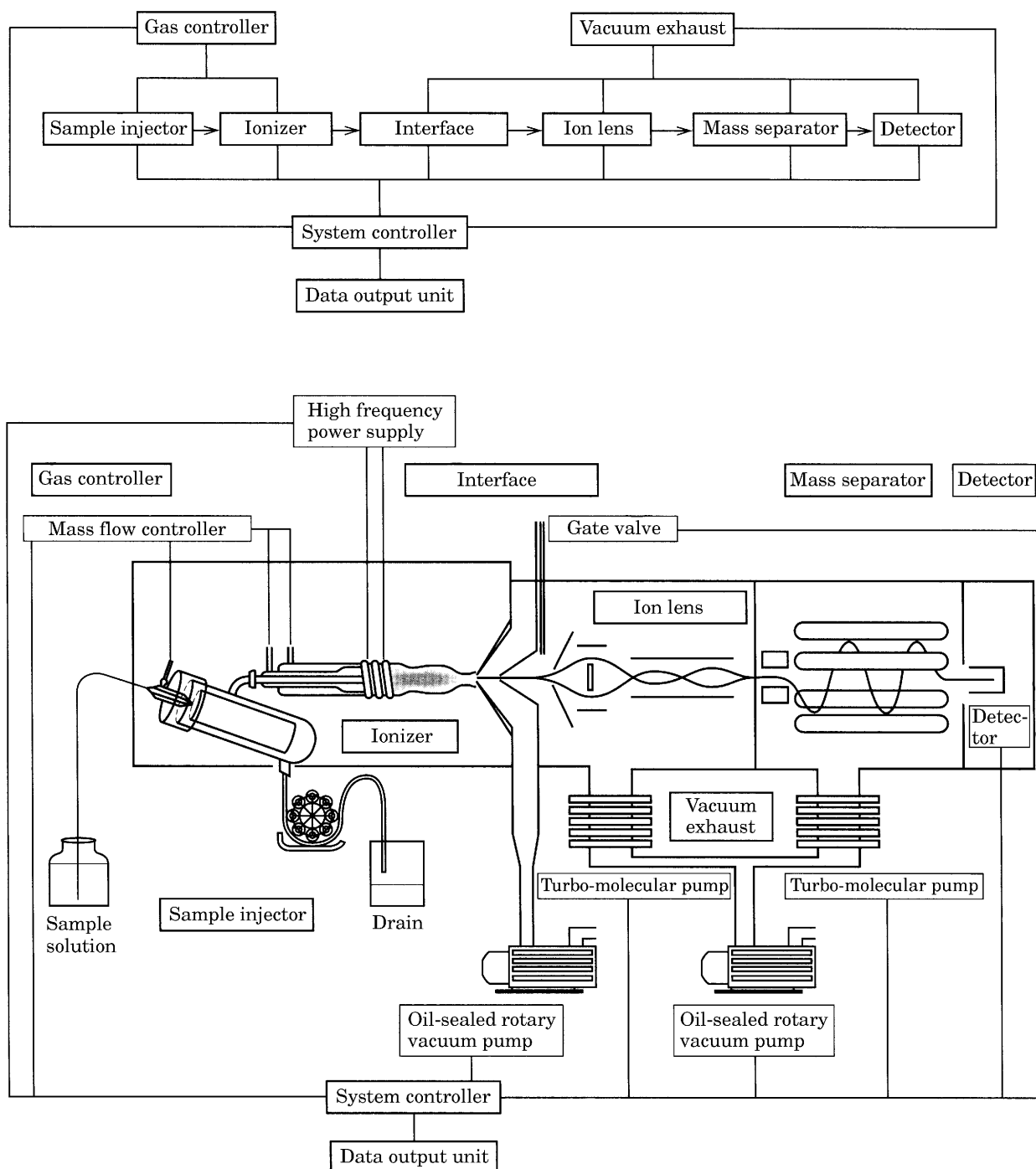
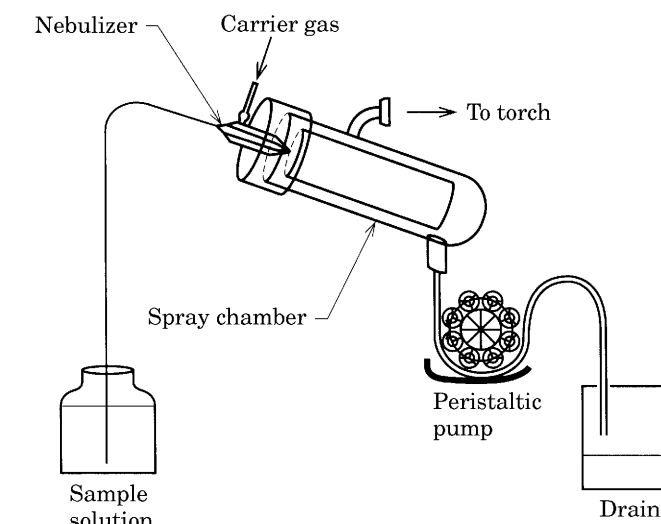


