ICP-MS Analysis in the Industrial Field

Shin-ya Ichikawa, Kazunori Onabe

Inductively coupled plasma mass spectrometer(ICP-MS) is an elemental analyzer with high sensitivity and high selectivity, and is one of the analytical instruments used in the industrial field. Recently, new analysis methods that connect laser ablation or high-performance liquid chromatograph with ICP-MS have been attracting attention. This paper provides an overview of ICP-MS analysis and introduces various ICP-MS analysis examples in the industrial field.

1. Introduction

In the field of analytical chemistry, inductively coupled plasma atomic emission spectrometry (ICP-AES) and ICP-MS are used as analytical instruments that use inductively coupled plasma. Both are elemental analyzers capable of simultaneous analysis of multiple elements with high selectivity, and in the industrial field, not only ICP-AES but also the more sensitive ICP-MS is becoming increasingly popular. Recently, analytical methods that take advantage of the high sensitivity and selectivity of ICP-MS have attracted attention, including laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) connected to laser ablation and liquid chromatography inductively coupled plasma mass spectrometry (LC-ICP-MS) connected to a high-performance liquid chromatograph¹⁾²⁾. In this report, we introduce the overview and features of ICP-MS, as well as examples of LA-ICP-MS and LC-ICP-MS analysis in the industrial field.

2. Overview and characteristics of ICP-MS

ICP-MS is basically an elemental analysis device that measures liquid samples. An overview of an ICP-MS is shown in Fig.1. The liquid sample is atomized by a liquid delivery pump, nebulizer, and carrier gas, and only small particles are selected in the spray chamber and introduced into the inductively coupled plasma (ICP), which is the ionization section. In the ionization section, the gas used for the plasma is introduced into a quartz torch, and the gas is discharged in a high-frequency induction coil, forming a high-temperature ICP at atmospheric pressure, which atomically ionizes the elements in the sample introduced into the ICP from the spray chamber. The gas that forms this plasma, and the aforementioned carrier gas, are primarily argon, but when measuring samples that contain organic solvents, a mixture of argon and oxygen is used, and there are also cases where helium or nitrogen gas is used. When measuring samples that contain high concentrations of metal elements, there is a risk that the

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sensitivity of the downstream mass spectrometer will decrease due to contamination, so some models have a function to eliminate the aforementioned problem by installing an argon gas inlet line between the spray chamber and the ionization section and controlling the amount of sample introduced into the ionization section.

Next, the atomic ions generated in the ionization section are extracted from the interface section to the ion lens section and then guided to the mass separation section. The interface section is composed of a sampling cone and a skimmer cone. The ion lens section is composed of an extraction electrode and a focusing electrode, and plays the role of efficiently guiding the atomic ions to the mass separation section. The mass separation section is available in quadrupole, magnetic field, time-of-flight, and triple quadrupole types.

Until now, quadrupole types have been the mainstream, but recently triple quadrupole types have been attracting attention. The mass-separated atomic ions are detected by a secondary electron multiplier detector.

In addition, the vacuum exhaust section that keeps the interface section, ion lens section, and mass analysis section in a vacuum state is evacuated in two stages using an oil rotary pump and a turbomolecular pump, since ICP is an atmospheric pressure ionization method. Many quadrupole ICP-MS models are equipped with a collision reaction cell (CRC) between the ion lens section and the mass separation section. This CRC allows for selective detection of analytes by introducing gases such as helium, hydrogen, and ammonia into the cell to remove or reduce interfering ions, thereby improving sensitivity.

ICP-MS has become increasingly popular in recent years due to its advantage of enabling highly sensitive analysis of many types of elements at the ppt level. In addition to being a useful analytical method when used alone, development of analytical methods using hyphenated techniques that connect ICP-MS to other analytical instruments, such as the aforementioned LA and HPLC, gas chromatograph(GC), ion chromatograph(IC), and capillary electrophoresis(CE), is also progressing.

Abbreviations, Acronyms, and Terms.

ICP-MS—inductively coupled plasma mass spectrometer

A mass spectrometer that ionizes analytes using inductively coupled plasma and detects the ions produced.

- ICP-AES—inductively coupled plasma atomic emission spectrometer An optical emission spectrometer that uses inductively coupled plasma as an excitation source.
- LA—laser ablation

A device that irradiates a solid sample with laser light to vaporize or granulate the sample.

