

Analysis of Samarium and Europium in Wheat by ICP-MS after On-Line Separation and Preconcentration

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Summary: Europium and Samarium in wheat were determined by inductively coupled plasma mass spectrometry (ICP-MS) after flow injection on-line separation and preconcentration with P₅₀₇ resin micro-column. The enhancement factors of 20 and 17 were achieved for samarium and europium, respectively. The instrumental detection limits were 0.00016 ng/ml and 0.000058 ng/ml for samarium and europium, respectively. The sample throughput was 13 s/h. The developed method was applied to analyze GBW 07605 certified tea reference material and the results were in good agreement with the certified values. The method was also assessed for determination of samarium and europium in wheat samples and the distribution of europium and samarium in different parts of wheat were discussed.

Keywords: ICP-MS, P₅₀₇, GBW 07605

Introduction

With the application of rare earth elements (REEs) in agriculture, more and more attention were paid to their biological toxicity and environmental effects [1-4]. Suitable amount of REEs can enhance the growth of plants, but too much REEs also can cause some health and toxicological problems. Information about REEs distribution in biological samples is basic to an understanding of their physiology and is useful in agronomy, as well as environmental pollution assessments or studies of biochemical process [5]. So, accurate determination of REEs in crops is very important.

ICP-MS, with the advantages of high sensitivity and low detection limits for REEs, simple spectra, wide dynamic range, capable of simultaneous multi-element determination and rapid isotope analysis, has been widely used in REE analysis since its emergence in 1980s [3, 6-22]. But during REE analysis, formation of polyatomic ions interferences, such as ¹³⁵Ba¹⁶O⁺ on ¹⁵¹Eu⁺ and ¹³⁰Ba¹⁶OH⁺ on ¹⁴⁷Sm⁺ in this work, will affect the accuracy [8-13]. Furthermore, under some circumstances, the contents of some REEs were very low, which is beyond detection ability of some ICP-MS instruments. To solve the above problems, some traditional off-line separation methods such as ion-exchange column separation [14-16] and solvent extraction [17, 18] method have been proposed. But these methods have the disadvantages of tediousness, time consuming and high cost. The on-line separation

methods, with the advantages of rapidness and low cost, have drawn more attention from the analyst in recent years. On-line ion-exchange micro-column separation [19-21] and on-line precipitation [22] have already been utilized in REEs analysis by ICP-MS. P₅₀₇ extraction resin can separate different REEs and between REEs and some other interfering elements and has already been applied to preconcentrate trace REEs in sea water [14], geological samples [15] and high purity Tb₄O₇ [16]. In this paper, a method was developed to determine trace samarium and europium by ICP-MS after flow injection on-line separation and preconcentration with P₅₀₇ micro-column. Comparing with the off-line preconcentration method, this method has the advantages of accuracy, fastness and low consumption of samples and solvents.

Results and Discussion

Effects of Loading Acidity, Loading Flow Rate and Loading Time

In off-line chemical procedures, P₅₀₇ resin can adsorb REEs almost completely at pH=2.0-3.0 [14-16]. The effect of loading acidity in the on-line separation and pre-concentration system was studied in the 0.001 mol/l ~ 0.10 mol/l HCl range. The adsorption of the analytes by the P₅₀₇ resin in the micro-column was investigated by analysis of the Sm and Eu in the loading effluent, the waste liquid after the sample flow through the P₅₀₇ micro-column. When the analytes signal intensity in the effluent

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became apparently higher than the blank, it signified that some analytes flow through the micro-column. The results showed that the analytes was completely absorbed on the P₅₀₇ micro-column when the loading acidity were in the 0.001 to 0.01 mol/l range. As the loading acidity exceeded 0.01 mol/l HCl, part of the analytes were not retained on the micro-column and flowed through it. According to the above results, 0.01 mol/l HCl was chosen as the loading acidity in the further experiments.

The effects of the loading flow rate on the sensitivity of the analytes were investigated from 1 to 5 ml/min. The results showed that when the loading flow rates were in the 1-4 ml/min range, the analytes can be completely adsorbed by the P₅₀₇ micro-column and when the sampling flow rate is higher than 4 mL/min, part of the analytes can flow through the micro-column. At the same time, the analytes signal intensity increased with the increase of the loading flow rate in the 1-4 ml/min range which is due to the increase of analytes adsorbed by the micro-column. When the loading flow rate is higher than 4 ml/min, the increase of the analytes signal intensity became not apparent. Based on these results, 4 ml/min was chosen as the loading flow rate to obtain maximum analytes signal intensity.