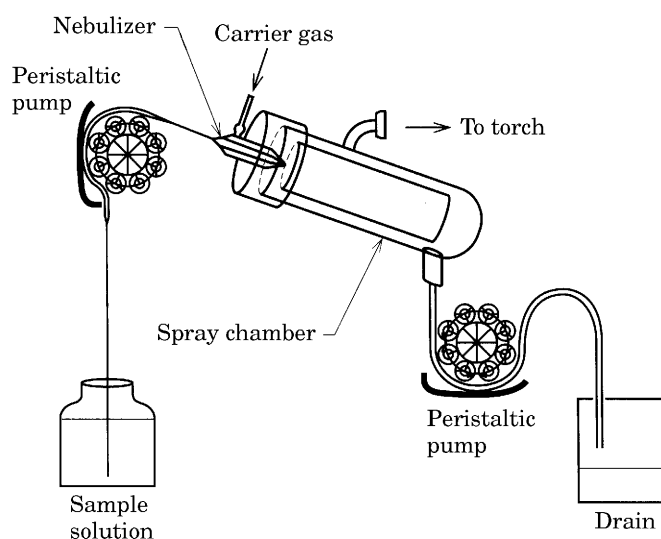
Figure 1 Basic construction of instrument (example)

5.1.1 Sample injector

This part injects samples into high frequency plasma. For injection of liquid samples, it consists of a nebulizer and a spray chamber. A peristaltic pump may be used together. Figure 2 shows an example of a sample injector. It is necessary to accurately control the flow rate and pressure of carrier gas used to inject the samples.



a) Natural suction of sample solution



b) Injection of sample solution by a feeding pump

Figure 2 Sample injector (example)

- a) **Feeding pump** A feeding pump is used for introducing the sample in a constant flow rate into a nebulizer which is structurally incapable of natural suction. In the case of the nebulizer capable of natural suction, the pump is used for the special purpose of limiting the influence of viscosity. A peristaltic pump is most typically used for this purpose, but a syringe pump or a gas pressure can be used.

- b) **Nebulizer** The nebulizer is the apparatus by which the liquid sample is changed to mist by the high pressure and high speed of gas flow. There are those nebulizers capable of natural suction or those that require a feeding pump, the former typically being of a coaxial type or a cross flow type, and the latter, a V groove type or parallel type. Those of coaxial type are most commonly made of glass or quartz, but they can be made of resin such as PFA (perfluoro-alkoxy ethylene tetrafluoro-ethylene copolymer). Cross flow type nozzles are often made of glass, quartz, platinum or sapphire. V groove type and parallel type nozzles made of synthetic resin are commonly used. The introduction amount of liquid sample is approximately 20 μ l to 2 ml. When the introduction amount is larger, the sensitivity becomes higher. However, since mists of the liquid mutually collide and combine, and are caught in the spray chamber as shown in **c)**, the amount that actually reaches the plasma is not proportional to the amount introduced through the nebulizer. Nebulizers of low flow rate are generally more efficient. An example of a nebulizer is shown in figure 3.