- HPLC—high performance liquid chromatograph An instrument that uses a liquid as the mobile phase to introduce a sample into a column and perform high-performance separation and detection by utilizing differences in interactions between the analytes and the stationary phase (adsorption, distribution, ion exchange, size exclusion, etc.).
- LC-ICP-MS—liquid chromatograph inductively coupled plasma atomic emission spectrometer

A liquid chromatograph with an inductively coupled plasma mass spectrometer (ICP-MS) connected to the detector.

CRC—collision reaction cell

A device for removing or reducing spectral interference caused by ions other than those of the target element. The main gases used to remove interference are helium and hydrogen, which are called He mode and H2 mode, respectively. CRC that does not use gas is called no gas mode.

GC—gas chromatograph An apparatus for performing chromatography using a gas as the mobile phase. IC—ion chromatograph

A high performance liquid chromatograph manufactured or assembled specifically for the analysis of ionic species components.

- CE—capillary electrophoresis Electrophoresis using a capillary as the migration field. It can be performed without a carrier or with a support such as polyacrylamide gel as the migration field.
- XRF—X-ray fluorescence spectrometry A method in which a sample is irradiated with X-rays and the fluorescent X-rays generated are measured to qualitatively and quantitatively identify the substance.
- separation column—separation column A tubular chamber in which separation of sample components takes place. It may be packed with a packing material or have a stationary phase supported on the capillary wall.
- retention time—retention time The time from when the sample is introduced into the column until the apex of the peak of the target

component appears. eluent—eluent

A liquid for developing and eluting the sample components held in the column.

m/z—mass to charge ratio

The value obtained by dividing the mass (m) of an ion by the charge (z). It is also called the mass-to-charge ratio. The horizontal axis of a mass spectrum is displayed as m/z.

analyte—analyte

The component to be examined in an analytical sample or sample solution. Also called the analyte.



Fig.1. Schematic diagram of ICP-MS.

3. ICP-MS analysis in the industrial field

3.1 Elemental analysis by ICP-MS

ICP-MS allows for elemental analysis of liquid samples with relatively simplified procedures. For example, aqueous solutions such as cleaning water and wastewater can be measured by adding a certain amount of nitric acid during the sample dilution process. Additionally, water-soluble samples that contain high concentrations of metal elements, such as plating solutions, can be measured if the metal concentration is diluted to a range that can be measured by ICP-MS. For samples that contain large amounts of organic solvents or organic matter, measurements are performed using an ICP-MS that is designed to analyze organic solvents.

On the other hand, solid samples can be measured by ICP-MS by pretreating them with acid or alkali reagents and turning them into a solution. Specifically, typical metals such as copper and aluminum, and metal materials mainly composed of iron can be turned into a solution by heating them using a solution of hydrochloric acid, nitric acid, and water in any ratio. However, if the sample contains elements that are insoluble in either hydrochloric acid or nitric acid, other acid or alkali reagents may be used in the pretreatment. In addition, organic materials such as resins and rubber materials can be turned into a solution by adding the sample and nitric acid to a closed container and heating it to decompose the organic matter. There are also several other pretreatment methods for organic materials, such as a method of thermal decomposition with sulfuric acid and a method of high-temperature heating in a platinum crucible using an alkali reagent. In any case, when performing elemental analysis using an analytical device that measures liquid samples such as ICP-MS, pretreatment to turn the sample into a solution is important, and experience and know-how are required because the pretreatment conditions, such as the equipment and reagents used, vary depending on the material of the sample and the elements to be measured.

3.2 Elemental analysis by LA-ICP-MS

As mentioned above, ICP-MS is designed to measure liquid samples, but elemental analysis is also possible for gaseous or particulate matter if it can be introduced into the ICP using a carrier gas. One analytical method that takes advantage of this feature is LA-ICP-MS, in which an LA is connected before the ICP-MS. Fig.2 shows an outline of a typical LA-ICP-MS, in which a sample stage is attached to an Nd/YAG laser.





LA-ICP-MS can perform elemental analysis of solid samples by irradiating the solid sample with a laser to vaporize and atomize the elements contained therein, and then introducing the samples into the ICP-MS using a carrier gas. In addition, line analysis and elemental imaging of the sample are possible by scanning the stage. As such, LA-ICP-MS has the advantage of being able to perform elemental analysis of solid samples without pretreatment, and does not cause the charge-up that is a problem with analytical devices that use electron beams such as scanning electron microscope energy dispersive X-ray analyzers (SEM-EDS).

