

STUDY OF SEPARATION OF RUBIDIUM AND STRONTIUM BY ION-EXCHANGE CHROMATOGRAPHY IN HNO₃ AND HCl MEDIA FOR DETERMINATION OF THEIR CONTENT AND ISOTOPIC COMPOSITION USING ICP-MS

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ABSTRACT

Chromatographic methods for separation of rubidium and strontium from each other and from matrix on cationit resin Biorad AG 50Wx8, 200-400 mesh are proposed. The elements were determined by ICP-MS Agilent 7500a. Rubidium, strontium and some of other elements were absorbed to the resin in 0.7 M HNO₃ medium. Then, rubidium and strontium could be eluted at the same time or one after another with HCl solution, that has the different concentrations. The methods can be well applied for analysis of the content and isotopic composition of rubidium and strontium by ICP-MS.

Keywords. *ICP-MS, Biorad AG 50Wx8, content, isotopic composition, ion-exchange chromatography.*

I - INTRODUCTION

The content and isotopic composition of rubidium and strontium are important parameters for geochemistry, geochronology [3, 6]. The Rb-Sr age dating technique is often applied in geochronology to date both igneous and sedimentary rocks [3]. The strontium isotope ratio ⁸⁷Sr/⁸⁶Sr has been suggested to be a promising fingerprint for provenance identification. Sr-isotope stratigraphy is based on Sr-isotope measurements of marine fossils in conjunction with the changing Sr-isotopic composition of seawater through time to provide an age for the fossil. This technique can also be used to determine ages for of other geologic processes, such as dolomitization.

Isotope ratio studies are traditionally done by thermal-ionization mass spectrometry (TIMS) with very high accuracy but analyses

are time-consuming, fairly expensive and difficult to perform. Inductively coupled plasma-mass spectrometry (ICP-MS) provides the determinations of content and isotopic composition of the elements with high sensitivity and precision. Although this technique does not offer the same precision as TIMS, it has the advantage of high number of samples throughput and ease of operation. ICP-MS has been used in a variety of rubidium and strontium isotope studies, including provenance determination and geological studies [1, 6].

However, rubidium and strontium have the isotopes with the same mass - Rb and Sr, so the determination of rubidium and strontium could be a difficult task. The isobaric overlap of ⁸⁷Rb and ⁸⁷Sr can be avoided by separating rubidium and strontium before analysis [3, 4]. These elements can be separated by some ways such as solvent extraction, extraction-chromato-

graphy or ion-exchange chromatography but the latter is often applied the most. Jitka Mikova studied on separation of strontium continuously on two chromatographic columns with two kinds of resin Sr. spec and TRU. spec [5]. Christian Pin used PHOTI resin (or PHOZIR) for separation of Rb, Sr, Ba and Pb in geological samples [1]. Keizi Misawa separated Sr and the rare earth elements with Sr resin [7]. Ciro Teixeira Correia, W. Siebel,... have been using resin AG 50Wx8 for the same purpose [2, 8]. The separation of rubidium and strontium have been studied by the same authors on cationit resin Biorad AG W50x8, 200-400 mesh using HCl acid as an absorption medium as well an eluent [9].

This research focuses on separation of rubidium and strontium on cationit resin Biorad AG W50x8, 200-400 mesh in HNO₃ medium and using HCl solution as an eluent. The elements were then determined by ICP-MS Agilent 7500a.

II - EXPERIMENTAL

1. Instrumentation and reagents

- ICP-MS Agilent 7500a;
- Quartz-glass chromatography column;
- Cationit resin Biorad AGW50x8, 200-400 mesh;
- Rubidium standard solution for ICP-MS, 1 µg/ml;
- Strontium standard solution for ICP-MS, 1 µg/ml;
- Multi element standard solution for ICP-MS, 1 µg/ml (include As, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Mg, Mn, Nd, Ni, Pb, Rb, Se, Sm, Sr, Ti, U, V, Zn);
- HNO₃ 65%, HCl 37%: Supra pure, Merck;
- Ultra pure water 18.2 MΩ.

2. Method

⁸⁵Rb, ⁸⁶Sr, ⁸⁸Sr and isotopes of all elements in standard solutions were measured by ICP-MS

Agilent 7500a to evaluate the separation of rubidium and strontium on the resins. The experiments were carried out on a quartz-glass chromatography column with the internal diameter of 8 mm and 200 mm height. The column was filled with 5 gr. of previously washed Biorad AGW50x8, 200-400 mesh resin.