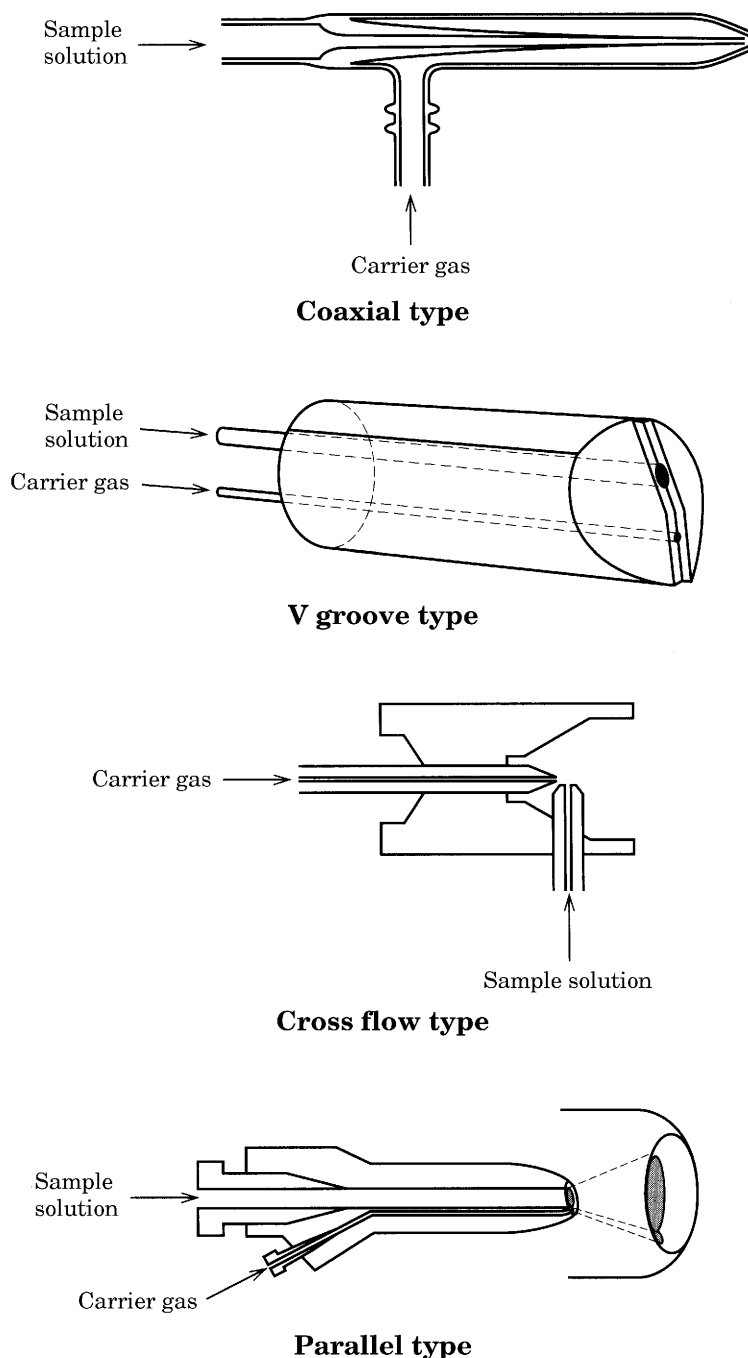
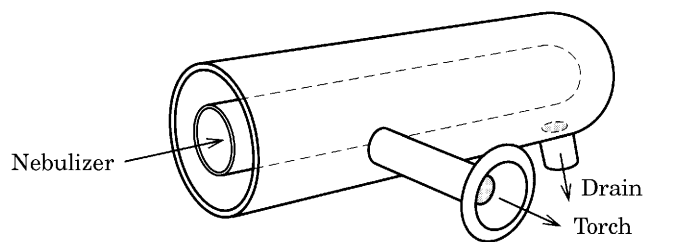
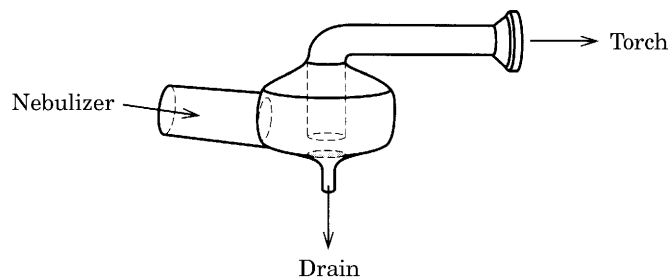


