Application of ICP-MS Method in Environmental Field

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Abstract. ICP-MS is a new technology for environmental monitoring and analysis. This article summarizes the characteristics of ICP-MS and its application in the analysis of environmental samples such as soil and water, and summarizes mass spectrometry interference factors such as isobaric, oxide, double charge, and polyatomic ions, with a view to future ICP-MS.

Keywords: ICP-MS, Environment, Application.

1. Introduction
Inductively coupled plasma mass spectrometer (ICP-MS) is an analytical instrument that combines the high temperature characteristics of ICP with the sensitive and fast scanning characteristics of MS. It has high sensitivity, low detection limit, small sampling volume, wide linear range, and multiple elements simultaneously and fast. The characteristics of the determination, at the same time because of its morphology and isotope analysis, play an important role in revealing the migration and transformation of inorganic elements, environmental behavior, and pollution sources [1-4]. In environmental monitoring, ICP-MS is widely used for the analysis of metals and metalloids in media such as water quality, soil, and ambient air [5-8].

2. Advantages of ICP-MS
ICP-MS is a mass spectrometry chemical composition analysis method that uses ICP as the ionization source. It is one of the modern methods for trace and ultra-trace analysis. It has the following characteristics.

a) High sensitivity, 1 to 3 orders of magnitude higher than the general ICP-AES analysis method (depending on the elements analyzed), especially when the mass number is above 100, the sensitivity is higher and the detection limit is lower, as shown in the table 1 shown.
b) In mass scanning measurement, when the measurement range is m/z 0~800, scanning can be performed at a high speed of 10~100 Ls. Therefore, the simultaneous determination of multi-element components can be easily achieved.

c) Various isotopes of each element can be measured simultaneously, so it can be used as an isotope dilution method.

d) With the development and development of new technologies, it is obviously not enough to measure the total amount of certain pollutants in environmental monitoring. This is because the toxicity of heavy metals and other existing forms is very different. The ICP-MS method is used for elements. The chemical form identification of is very effective.

e) Utilizing the high sensitivity and high selectivity of ICP-MS, it can be combined with multiple machines. For example, ICP-MS is used as the LC detector. Various chemical forms of, Sn, Hg and Pb.

3. Mass interference
Mass spectrum interference is divided into isobaric interference, oxide and double charge interference, signal fluctuations, interface effects and matrix effects.

3.1. Isobaric interference
Isobaric interference refers to the mass spectrum overlapping interference caused by the isotope of other elements in the sample with the same mass-to-charge ratio as the ion to be measured, and this interference cannot be resolved by the quadrupole mass spectrometer. The isobaric interference of 20 elements in the environmental standards is shown in Table 1. Except for 7 elements such as Be, B, Mn, Co, Cu, As, and Tl, there is no isobaric interference. The remaining 65% of the elements are at least. It is interfered by one isobaric, such as 123 Sb interfered by 123 Te, 50V is interfered by 50 Ti and 50 Cr, and Ba is interfered by isobaric up to seven. Isotopes with even mass numbers are more susceptible to isobaric interference than odd mass numbers. The isobaric interference mainly comes from the sample matrix or the acid used to digest the sample. In addition, there are impurities in the ICP-MS carrier gas and collision/reaction gas, such as Kr, Xe, etc.

3.2. Double charge interference
The interference of oxide and double charge is related to bond energy and ionization energy. The oxide interference is caused by the incomplete dissociation of the sample matrix or the recombination of dissociated elements in the plasma plume. The result is that the mass of the ion matrix (M) is M’ 16−18, M’ 32−36 Or interference peaks appear at M + 48 to 54, with M^{16}O^{+} being the most. As long as the plasma is not enough to break the oxide bond energy, oxide interference will occur. Therefore, the higher the oxide bond energy of the element to be measured, the smaller its signal intensity loss; meanwhile, M’ plasma plume and O atoms have been formed Recombination to form M^{16}O^{+}, which increases the signal intensity for measuring other elements. The 20 inorganic elements in the environmental field are subject to the interference of oxides. The interference of oxides depends on the plasma temperature and the amount of H_{2}O entering the ICP. Associated with oxide interference is double charge interference. The condition for the formation of double charge interference is that the second ionization energy of the element is lower than the first ionization energy of Ar. On the one hand, double charge interference reduces the ionic strength of the element to be measured, and on the other hand causes the double charged ions formed by other elements to increase the element to be measured. The ionic strength.

