

Advances in high resolution inductively coupled plasma mass spectrometer technology and applications

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Abstract

Rapid and accurate detection of low-content element samples, element isotopes and in situ microanalysis information about element has always been the focus and difficulty of ICP-MS technique. High resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) is an improved ICP-MS technology with the characteristics of a wide detection range, high resolution, high precision and low detection limit. This paper simply introduced the high resolution inductively coupled plasma mass spectrometer technology applications and the latest progress on the application of the technique made some reviews, including high resolution inductively coupled plasma mass spectrometer technology introduction, metal and nonmetal elements analysis, isotope ratio analysis and so on, mainly in the low-content of complex matrix samples of some new methods were introduced.

Keywords

HR-ICP-MS; Element concentration; Elemental isotope; Laser ablation system.

1. Introduction

Inductively coupled plasma mass spectrometer (ICP-MS) is the most common instrument in chemical analysis. Since it was put into commercial use in 1983, it has been widely used in many fields such as geology, environment, medicine, materials, chemical industry and so on. However, due to the use of argon plasma to ionize elements, ICP-MS has many disadvantages, such as Polyatomic Ion interference and matrix effect, so the application of ICP-MS has always been shackled. Polyatomic Ion interference can be solved in many ways, such as sample pretreatment, collision cell technology, reaction cell technology, etc., but these technologies are more complex or introduce more uncertainty. The most direct and effective solution to Polyatomic Ion interference in ICP-MS is to improve the resolution of the instrument. For example, in the process of testing ^{56}Fe , it is often strongly disturbed by $^{40}\text{Ar}^{16}\text{O}^+$ and $^{40}\text{Ca}^{16}\text{O}^+$.

when the resolution above 2500, interference peak can be carried out directly. But the common Quadrupole Inductively coupled plasma mass spectrometer (Q-ICP-MS) can only reach the resolution of 300. Therefore, based on this need, the high-resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) has been developed. HR-ICP-MS has the characteristics of a wide element detection range, high resolution, high accuracy and ultra-low detection limit. It can accurately measure the major, trace and even ultra trace elements and their isotopes. This paper reviews the application progress of HR-ICP-MS in the field of analysis and detection.

2. Determination of element content

In the research of HR-ICP-MS for sample analysis, the most reported is the determination of the content of major and trace elements in the sample. In the ICP-MS test process, the factors that affect the test results usually include the working state of the plasma, the effect of instrument quality discrimination, the interference of isotopes and polyatomic ions, etc. The working state of the plasma remains basically constant during the one test and can be ignored. The Mass discrimination effect refers to the phenomenon that only positively charged ions are left when charged ions of different masses pass through the interface of the instrument, and light ions are excluded at the edge of the ion beam, making it more difficult to enter the instrument [1] [2]. The mass discrimination effect can be corrected by the element internal standard method and the external standard method. Isotopic interference refers to the phenomenon that the isotopes of different elements are similar in mass and superimposed at the same mass position during the test process to cause interference. For example, ^{204}Hg interferes with ^{204}Pb . Polyatomic ion interference is the formation of polyatomic ions by isotopes of different elements (Two-atom ions, three-atom ions, etc.). The phenomenon of interference caused by the superposition of the mass position of the measured element during the test, such as the interference of $^{40}\text{Ar}^{16}\text{O}$ on ^{56}Fe , due to the complex matrix in the ICP-MS test process, the isotopes and Polyatomic ion interference will affect the test results of multiple elements [3]. Therefore, how to solve the isobaric and polyatomic ion interference in the test process has always been a major problem in the development of ICP-MS instruments and the construction of detection methods.