Figure 3 Nebulizers (examples)

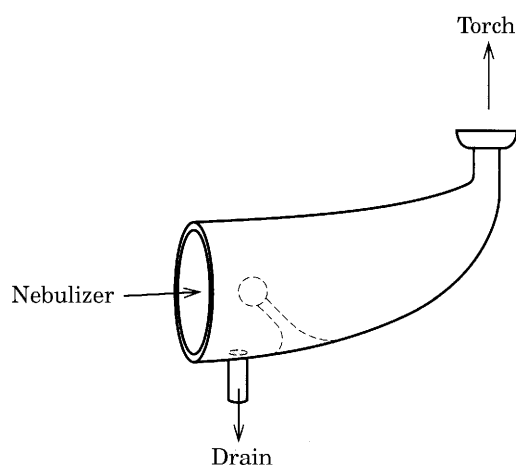
- c) **Spray chamber** Spray chambers are provided for the purpose of allowing only the mists of sufficiently small particle size to be introduced through the nebulizer, preventing mists of large size particles that cannot be decomposed at the plasma. They are available in double tube type, cyclone type, horn type and the like. A typical spray chamber would condense the mists of particles larger than $5\ \mu\text{m}$ to $20\ \mu\text{m}$ on the chamber wall and let any mists smaller than that pass. However, some spray chambers have an impactor to pulverize the large-sized mists. In addition to selecting and transferring the mists, the spray chambers also function as the damper against the fluctuation of the gas flow. Figure 4 shows an example of a spray chamber.



Double tube type



Cyclone type



Horn type

Figure 4 Spray chambers (examples)

5.1.2 Ionizer

The ionizer consists of the ionization source (high frequency plasma) which decomposes the sample to atom and furthermore excites and ionizes it, and the power supply and control circuits to maintain plasma. The high frequency plasma is either an inductively coupled plasma (ICP) or a microwave induce plasma (MIP). The power supply frequency is 27.12 MHz or 40.68 MHz for ICP, and 2.45 GHz for MIP. These frequencies are controlled by a quartz-crystal radiator or self-excited oscillation.

- a) **Inductively coupled plasma (ICP)** ICP is, as shown in figure 5, generated in the torch of quartz enclosed by high frequency induction coil. The torch consists of triple tubes and the central tube (injector) can be made of alumina, sapphire, platinum or others in addition to the most typical quartz. The sample

is introduced through the injector, together with the carrier gas. For the gas generating plasma, argon is generally used. However, nitrogen, helium, oxygen or the gas consisting of the mixture of these gases with argon can be used. The flow rate or the pressure of gas needs to be controlled with precision.