Effects of loading time on the analytes sensitivity were studied in the 20~140 s range with a 0.1 ng/ml standard mixture in 0.01 mol/l HCl. As shown in Fig. 1, the signal intensity of the analytes increased almost linearly from 20 to 140 s of loading time. These results indicates that a higher enrichment factor for the analytes could be achieved by increasing loading time. But as the loading time

increases, the analysis time become longer. To make a compromise between high sensitivity and short analysis time, a loading time of 120s was selected.

Rinsing of the Micro-Column

After samples being loaded on the P₅₀₇ micro-column, the residues of the sample solution on the micro-column may contain sample matrix with high contents of dissolved salts and interfering species, such as Ba in this work. Introduction of such complex material with the eluate into the ICP-MS system could block the sampling and skimmer cone and produce severe interferences. The residue material may also deposit on the ion lens to degrade the analytical performance. So a rinsing step was employed to remove the residual matrix on the micro-column before elution and introducing the eluate to the ICP-MS instrument.

In this work, 0.01mol/l HCl, the same as loading acidity, was used for rinsing and flow rate of 2.25 ml/ min was used for rinsing. A solution of Ba with concentration of 200 ng/ml in 0.01 mol/l HCl (comparable to that of Ba in the sample) was used to study the rinsing of the micro-column after sample loading. The Ba signal was used as index to investigate the rinsing efficiency. The results showed that the intensities of ¹⁵¹Ba can decreased from two hundred thousands cps to below 2000cps after 30s rinsing. In this work, the production rates of ¹³⁵BaO⁺ and ¹³⁰BaOH⁺ were 0.42% and 0.29%, respectively. As Ba signal, intensity is so low after 30s rinsing, their interferences on ¹⁵¹Eu and ¹⁴⁷Sm were negligible. As a result, a rinsing time of 30s was selected.

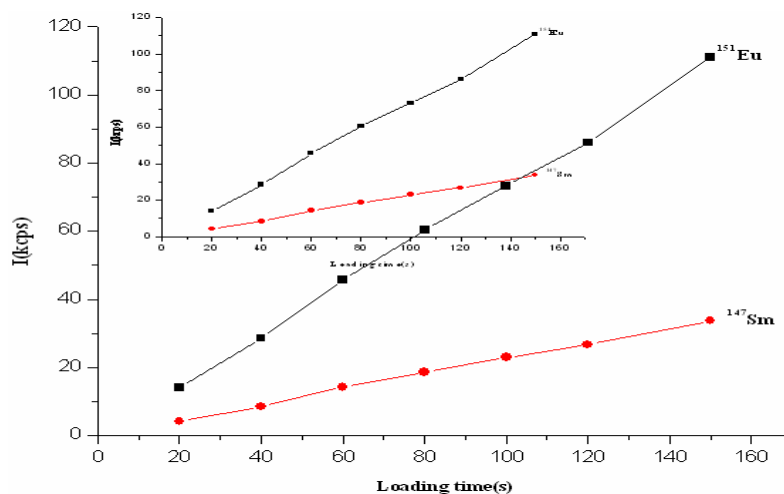


Fig. 1: Effects of sampling time on the signal intensity of the analytes.

Effects of Eluent Concentration and Elution Flow Rate

In the off-line operations, 6 mol/l HCl was often used to elute REEs from the P₅₀₇ column [14-16]. But in the on-line system, the eluent solution will be introduced into the ICP-MS system. When HCl of high concentration was used as eluent, the sampling cone and skimmer cone will be hurt. So, the effects of eluent concentration were investigated. In this work, 0.25 ~ 4 mol/l HCl as eluent with 0.1 ng/ml standard mixture, other conditions the same as the above optimized, was used to investigate the effect of eluent(HCl) concentration. The results was shown in Fig. 2, when the eluent was HCl of concentration below 1 mol/l, with the increase of HCl concentration, the analytes sensitivity increased rapidly. At the same time, when HCl concentration became higher than 1 mol/l, no significant changes were found for the analytes sensitivity. At the same time, with the increase of HCl concentration, the elutions of other REEs become faster. When the concentration of HCl is 2 mol/l, all the REEs can be almost totally eluted in 80 s. For the above reasons, 2 mol/l HCl was selected as eluent.