There are usually three ways to solve the interference of isobaric and polyatomic ions: pre-processing for sample separation and purification, using collision cell/reaction cell technology, and improving instrument resolution. The pretreatment of sample separation and purification, namely, the separation of matrix elements by the chemical properties of different elements, can effectively remove the interfering elements and reduce the matrix effect, but only a small number of elements can be treated each time, which is susceptible to the influence of personnel operation level, reagent and environmental pollution in the process. At present, Pretreatment of sample separation and purification is commonly seen in Multi-receiving cup inductively coupled plasma mass spectrometer for element isotope testing or concentration low-content sample [2]. Collision cell and reaction cell technology are more common in conventional ICP-MS testing. By setting up a collision cell or reaction cell in the ion beam transmission path, the isotopes and polyatomic ions in the ion beam are combined with the collision gas. The reactant gas undergoes physical collision or chemical reaction, thereby reducing or even removing its interference. However, the physical collision or chemical reaction in the collision/reaction process will inevitably lead to the reduction of ion beam intensity, resolution and unknown reaction products[4], requiring a lot of verification and debugging process. Improving the resolution of the instrument is the most direct way to solve the interference of isotopes and polyatomic ions. For example, the target element peak of the iron content test in the ICP-MS test is usually the ^{57}Fe peak with an isotope ratio of only 2.12%, and ^{56}Fe peak accounting for 91.75% cannot be used. And if the instrument resolution ($R=M/\Delta M$) can reach more than 2500, the

$^{16}\text{O}^{40}\text{Ar}^+$ peak can be separated, ^{56}Fe can be directly tested, and the best test results can be obtained. Another example, in the process of ICP-MS analysis of rare earth elements, light rare earth elements such as oxides interfere with heavy rare earth elements, and barium hydrogen, oxygen and chlorine interfere with rare earth elements [5]. Using high resolution mode can also minimize these disturbances and obtain good test results. Combined with the high sensitivity of HR-ICP-MS, even the sensitivity in HR mode is about 1/50 of that in LR mode, it still has good test precision. Table 1 shows the element isotopes and instrument resolution of 51 common elements selected in HR-ICP-MS test.

Cullen et al. [6] tested the content of trace elements in seawater particles in the ocean using HR-ICP-MS at low and medium resolution, and successfully reduced the sample amount of thousands or even tens of thousands in the original process to 0.2-5.0L, without the need for separation and purification process. Al, P, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, Ag, Cd, Ba, Pb and U were simultaneously measured by this method. The accuracy of this method is better than 4%, and the accuracy deviation of most elements is less than 10% when using an external standard curve method.

Gellein et al. [7] used HR-ICP-MS to measure the content of 12 elements including Ag, As, Au, Cd, Cu, Hg, Fe, Pb, Se, Sr, U and Zn in single strands of human hair. At the same time, through the analysis of trace elements in human hair, Gellein obtained information on the essential elements and toxic elements, and speculated that for some elements, it may be related to diet and seasonal changes at the time of exposure.

Yuan Yuan et al. [8] used HR-ICP-MS to complete the test of 49 elements in soil samples. To test the light rare earth elements La, Ce, Pr, Nd, Sm, use the HR mode with resolution greater than 4000, ^{169}Tm , ^{172}Yb , ^{175}Lu , and choose to use the LR mode. The precision of the test is 1.0~7.7%, and method accuracy (logarithmic error) $\Delta\lg C$ is between 0.00 and 0.07.

Wen Liang et al. [9] simultaneously used three methods of ultraviolet spectrophotometer (UV), high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) and digital PCR to quantify cell plasmids. Among them, HR-ICP-MS quantifies plasmid DNA by analyzing phosphorus in DNA molecules. Through the purification of DNA standards and the optimization of dPCR analysis methods, the consistency of UV, HR-ICP-MS and dPCR test results was successfully achieved, with a relative deviation of less than 10%.

Sambuddha Misra et al. [10] developed an accurate determination method of B/Ca in low-quality natural carbonate (<5 $\mu\text{g CaCO}_3$) based on HR-ICP-MS. The test range of the method: 9-250 $\mu\text{mol/mol}$, the detection limit: 2 $\mu\text{mol/mol}$ (the detection limit in the previous method: 10 $\mu\text{mol/mol}$), and the long-term test accuracy error is less than 3.9% (2σ). This method helps researchers directly test the B/Ca ratio and trace element content of foraminifera shells.