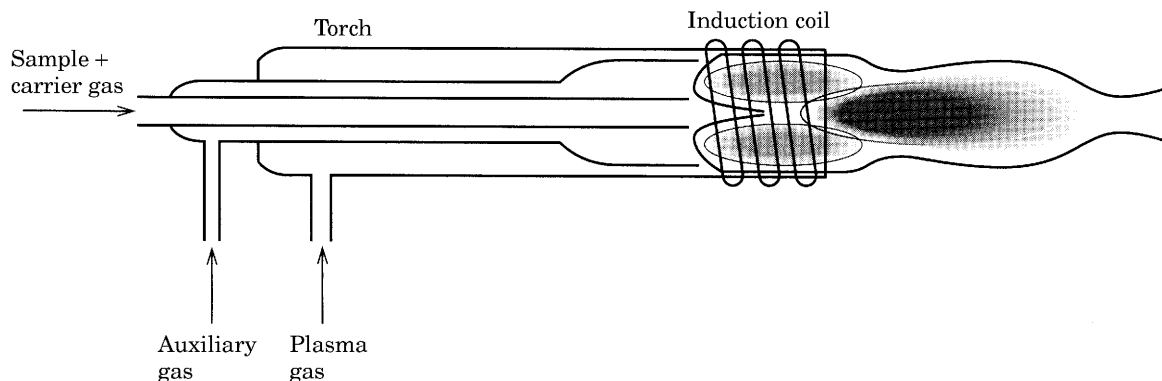


Figure 5 Inductively coupled plasma (example)

- b) **Microwave induced plasma (MIP)** MIP is, as shown in figure 6, generated in a torch equipped with a cavity. The torch generally consists of double tubes, and introduces the sample, together with the carrier gas, from the central tube. For the gas generating plasma, nitrogen is most commonly used. However, mixture gas of nitrogen with argon, helium, or oxygen can be used. The flow rate or the pressure of gas needs to be controlled with precision.

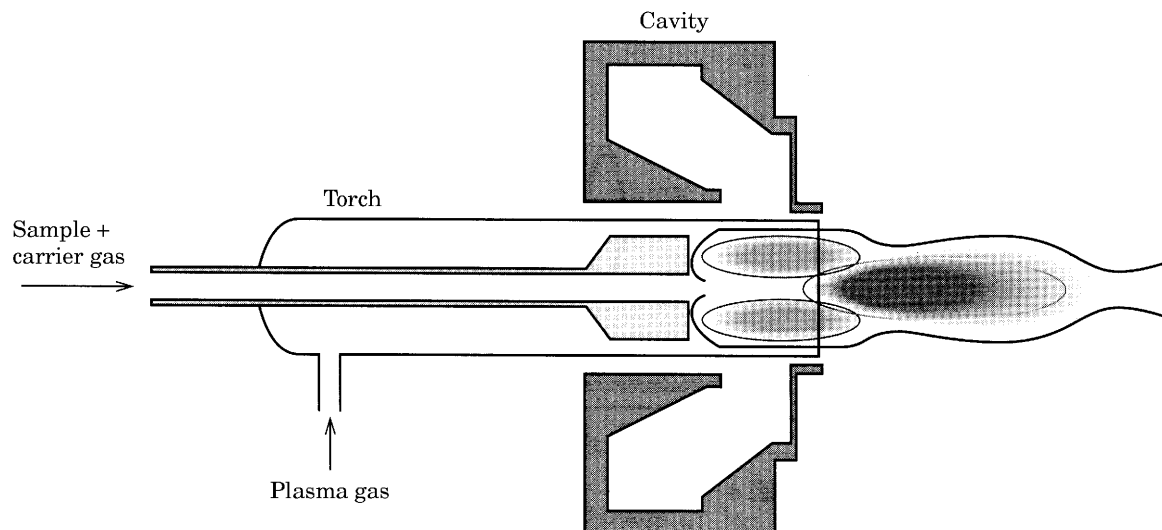


Figure 6 Microwave induced plasma (example)

5.1.3 Interface

The interface constitutes the boundary which connects the plasma under atmospheric pressure to the mass separator under vacuum state, and is the quasi-vacuum region of approximately 200 Pa to 400 Pa, consisting of a sampling cone, skimmer cone and a gate valve. It serves to lead the ion generated in plasma efficiently to the mass separator.