Mix standard solution of rubidium and strontium or multi element standard solution in 0.7M HNO₃ medium was loaded onto the column. The column was previously conditioned with 0.7 M HNO₃ solution. The standard solution passed through the column at the rate of 0.6 ml/min. The column was then rinsed with 0.7 M HNO₃ solution. The rinse solution passed through the column at the same rate. The effluent from loading and the rinse fractions were collected combined (combined solution) and measured to determine the elements.

The combined solution and each of 2.5 ml fractions of the elution solution were evaporated to dryness. The residues were again dissolved in 25 mL of 0.3 M HNO₃ acid and the solutions were measured by ICP-MS Agilent 7500a for determination of the elements.

III - RESULTS AND DISCUSSION

1. Investigation of optimal plasma operating parameters for measuring isotopes of rubidium and strontium by ICP-MS

The isotopes were measured on ICP-MS with mode ISOTOPE ANALYSIS. The parameters of ion lens, quadruple system, and detector are often fixed since the device was established. The plasma operating parameters were investigated to ensure the measures have high sensitivity and the lowest formation of poly-atom pieces.

The optimal main plasma operating parameters of the device for measuring the isotopes of rubidium and strontium are as follows:

Radio frequency power: 1530 W

Carrier gas flow rate: 1.22 L/min.

Sample depth: 6.0 mm

Peripump rate: 0.1 rps.

HNO₃ acid was chosen as the environment for sample solution. The acidic concentration of sample solution does not much influence the sensitivity of an analysis.

2. Study on separation of rubidium and strontium from each other

Mix standard solution of rubidium and strontium in 0.7 M HNO₃ medium (5 µg of each element) was loaded onto the column. Both of rubidium and strontium was not found in the combined solution. It proved that they were absorbed to the resin well.

The elements were eluted with 50 ml of 1.5 M HCl; 2.0 M HCl; 2.5 M HCl; 3.0 M HCl solution at the rate of 0.6 ml/min. All of these solutions could elute rubidium from the column and the recovery of rubidium was 92% (figure 1). Strontium was remained on the column, not eluted with 1.5 M HCl solution even 62.5 ml of elution solution was used. Strontium was eluted well with 2.0 M HCl; 2.5 M HCl; 3.0 M HCl solution. The recoveries of strontium were 92%. The elution of strontium began when the elution of rubidium had finished. The elution curves for rubidium and strontium were isolated from each other. They were far away in the case of using 2.0 M HCl solution as an eluent and had the

tendency to be more closed each other when the concentration of HCl solution was increased.

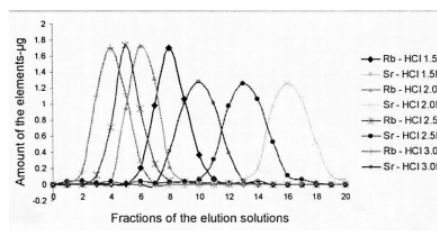


Fig. 1: Elution curves for Rb and Sr

When using 1.5 M HCl solution for eluting rubidium and then using 3.0 M HCl solution for eluting strontium, rubidium and strontium were separated well one after another. Furthermore, it was easier to execute the separation of rubidium and strontium by this way.

3. Study on separation of rubidium and strontium from matrix

Multi element standard solution (5 µg of each element) in 0.7 M HNO₃ medium was loaded onto the column. The combined solution was measured to determine the elements. The results (table 1) showed that almost of the elements in standard solution was absorbed to the resin except arsenic and selenium. These elements were not absorbed to the resin and washed out from the column.

Table 1: Amount of the elements found in the combined solution

Elem.	Amount, µg	Elem.	Amount, µg	Elem.	Amount, µg	Elem.	Amount, µg	Elem.	Amount, µg	Elem.	Amount, µg
Be	0.2	V	0.4	Co	0.2	Ga	0.2	Sr	0.1	Nd	0.1
Mg	0.6	Cr	0.2	Ni	0.2	As	4.8	Cd	0.2	Sm	0.1
Ca	0.3	Mn	0.3	Cu	0.1	Se	4-7	Cs	0.2	Pb	0.3
Ti	0.4	Fe	0.2	Zn	0.3	Rb	0.1	Ba	0.3	U	0.2

The elements were eluted with 50 ml of 1.5 M HCl solution at the rate of 0.6 ml/min. Rubidium and many of other elements were eluted. Their elution curves were shown in figure 2. Strontium, barium, samarium,

neodymium were remained on the column. There were the considerable amounts of beryllium, copper and vanadium and the certain amounts of cobalt, nickel, cesium in the fractions of rubidium. They will not influence

the determination of rubidium by ICP-MS if their amounts in the sample are not much larger than that of rubidium.