Table 1: Isotope selection and instrument resolution setting of 51 elements in HR-ICP-MS test

Tested isotope	Abundance (%)	Interference	Resolution requirements	Instrument model
^7Li	92.41	$^6\text{Li}^1\text{H}^+$	1010	LR
^9Be	100.00			LR
^{24}Mg	78.99	$^{12}\text{C}_2^+$	1604	MR
^{45}Sc	100.00	$^{14}\text{N}^{31}\text{P}^+$, $^{28}\text{Si}^{16}\text{O}^1\text{H}^+$	2149, 1892	MR
^{47}Ti	7.44	$^{31}\text{P}^{16}\text{O}^+$	2777	MR
^{51}V	99.75	$^{35}\text{C}^{16}\text{O}^+$	2573	MR
^{52}Cr	83.79	$^{12}\text{C}^{40}\text{Ar}^+$, $^{35}\text{Cl}^{16}\text{O}^1\text{H}^+$	2375, 1671	MR
^{55}Mn	100.00	$^{39}\text{K}^{16}\text{O}^+$	2671	MR
^{56}Fe	91.75	$^{40}\text{Ar}^{16}\text{O}^+$, $^{38}\text{Ar}^{18}\text{O}^+$	2502, 2075	MR
^{59}Co	100.00	$^{43}\text{Ca}^{16}\text{O}^+$, $^{42}\text{Ca}^{16}\text{O}^1\text{H}^+$, $^{24}\text{Mg}^{35}\text{Cl}^+$	2878, 2093, 2856	MR

⁶⁰ Ni	26.22	⁴⁴ Ca ¹⁶ O+	3058	MR
⁶³ Cu	69.17	²³ Na ⁴⁰ Ar+, ⁴⁷ Ti ¹⁶ O+	2791,3687	MR
⁶⁶ Zn	27.90	⁵⁰ Ti ¹⁶ O+	4826	HR
⁶⁹ Ga	60.11	¹³⁸ Ba ₂ +	2549	MR
⁷⁴ Ge	35.94	¹⁴⁸ Nd ₂ +, ¹⁴⁸ Sm ₂ +	1983,2040	MR
⁷⁵ As	100.00	³⁵ Cl ⁴⁰ Ar+, ¹⁵⁰ Nd ₂ +	7780,1928	HR
⁸² Se	8.73	⁸² Kr	25393	LR
⁸⁵ Rb	72.17			LR
⁸⁸ Sr	82.58	⁸⁶ Kr, ⁸⁵ Rb ¹ H+	8299	LR
⁸⁹ Y	100.00			LR
⁹⁰ Zr	51.45			LR
⁹³ Nb	100.00			LR
⁹⁵ Mo	15.92			LR
¹¹⁴ Cd	28.73	¹¹⁴ Sn, ⁹⁸ Mo ¹⁶ O+	196182, 37468	LR
¹¹⁵ In	95.71	¹¹⁵ Sn	212619	LR
¹¹⁸ Sn	24.22			LR
¹²¹ Sb	57.21			LR
¹²⁶ Te	18.95			LR
¹³³ Cs	100.00			LR
¹³⁷ Ba	11.23			LR
¹³⁹ La	99.91			LR
¹⁴⁰ Ce	88.45			LR
¹⁴¹ Pr	100.00			LR
¹⁴⁶ Nd	17.17			LR
¹⁴⁷ Sm	14.99			LR
¹⁵³ Eu	52.19	¹³⁷ Ba ¹⁶ O+	7456	HR
¹⁵⁷ Gd	15.65	¹⁴⁰ Ce ¹⁶ O ¹ H+, ¹⁴¹ Pr ¹⁶ O+	9938, 7333	HR
¹⁵⁹ Tb	100.00	¹⁴³ Nd ¹⁶ O+	7707	HR
¹⁶³ Dy	24.90	¹⁴⁷ Sm ¹⁶ O+	8611	HR
¹⁶⁵ Ho	100.00	¹⁴⁹ Sm ¹⁶ O+	9047	HR
¹⁶⁶ Er	33.61	¹⁵⁰ Nd ¹⁶ O+, ¹⁵⁰ Sm ¹⁶ O+	11443, 9162	HR
¹⁶⁹ Tm	100.00	¹⁵³ Eu ¹⁶ O+	9344	LR
¹⁷² Yb	21.83	¹⁵⁶ Gd ¹⁶ O+	8886	LR
¹⁷⁵ Hf	27.28			LR
¹⁸¹ Ta	99.98			LR
¹⁸² W	26.49			LR
²⁰⁵ Tl	70.48			LR
²⁰⁸ Pb	52.35			LR
²⁰⁹ Bi	100			LR
²³² Th	100			LR
²³⁸ U	99.27		1010	LR