- a) **Sampling cone** The sampling cone is a cone having the orifice of about 1 mm diameter at the tip and is cooled by water or gas. The one made of nickel or copper is generally used. Some sampling cones are made of platinum at the vicinity of the orifice. Platinum-made sampling cones are used for introduction of sulfuric acid, phosphoric acid and organic solvent.
- b) **Skimmer cone** The skimmer cone is a cone having the orifice of about 0.3 mm to 1 mm diameter at the tip. The cone angle is generally smaller than that of the sampling cone. Similarly to the sampling cone, it is typically made of nickel, copper, platinum and the like. The cone angle and the orifice diameter of the skimmer cone, since they greatly influence the sensitivity of the analysis, need to be maintained to be constant.
- c) **Gate valve** The gate valve is the mechanism by which the vacuum condition of mass separation part is maintained when the apparatus is under the suspension condition. While in the suspension condition, the interface is under the atmosphere pressure.

5.1.4 Ion lens part

The ion lens part is the part in which ions are efficiently extracted from plasma and led to the mass separator. It also serves to shut off the neutral particles and the ultraviolet ray so that they are not detected. These particles and photons may cause the background. It consists of one or two extraction electrodes, the apparatus for shutting off particles and photons and a focusing electrode. Some apparatus are without an extraction electrode and have only the focusing electrode, which also serve as the extraction electrode. The shielding apparatus (see figure 7) can be a screen, an axis-shifted ion lens, a 90°-polarized electrode, a 90°-polarized mirror, and oblique ion guide and the like.