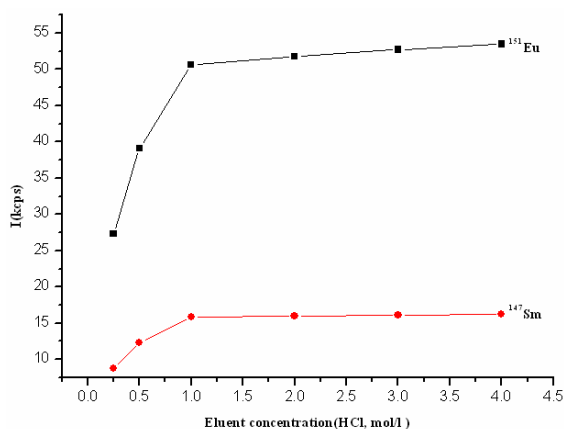


Fig. 2: Effects of eluent concentration on the signal intensity of the analytes.

The selection of elution flow rate is very important, because elution flow rate not only affects the nebulizer efficiency, but also control the efficiency of desorption of REEs from the P₅₀₇ extraction resin. Eluent flow rates from 1 ml/min to 5 ml/min was investigated. As shown in Fig. 3, with the increase in elution flow rate, the analytes sensitivity decreased in the investigated flow range. The reason may be that, with the increase of elution flow rate,

contacting time and exchanging reaction between the eluent and the resin became inadequate. At the same time, with the increase of elution flow rate, more solvent will be introduced into the ICP-MS instrument, the gasification of the solvent will consume more energy of the plasma and the nebulization efficiency was also affected. Due to the above reasons, the analytes signal intensity became low with the increase of elution flow rate. It should be noted the precision of the flow rate degraded when it was below 1 ml/min for the FI-3100 flow injection system. To make a compromise between nebulization efficiency, analytes sensitivity and flow rate precision, 1.5 ml/min was used as the elution flow rate in the further experiments.

The Analytical Performance of the Method

The developed method was verified by application to the determination of samarium and europium in tea certified reference material GBW07605. As shown in Table-1, the results were in good agreement with the certified value and the precision is acceptable. Based on 10 replicate determination of 0.1 ng/ml standard mixture, the precision is 3.9% and 4.5% for samarium and europium, respectively. Based on three times the standard deviation for 10 replicate determinations of 0.01 mol/ml HCl, the detection limit was 0.00016 and 0.000058 ng/ml for samarium and europium, respectively. The enhancement factors calculated from the signal intensities for a 0.1 ng/ml standard mixture in comparison with the results obtained with continuous nebulization aspiration were 20 and 17 for samarium and europium, respectively. The sample throughput was 13 s/h and the micro-column can be used at least 60 times for the same kind of plant samples.

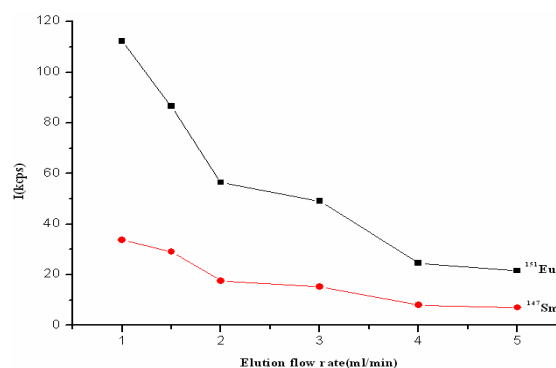


Fig. 3: Effects of elution flow rate on the signal intensity of the analytes

Table-1: Analytical results of GBW 07605 standard tea reference material ($\mu\text{g/g}$, $n=3$).

| Elements | Found | RSD(%) | certified |
|----------|-------|--------|-------------------|
| Sm | 0.092 | 5.5 | 0.085 \pm 0.017 |
| Eu | 0.015 | 7.2 | 0.018 \pm 0.002 |

Sample Analysis

With the popularization of REEs application in agriculture, the investigation of REEs in crops became increasing important. In this work, wheat samples collected from wheat field in Zizhen, Lingxian, Shandong Province, China, was analyzed. The results were shown in Table-2. As shown in Table-2, the contents of samarium and europium in wheat samples increased with the following order: wheat seeds, wheat stems, wheat shells, wheat leaves and wheat roots, which is in agreements with their reported distributions in rice [12].