In the case of eluting the elements with 50 ml of 2.0 M HCl solution at the rate of 0.6 ml/min, rubidium, strontium and many of other elements were eluted. Their elution curves were shown in figure 3. Barium, samarium, neodymium were still remained on the column. There were the considerable amounts of cobalt, nickel and the certain amounts of beryllium, copper, vanadium, cesium and uranium in the fractions of rubidium. The elution of strontium began when the elution of almost all other elements had finished. The elution curve for strontium was isolated from those for other elements. By this way, strontium was separated well from rubidium and from almost all the elements involved in this study.

When using 50 ml of 2.5 M HCl solution as an eluent, the elution of the elements was almost the same in the case of using of 2.0 M HCl solution as an eluent. The difference was that strontium was eluted earlier.

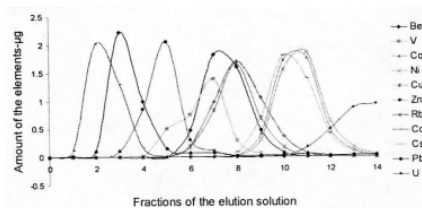


Fig. 2: Elution curves for the elements with 1.5 M HCl solution

Geological samples such as feldspar, k-feldspar, biotite and muscovite are often used for the Rb-Sr age dating technique in geochronology. These samples contain high contents of calcium and magnesium, those could affect rubidium and strontium elution. In order to test the effect of increased calcium and magnesium concentrations on the described separation method, mix standard solution containing 1 µg Sr, 7 µg Rb, 700 µg Ca, 700 µg Mg was loaded onto the column. The elements

were absorbed to the resin well.

The elements were first eluted with 1.5 M HCl solution. Rubidium and magnesium were completely eluted with 12 fractions of elution solution (30 ml of 1.5 M HCl solution) while calcium and strontium were remained on the column. Their elution curves were shown in figure 4. Rubidium and magnesium were eluted almost at the same time and magnesium did not affect Fig. 3. Elution curves for the elements with rubidium elution.

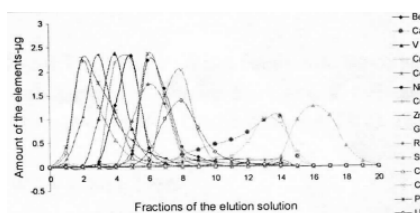


Fig. 3: Elution curves for the elements with 2.0 M HCl solution

The elements were then eluted with 3.0 M HCl solution. Calcium and strontium were completely eluted with 8 fractions of elution solution (20 ml of 3.0 M HCl solution). Their elution curves were shown in figure 5. The elution of strontium began as the elution of calcium had near finished, so there was not large amount of calcium in the elution fractions of strontium. The results show that calcium and magnesium with their large amount did not influence the separation of rubidium and strontium by ion-exchange chromatography with Biorad AGW50x8, 200-400 mesh resin and the determination of rubidium and strontium by ICP-MS.

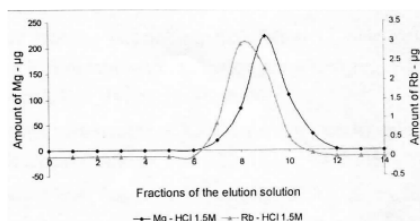


Fig. 4: Elution curves for Mg and Rb with 1.5 M HCl solution

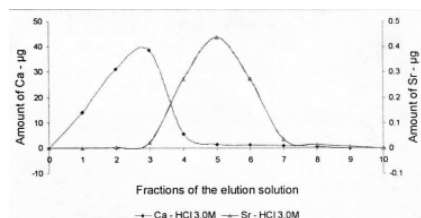


Fig. 5: Elution curves for Ca and Sr with 3.0 M HCl solution

IV - CONCLUSION

The methods for separation of rubidium and strontium from each other and from matrix on cationit resin Biorad AG 50Wx8, 200-400 mesh were investigated. Rubidium and strontium were well absorbed to the resin in 0.7 M HNO₃ medium. Strontium was eluted from the column with 3.0 M HCl solution after eluting rubidium and many of other elements with 1.5 M HCl solution. Rubidium and strontium were also eluted using 2.0M HCl solution as an eluent. By both ways, strontium was well separated from rubidium and from all other elements involved in this study but rubidium was not well separated from cobalt, nickel, beryllium, copper, vanadium, cesium and uranium. Anyway, these elements will not influence the determination of rubidium by ICP-MS if their amounts are not much larger than that of rubidium in the sample.

The methods can be well applied for

analysis of the content and isotopic composition of rubidium and strontium using ICP-MS.

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