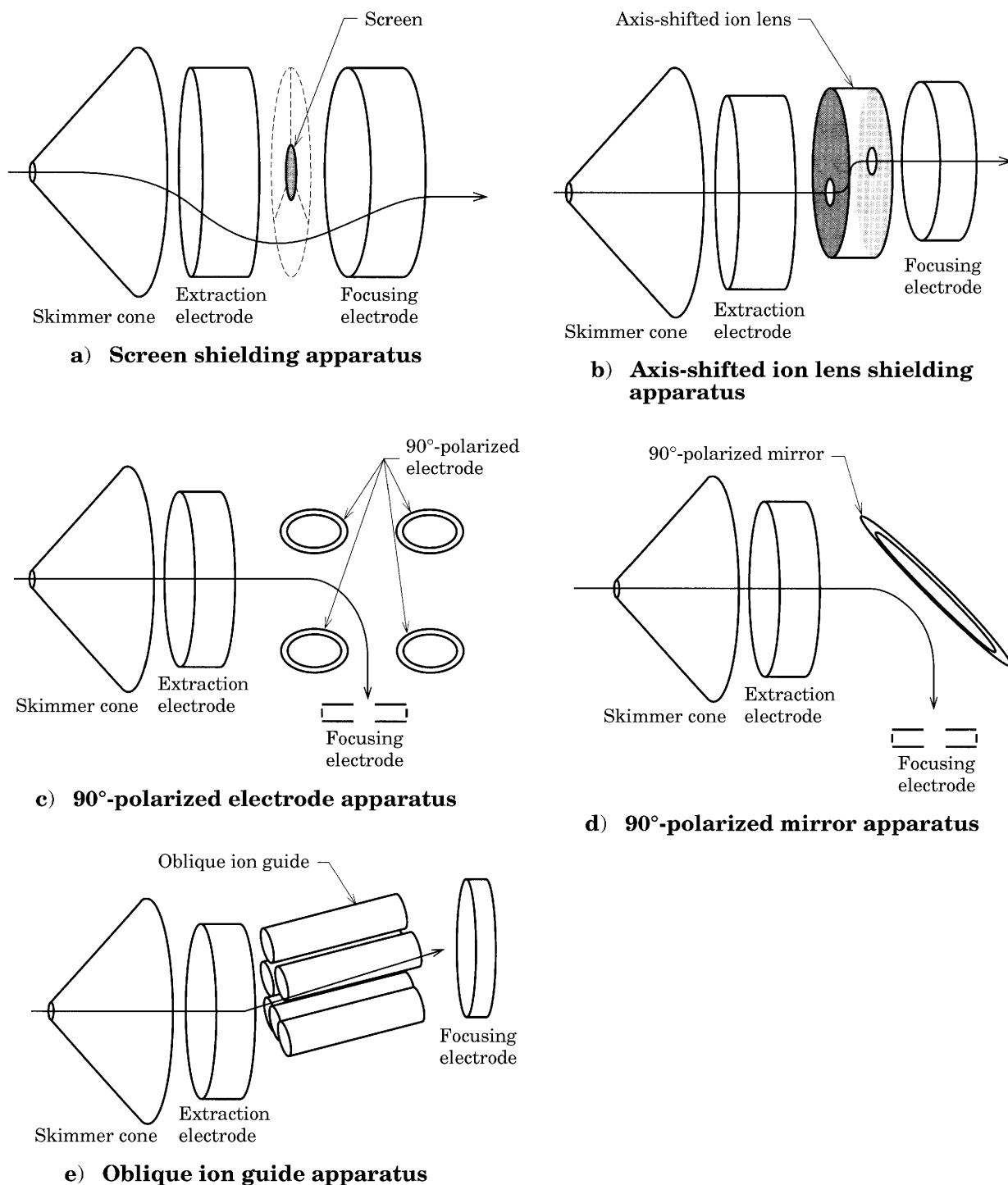


Figure 7 Ion lens part using various shielding apparatus

5.1.5 Mass separator

A mass separator separates ions that have entered from the ion lens. It employs electromagnetic action of electric and magnetic fields on ions in vacuum, and separates ions temporarily and spatially according to each mass. It is available in several types: quadrupole mass spectrometer, magnetic sector type double-focusing mass spectrometer, time-of-flight mass spectrometer, three-dimensional quadrupole mass spectrometer, etc. Typical ones are explained below.

- a) **Quadrupole mass spectrometer** A quadrupole mass spectrometer, by filtering action of passing quadrupole electrodes, mass-separates only ions of target elements. Figure 8 shows a principle of separation. A high frequency electric field is formed by positive and negative direct current voltage (U) and high frequency voltage ($V\cos\omega t$). This field has a hyperbolic surface and is formed within space surrounded by quadrupole electrodes. Ions are forced to oscillate. Ions of target elements are oscillated stably only if they meet the relation of the frequency, voltage, and radius (r) of inscribed circle of high frequency electric field. These ions are moved along the centre of high frequency field. Other ions are forced to oscillate with increasing amplitude and they are removed. As a result, only ions of the target elements can pass the quadrupole electrodes. The mass of passing ions is correlated linearly to high frequency voltage. Accordingly, mass spectrum can be measured by changing the high frequency voltage.