Table-2: Results of wheat sample analysis ($\mu\text{g/g}$, $n=3$).

| Elements | Wheat seeds | Wheat stems | Wheat shell | Wheat leaves | Wheat roots |
|----------|------------------------|------------------------|------------------------|------------------------|----------------------|
| Sm | 0.0029 \pm 0.0002 | 0.0080 \pm 0.0006 | 0.0084 \pm 0.0007 | 0.0170 \pm 0.0013 | 0.192 \pm 0.014 |
| Eu | 0.0014 \pm 0.0001 | 0.0031 \pm 0.0003 | 0.0029 \pm 0.0003 | 0.0053 \pm 0.0005 | 0.049 \pm 0.004 |

Conclusions

A method of determination of samarium and europium by ICP-MS after on-line separation and preconcentration with a P_{507} micro-column was developed. Using this method, the interference of $^{135}\text{Ba}^{16}\text{O}^+$ and $^{130}\text{Ba}^{16}\text{OH}^+$ on $^{151}\text{Eu}^+$ and $^{151}\text{Sm}^+$ can be efficiently eliminated. The sensitivity of samarium and europium were enhanced 20 and 17 times, respectively. The validity of the developed method was verified by analysis of GBW 07605 tea certified reference materials and the results was in good agreement with the certified value. To further verify the developed method, wheat samples were analyzed and the results are acceptable. The distributions of samarium and europium in wheat were in agreements with those in rice [12].

Experimental

Instrumental

The ICP-MS instrument used was a DRC-E (Perkin-Elmer Corporation, USA) quadrupole-based ICP-MS instrument. The instrumental parameters are listed in Table-3. A FI-3100 flow injection system

(Beijing Titan Instruments Co., Beijing) was used for the on-line pre-concentration and separation. The FI-3100 system consists of two peristaltic pumps and a rotary injector valve (eight ports on the rotor and eight ports on the stator). The rotation speed, actuation sequences of the two pumps and the actuation of the injector valve were controlled by the SCM in the FI-3100. The FI manifold used for the separation and pre-concentration is shown in Fig 4. Tygon peristaltic pump tubing was used to aspirate the sample solutions and reagents. PTFE tubing (0.8mm i.d.) was used for all connections. These connections were kept as short as possible to minimize the dead volume.

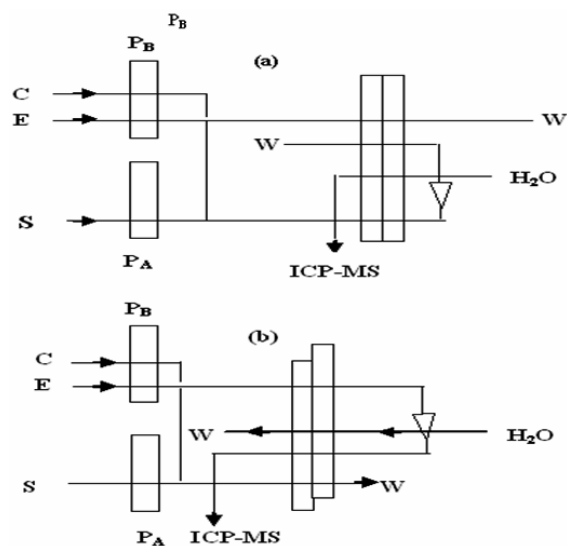


Fig.4: Manifold for on-line micro-column separation and preconcentration system coupled to ICP-MS:(a) Loading; (b) Injection; P_A , pump A; P_B , pump B; C, carrier (0.01 mol/l HCl); E, Eluent(2 mol/l HCl); S, sample solution; W, waste.

The micro-column was made from the tip of a plastic pipette commonly used in dropping of the sample in graphite furnace AAS. The sharp end of the conic column was fitted with 100-mesh nylon screen to retain the resin in the tubing, which was later sealed with a drop of cyclohexanone. With one end fitted with nylon screen, the column was filled with slurry of 60~100 mesh P_{507} resin by a syringe. Then some nylon screen was put on the resin surface and the micro-column was sealed. The total volume of the column was about 75 μl . The micro-column was then placed in the injector manifold in a position where

the sample was loaded in one direction (from sharp end to the other end) and eluted in the reverse direction. This counter-flow design prevented the resin from packing into one end of the column and was easy to elute the analytes from the column. The micro-column was ready for use after several alternating washings with eluent and rinsing solution.