3. Isotope determination

Isotopes refer to atoms with the same number of protons but different numbers of neutrons. Isotopic testing can be used in many research fields such as medicine, environment, minerals, and archaeology. However, the mass difference between isotopes is very small, and the change

of isotope ratio can be observed is also very small, so the instrument used for testing is also put forward higher requirements. Accuracy of the early quadrupole ICP-MS analysis and testing of the isotope ratio was poor, and it was subject to strong isotopic interference. It can only be applied to some applications with large changes in the isotope ratio and slightly lower accuracy requirements, such as zircon U-Pb dating, etc., isotope ratio tests are usually performed using thermal ionization mass spectrometer (TIMS), secondary ion mass spectrometry (SIMS) and other instruments [11]. With the improvement and upgrade of the instrument, the isotope measurement accuracy of the improved ICP-MS instrument, led by MC-ICP-MS, has been significantly improved. HR-ICP-MS is equipped with electrostatic and magnetic focusing analyzers at the same time, which has the characteristics of high resolution and high sensitivity, so that HR-ICP-MS can obtain more accurate isotope ratio information without interference, and the accuracy of testing isotope can be Reach 0.02%-0.3% (RSD) [12].

Frank Vanhaecke et al. [13] used the medium resolution mode of MAT Element HR-ICP-MS to test $^{63}\text{Cu}/^{65}\text{Cu}$ and $^{206}\text{Pb}/^{207}\text{Pb}$. The interference of $^{40}\text{Ar}^{23}\text{Na}^+$, $^{28}\text{Si}^{35}\text{Cl}^+$ and $^{23}\text{Na}_2^{16}\text{OH}^+$ on ^{63}Cu and $^{30}\text{Si}^{35}\text{Cl}^+$, $^{28}\text{Si}^{37}\text{Cl}^+$ and $^{23}\text{Na}_2^{19}\text{F}^+$ on ^{65}Cu are greatly reduced in medium resolution mode. Accuracy of testing the ratio of $^{63}\text{Cu}/^{65}\text{Cu}$ and $^{206}\text{Pb}/^{207}\text{Pb}$ is 0.1% (RSD, n=10).

Stürup et al. [14] used HR-ICP-MS to simultaneously determine the zinc isotope ratios ($^{64}\text{Zn}/^{66}\text{Zn}$, $^{67}\text{Zn}/^{66}\text{Zn}$, $^{68}\text{Zn}/^{66}\text{Zn}$ and $^{70}\text{Zn}/^{66}\text{Zn}$) and total zinc content in human feces, urine and serum. The relative standard deviation (RSD) of $^{67}\text{Zn}/^{66}\text{Zn}$, $^{68}\text{Zn}/^{66}\text{Zn}$ and $^{70}\text{Zn}/^{66}\text{Zn}$ is 0.7%, and the relative standard deviation (RSD) of $^{64}\text{Zn}/^{66}\text{Zn}$ is 1.2%. When using a mass resolution of 6000, except for ^{64}Zn by monitoring the Ni content to subtract the overlap of ^{64}Ni , all other zinc isotopes can be measured without interference. The use of different mass resolution settings ensures a good identification of all spectral interference of zinc isotopes in feces, urine and serum and a balance of test accuracy.