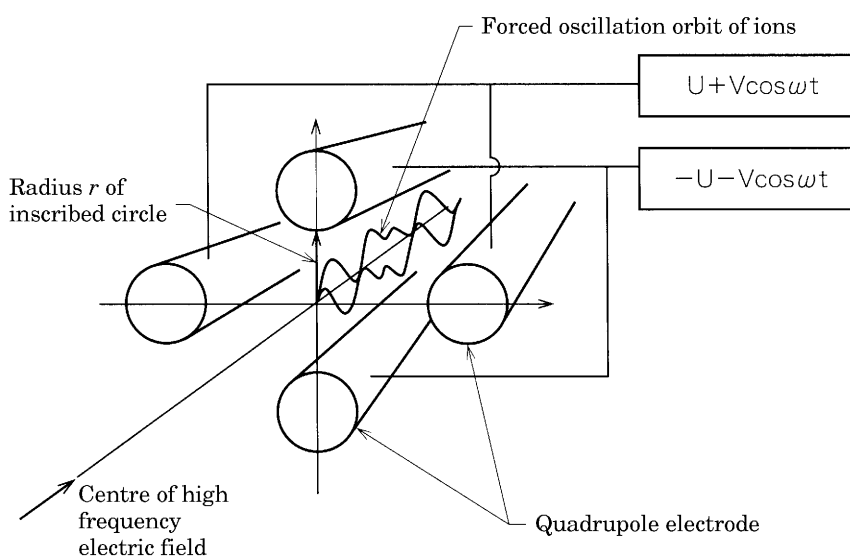


Figure 8 Illustrated separation principle of quadrupole mass spectrometer

- b) **Magnetic field type double-focusing mass spectrometer** The magnetic field type double-focusing mass spectrometer separates ions as corresponding to their mass by using the magnetic field sector and electric field sector. The orbit which ion follows is dependent on the mass and kinetic energy (velocity) of the ion. Accordingly, for the separation of ions corresponding to their mass, the difference of kinetic energies that the ions have makes a problem. In the magnetic field type mass spectrometer, the difference of kinetic energies among ions can be the direct cause of the decrease of mass resolution. Therefore, if a higher mass resolution is to be obtained, selection of energy by electric field is necessary. This type of mass spectrometer, combining the electric field with the magnetic field, is called the magnetic field type double-focusing mass spectrometer, because it is capable of focusing both the extension of the initial direction of ion and the extension of energy. Those arranged in the order of electric field to magnetic field from the ion source is called the positive arrangement type double focus and those arranged in the order of the magnetic field to the electric field is called the reverse arrangement type double focus (figure 9). Both arrangements are available on the market. Generally, for obtaining high resolution the reverse arrangement type is used.

The reverse arrangement type is favoured because it is capable of shortening the distance between the electric field and the ion detector. When the ion collides with the residual gas, the ion loses part of its kinetic energy, and consequently the mass resolution is lowered. By adopting the reverse arrangement, the selection of energy is possible at a position closer to the detector, and the frequency of energy loss is diminished and a higher mass resolution can be obtained. In the magnetic field type mass spectrometer, the mass resolution can be generally adjusted by the width of object slit and image slit. Higher resolution can be obtained by the narrowing of the slit, which, however, would then lead to the decrease of the sensitivity of analysis.

- 1) **Single detector type mass spectrometer** The single detector type mass spectrometer, which has only one detector, measures the analytical target element successively by scanning the mass of ion every time that the ion enters the detector. For the mass scanning, there are the case where the elements of different mass numbers are detected in order by changing the strength of the magnetic field and the case where the mass number of ion is changed by changing the acceleration energy of ion. The former is characteristic in that the transmission efficiency of ion within the mass spectrometer does not fluctuate greatly depending on the mass of ions, because the kinetic energy of ions is not changed. However, its mass scanning velocity is slower than the quadruple mass spectrometer by one place. In the latter system, the high speed of mass scanning and successive detection are possible because the strength of magnetic field is fixed. On the other hand, the corresponding mass number range is about $\pm 30\%$ of the specific mass number, therefore it is required to change the strength of magnetic field several times for the measurement all over the district of mass number (mass number 6 to 260). In the system in which the mass scanning is carried out by changing the acceleration energy of ion, the arrangement of reverse arrangement type is required. When the measurement of isotope ratio is carried out, the strength of isotope signal is measured in order while changing the magnetic field strength or ion energy. Double-focusing type mass spectrometer enables the observation of the peak of the flat type and thus increased measurement precision can be expected compared to the quadruple type. In the case where the signals of the analysis element are transient, or there are changes with time that can not be neglected, the decrease of the isotope analysis precision is inevitable.