Therefore, there is no need for electrical conduction treatment even with organic materials such as resins and rubber materials, and it is also possible to evaluate the element distribution over a wide area of several centimeters.

Below are some examples of LA-ICP-MS analysis in the industrial field. First, Fig.3 shows an example of elemental imaging evaluation of the solder mounted on a flexible printed circuit board (FPC). Because there is a polyimide film around this solder, Br detected on the left side of the solder suggests that it is a bromine-based flame retardant, and Sb suggests that antimony trioxide (Sb₂O₃), a flame retardant assistant, is present in the adhesive layer below

the polyimide film. In addition, because there is flux in the upper right corner of the solder, a large amount of C, which is thought to be derived from the organic components of the flux, was also detected as an element other than Sn. Note that since this solder mounted is lead-free solder that complies with the RoHS Directive, which is a regulation of the EU, the amount of Pb detected in this result was small, but even such a small sample can be more clearly judged if it contains a high concentration of Pb exceeding the RoHS Directive threshold (Pb: 1000 ppm).



Fig.3. Elemental imaging of mounted solder by LA-ICP-MS.

Next, Fig.4 shows an example of elemental imaging evaluation of foreign matter attached to a cable using LA-ICP-MS.



Fig.4. Elemental imaging of foreign matter cable by LA-ICP-MS.

Details of this cable are unknown, but XRF analysis of the foreign object revealed that it was stainless steel composed mainly of Fe, Ni, and Cr, but it was difficult to identify the type of steel. On the other hand, LA-ICP-MS analysis is capable of performing elemental analysis of smaller samples than XRF, and can identify the type of steel using a calibration curve method using standard substances, and the results showed that the foreign object was equivalent to JIS standard steel type SUS304, as shown in Table 1.

Table 1. Quantitative	value of foreign matte	r by LA-ICP-MS.
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V	Cr	Mn	Fe	Со	Ni	Мо
0.08	18.36	1.13	71.87	0.16	8.31	0.1
						(wt%)

3.3 Elemental analysis by LC-ICP-MS

ICP-MS is capable of selectively detecting target elements with relatively high sensitivity, and as an analytical method that takes advantage of this advantage, elemental analysis using LC-ICP-MS, in which HPLC is connected before the ICP-MS, is also attracting attention. Fig.5 shows an overview of the LC-ICP-MS used when examining the analytical examples introduced below.



Fig.5. Schematic diagram of LC-ICP-MS.

LC-ICP-MS is mainly used as a method for simultaneous analysis of arsenic and selenium compounds in aqueous solutions. Analytes can be separated by chemical form using HPLC, and then detected as elements by ICP-MS. This analysis by chemical form is called elemental speciation. In the case of simultaneous analysis of arsenic compounds, instead of preparing a standard solution for each analyte, it is possible to quantitatively analyze many types of arsenic compounds using an elemental standard solution containing arsenic. This has the advantage that even unknown analytes or analytes for which standard solutions are difficult to obtain can be quantitatively analyzed using elemental standard solutions. In addition, LC-ICP-MS has various advantages, such as the ability to measure small amounts of samples using HPLC autosamplers and injectors, and the ability to determine the presence of the analyte as a peak in the chromatogram obtained by separation analysis even if the analyte is subject to spectral interference. As an example of the application of this analysis method, an example of separation analysis of 18 elements using LC-ICP-MS is shown in Fig.6.



Fig.6. Chromatogram of 18 elements by LC-ICP-MS.

In this analysis of 18 elements, samples were used in which inorganic compounds were dissolved in HPLC eluent. In the diagram, S to Br are anions, and Na to Ca are cations; these are generally separated and analyzed using ion chromatograph in an anion column and a cation column, respectively. Other elements are analyzed using ICP-MS or ICP-AES.

In contrast, in this analysis using LC-ICP-MS, a separation column that can retain both anions and cations is used, which not only allows for the separation and analysis of anions, cations, and elements, but also allows for the simultaneous speciation of As, Se, Cr, and Fe.

4. Conclusion

ICP-MS is used as a highly sensitive elemental analyzer capable of simultaneously analyzing multiple elements, and analytical methods that connect it to LA or LC are also attracting attention. In this report, we have introduced some examples of LA-ICP-MS and LC-ICP-MS analysis, but we will continue to apply this method as an in-house analytical technique and to develop new analytical methods.

Reference

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