Table-3: Operating parameters of ICP-MS instrument.

| Inductively coupled plasma | |
|----------------------------|---|
| Forward power/w | 1100 W |
| Coolant flow rate (Ar) | 15.0 l/min |
| Auxiliary flow rate (Ar) | 1.20 l/min |
| Nebulizer flow rate(Ar) | 0.92 l/min |
| Sampling conditions | |
| Sampling cone orifice(Ni) | 1.1 mm |
| Skimmer cone orifice (Ni) | 0.9 mm |
| Nebulizer | cross-flow |
| Spray chamber | Scott dual-Channel |
| Sample uptake | 1.5 ml/min |
| Signal processing | |
| Isotopes monitored | ¹³⁵ Ba, ¹⁴⁷ Sm, ¹⁵¹ Eu |
| Data acquisition | peak hopping |
| Dwell time | 50 ms·AMU ⁻¹ |
| Sweeps | 3 |
| Resolution | standard |
| Replicate | 1 |

Chemicals

HNO₃ and HF are both MOS grade and were from Beijing Chemical Reagent Research Institute (Beijing, China). HCl of suprapure grade was from Beijing Huazhun Science and technology development department (Beijing, China.). HClO₄ of guaranteed grade was from Beijing Nan Shang Le Chemical Plant (Beijing China). Water of 18.2 mΩ·cm was from a Milli-Q water system. P₅₀₇ resin (60-80mesh) was purchased from Yuelong Metal Company of Shanghai. 1.0 mg/ml of each standard solution of Sm, Eu and Ba were from National research center of standard materials(Beijing, China). Samarium, europium and Barium standard solutions with appropriate concentrations used in this study were prepared by sequential dilution of the standard stock solutions with 0.01 mol/l HCl. GBW 07605 tea certified standard material from State Bureau of Metrology(Beijing, China) was used to verify method accuracy.

Sample Preparations

Wheat samples were collected from the mature wheat in wheat field, Zizhen, Lixian, Shandong Province, China. The samples were ground in mill and sieved to obtain particles of 0.25 mm in diameter. They were dried for 6 hours at 60 °C before use. 0.1 g dried samples were weighed accurately into a 30 ml PTFE vessel. After 3 mL HNO₃, 0.4 ml HClO₄ and 0.1mL HF was added, the cap for the

PTFE vessel was tightened. The PTFE vessel was put in a stainless airtight vessel. Then the stainless vessel was heated at 170 °C in a oven for 6 h and then the PTFE vessel was placed on a hot plate (at about 120 °C) after the cap was removed. When the solutions were evaporated to dryness, 0.4 ml HClO₄ was added. When the solutions were evaporated to dryness again, the residue was solubilized with 10 ml 0.01 mol/l HCl.

Procedure

The manifold was set up as shown in Fig. 4 and FI-3100 program and the sequence of operation with solution uptaking rate (ml/min) and function actuated time (seconds) were shown in Table-4. In the equilibration stage, the pump B activated and the valve was in the loading position. The micro-column was conditioned by the carrier (0.01 mmol/l HCl). In the pre-filling stage, pump A activated and pump B stopped and the valve was changed to the injection position. The tubing was filled with sample solution. This stage was used for flushing the line from sample up to the injector valve when a new sample was introduced. In preconcentration step, the valve was in loading position. The sample solution was pumped through the micro-column from the sharp end of the micro-column by pump A. In this step, Europium and samarium in the sample were adsorbed on the P₅₀₇ resin. In rinsing step, the valve was still in loading position, but pump A was stopped while pump B was activated, so that 0.01mol/l HCl was sucked through the micro-column to remove the residual sample matrix in the column and tubing. Meanwhile, Water of 18.2 mΩ·cm was introduced into ICP-MS system by the peristaltic pump inside the ICP-MS system to rinse the nebulizer, spray chamber and sampling cone. In the elution step, the valve was in injection position and a flow of 2 mol/l HCl was introduced by Pump B into the micro-column from the other end of the column to elute samarium and europium and carried it to ICP-MS system for detection.

Table-4: The operational procedure for flow injection separation and preconcentration.

| Step | Function | Valve position | Time/s | Pump active | Medium pumped | Flow rate ml/min |
|------|---------------|----------------|--------|----------------|---------------|------------------|
| 1 | equilibration | a | 20 | P _B | C | 4.0 |
| 2 | Prefilling | b | 10 | P _A | S | 4.0 |
| 3 | Loading | a | 120 | P _A | S | 4.0 |
| 4 | Rinsing | a | 30 | P _B | C | 2.25 |
| 5 | Elution | b | 90 | P _B | E | 1.5 |

C, carrier (0.01 mol/l HCl); E, Eluent(2 mol/l HCl); S, sample solution

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