Jenny-Burri [15] collected 24-hour urine from a population across Switzerland (n = 1393), used HR-ICP-MS to measure the ratio of $^{238}\text{U}/^{233}\text{U}$ in the sample, and performed isotope dilution calibration. The results of the study showed that the total median and 95th percentile of U content in the sample were 15 ng/24 h and 67 ng/24 h. Studies have shown that the place of residence has a significant impact on urine uranium excretion, but most of the areas with the highest levels of uranium excretion in urine were not associated with areas with high concentrations of uranium in drinking water. It is speculated that there are other sources of uranium besides local drinking water. At the same time, it was found that gender and albumin excretion also had a significant effect on uranium excretion.

4. Laser ablation combined system

A single ICP-MS can only undertake limited analysis and testing tasks, but it can fully explore the potential of ICP-MS through the combination of instruments. Laser ablation combined with ICP-MS has been widely used in various fields in recent years, especially in zircon U-Pb dating, mineral composition analysis and mineral inclusion research. The laser ablation system has high requirements for the combined equipment, and the small amount of the aerosol produced by laser shock can only be obtained with a fast detection equipment. In this case, when using Q-ICP-MS to scan by changing the voltage, the signal fluctuates greatly during the detection process [16]. Generally, MC-ICP-MS and Time-of-Flight ICP-MS are more suitable for combined laser ablation system due to the structural characteristics of the instrument. However, the early HR-ICP-MS used a transforming magnetic field for scanning, and the scanning speed was slow, so it was considered unsuitable for the combined laser ablation system. However, the latest models of instruments, such as ATTOM ES, use a combination of electric and magnetic fields, fast magnetic field scanning and other scanning methods to overcome the above shortcomings

to a large extent. Therefore, HR-ICP-MS can be more suitable for laser denudation with its advantages of high resolution, high sensitivity and anti-interference.

Barrelet et al. [17] used the HR-ICP-MS combined laser ablation system to test the sulfur, phosphorus, potassium and other elements in the Norwegian spruce core samples. The combination of the laser system and HR-ICP-MS allowed the researchers to measure low concentrations of elements at multiple points in a relatively narrow monolayer of rings. By analyzing the seasonal changes in the content of elements such as sulfur and phosphorus in wood, some new aspects of the metabolism of Norway spruce are revealed.

Hipley et al. [18] applied the LA-HR-ICP-MS method to the test of uranium oxide minerals in deposits in northern Australia, and compared the new data with the previously published data of thermal ionization mass spectrometry (TIMS) and the age of known important geological events. In the samples of El Sherena, Pallet, and Mount Isa, the age of U-Pb characterization measured in the previous study is very consistent with the LA-HR-ICP-MS measurement results. The results show that LA-HR-ICP-MS provides good spatial resolution and eliminates the interference of silver, phosphates, sulfides and halides, which may lead to incorrect data in the quadrupole ICP-MS test. The study found that the upper intercept U-Pb age of the $^{207}\text{Pb}/^{206}\text{Pb}$ crystalline uranium deposits in Adelaide River and Pallet is about 800 Ma, which may reflect the recrystallization of the crystalline uranium deposits during the Rodinia cracking process.

5. Conclusion

This article introduces the research and application progress of HR-ICP-MS instrument testing methods. It can be seen that the use of HR-ICP-MS to test low content complex samples is still the focus of HR-ICP-MS instrument test method research and application. Isotope testing and laser ablation combined system is still relatively weak. However, as the application of isotope and microanalysis in-situ research becomes more and more extensive, the advantages of HR-ICP-MS may be able to greatly improve the accuracy and test efficiency of isotope and microanalysis in-situ. HR-ICP-MS, as an instrument with high resolution, extremely low detection limit and fast magnetic field scanning, will show its great application value in more fields.

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