3.3. Signal fluctuations
One of the current shortcomings of ICP-MS is signal fluctuations, poor long-term stability, which affects the accuracy of the measurement results. The reasons for signal fluctuations are various, such as the rotation of the vacuum pump, the amount of sample extraction, the response of the detector, the ion optics system, etc. Unstable performance will cause fluctuations in the final signal.
3.4. Interface effects and matrix effects

The interface effect is inherent to the ICP-MS technology. It is a comprehensive effect of the complex physical and chemical reactions that occur at the interface between the ICP torch flame and the mass spectrometer and during the ion focusing transmission process. The physical reason is that the salt in the sample is deposited on the surface of the cone. The cone hole has a tendency to become smaller. The acidity of the plasma torch high temperature ablation solution makes the cone hole larger. The change of the cone hole causes a change in the number of ions extracted from the plasma to the mass spectrometer. The chemical reason is that in the process of ion flow passing through the cone hole, complex chemical reactions occur due to changes in temperature and pressure, and interactions between particles.

The matrix effect is due to the presence of a higher concentration of matrix elements, which disrupts the ionization balance of the various elements in the plasma, resulting in an enhancement or suppression effect of the ionization process of the measured element.

4. Application of ICP-MS

4.1. ICP-MS determination of rare earth elements

During the "Seventh Five-Year Plan" period, my country used extraction resin to separate and concentrate in the soil background value survey, and ICP-AES to determine the content of each rare earth element in the soil. Not only the procedures are complicated, but also matrix interference is easily introduced, which leads to measurement errors. Using the HR-ICP-MS method, the soil does not need to be concentrated and separated after digestion, and it can be directly measured with high sensitivity.

4.2. ICP-MS determination of natural water

In 1993, Japan promulgated a new surface water standard, in which the limit standards for Se, As, and Sb were 0.01, 0.01 and 0.002mg/L, respectively. Such low concentrations are also difficult to directly measure with conventional atomic absorption methods. In the new standard method promulgated by Japan, ICP-MS (or MIP-MS) is listed.

It is a standard method for determining Cr$^{6+}$, Cu, Cd, Pb, etc. Related scholars used continuous hydride generation-ICP-MS (Flow-HG / ICP-MS) to simultaneously determine Se, As, Sb, and Ge in natural water. The combination of continuous hydride generation and ICP-MS effectively overcomes the shortcomings of ICP-MS that are easily affected by the water sample matrix, and can carry out continuous automatic determination at the same time. EDTA was added as a masking agent during the measurement to overcome the influence of metal elements on the formation of hydrides.

4.3. Application of ICP-MS in other environmental analysis

In order to investigate the impact of environmental pollution on the ecological environment, environmental monitoring personnel often need to determine biological samples such as various animals and plants. Related scholars use HNO$_3$-H$_2$O$_2$-HF to digest human hair, tea, leaves, shellfish, rice noodles and other samples, and use ICP-MS measured V, Ni, Zn, Ge, As and Mo.

5. Outlook

At present, ICP-MS-related articles published in China mainly focus on general applications, online applications, and related sample preparation techniques and experimental conditions; while abroad, they focus on new ways to solve mass interference and non-mass interference, and improve isotope In-depth research on new methods of ratio analysis precision and other aspects is precisely the gap between China and foreign advanced technologies. ICP-MS, as a powerful tool for the analysis of inorganic elements, has obvious advantages, and the existing mass spectrum interference is also an unavoidable problem. The research and discussion on mass spectrometry interference of 20 inorganic
elements such as isobaric, oxide, double charge, and polyatomic ions in the environmental field is very valuable for the promotion and application of ICP-MS in the environmental field.

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