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การวิเคราะห์ปริมาณธาตุหายากในแร่โมนาไซต์ของไทยโดยวิธี ICP และเทคนิคทางนิวเคลียร์

DETERMINATION OF RARE EARTH ELEMENTS IN THAI MONAZITE BY INDUCTIVELY COUPLED PLASMA AND NUCLEAR ANALYTICAL TECHNIQUES

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บทคัดย่อ: ได้ทำการวิเคราะห์หาปริมาณธาตุหายากในแร่โมนาไซต์ของไทยโดยวิธี ICP-AES เปรียบเทียบกับวิธีอาบรังสีนิวตรอน(INAA) และวิธีกระตุ้นด้วยรังสีเอกซ์(XRF) โดยได้ตรวจสอบความถูกต้องและความแม่นยำของวิธี INAA และ ICP-AES กับสารมาตรฐานโมนาไซต์ SRM IGS-36 จากการศึกษาพบว่าวิธี INAA ได้ผลวิเคราะห์ใกล้เคียงกับค่าที่รายงานไว้ ส่วนวิธี ICP-AES นั้นส่วนใหญ่ได้ผลวิเคราะห์ใกล้เคียงกับค่าที่รายงานไว้ยกเว้นบางธาตุที่มีความเข้มข้นต่ำๆ และได้ทำการวิเคราะห์ธาตุหายากในแร่โมนาไซต์ของไทยจำนวน 2 ตัวอย่าง ซึ่งทางศูนย์วิจัยและพัฒนาธาตุหายาก กองเคมี สำนักงานปรมาณูเพื่อสันติได้เตรียมขึ้นสำหรับใช้เป็นสารมาตรฐาน พบว่าผลการวิเคราะห์ของทั้ง 3 วิธีได้ผลใกล้เคียงกัน

Abstract: The inductively coupled plasma atomic emission spectroscopy (ICP-AES) for the determination of individual rare-earth elements (REE) was evaluated by comparison with instrumental neutron activation analysis (INAA) and x-ray fluorescence spectrometry (XRF) . The accuracy and precision of INAA and ICP-AES were evaluated by using standard reference material IGS-36, a monazite concentrate. For INAA, the results were close to the certified value while ICP-AES were in good agreement except for some low concentration rare earth. The techniques were applied for the analysis of some rare earth elements in two Thai monazite samples preparing as the in-house reference material for the Rare Earth Research and Development Center, Chemistry Division, Office of Atoms for Peace. The analytical results obtained by these techniques were in good agreement with each other.

Methodology: 1. INAA: 1.1 standard Preparation:- Standard of CeO_2, La_2O_3, Pr_6O_{11} and Nd_2O_3 were prepared by direct weighing of the spec-pure oxides into high purity polyethylene vials, and heat-sealed. Other minor and trace rare-earth elements were prepared by dissolving spec-pure oxides in HNO_3 , pipetting into polyethylene vials, evaporating to dryness then heat-sealed. 1.2 Samples Preparation:- 50 mg of Standard Reference material IGS-36 were weighed into a polyethylene vials, heat sealed and irradiated with the oxide standards in the TRR1/M1 reactor. After irradiation, the gamma activities of the samples and standards were measured. Short-lived nuclides of Dy and Nd were first determined after 2 minutes irradiation. After a few days cooling, the samples and standards were again irradiated for long half-life isotopes. **2. ICP-AES**: 2.1 Standards Preparation:- Standard solutions of all rare earth elements containing 100 ppm each were prepared by dissolving appropriate amount of specpure oxides in HNO_3. 2.2 Sample Preparation:- Prior to weighing, Standard Reference material IGS-36 and Thai monazites were dried at 120°C for 1 hr and let cool in dessicator. About 1 g. of sample was accurately weighed and digested with 10 ml of concentrate H_2SO_4 at 250°C for 2 hrs.. After cooling, a 50 ml aliquot of 5% HNO_3 was added to the digested slurry, filtered and washed with deionized water. The filtered solution was adjusted to 250 ml with 5% HNO_3. The aliquot was measured directly for Eu, Gd, Dy, and Yb; after 10 times dilution. for Y, La, Pr, Nd and Sm; after 25 times dilution and for Ce after 1,000 times dilution. **3. XRF**: Monazite samples from southern part of Thailand were grinded to -325 mesh and dried at 100°C . About 4 gm. of samples were then pressed into pellets with the size of 30 mm in diameter and 5 mm thick. It was kept in an plastic wrap, then measured by a wavelength dispersive X-ray Fluorescence Spectrometer.

Results and Discussion: The analytical results of some rare-earth elements in the standard reference material (IGS-36) by INAA and ICP-AES are given in Table 1. The concentration of rare earth elements in two Thai monazite samples by INAA, ICP and XRF are show in Table 2. Each standard and samples were prepared five times and analyzed five times. INAA method for the analysis of some rare earth elements has been successfully tested for SRM IGS-36. The observed values are close to the certified values except Ho, the error is probably due to direct weighing of standard oxides and also to the inhomogenity of neutron flux distribution. The results from ICP-AES method are close to the certified value except for Sm, Eu, Gd and Yb, these elements shown some deviations from the certified values. The selected procedures were applied for the analysis of some rare-earth elements in Thai monazite samples.

As seen from Table 2, The analytical results obtained by these three techniques are in good agreement with each other and compiled data. INAA has the advantage of being very sensitive and free from problems of reagent blank and contamination after sample irradiation. The disadvantages are the irradiation facilities, the exposure to ionizing radiations for the analyst, the special working conditions due to the radioactivity induced in the geological material and the long delay time. ICP has the advantages of no mainpulations of radioactive material, a greater speed of analysis and lower capital cost. The disadvantages are the risks of contamination during analysis and incomplete recovery, especially when acid-resistant accessory REE-rich minerals are present. It should be noted that in the ICP procedure, 1 g of sample were used while only 50 mg were necessary for INAA. This should not be considered as a disadvantage for sample, since large samples were generally available. Furthermore, a 1-g sample were more likely representative than a 50-mg sample. For XRF, samples were prepared and measured by Brucker Company, Germany. It need more sample than the others two methods (4 g). The advantage is the XRF method permits simultaneous determination of many elements. If there is no overlap of X-ray peak , the possibility of determining two neighboring elements will depend only on the resolution of the detector. The disadvantages are the matrix effect of the sample and geometrical measuring. However, the XRF results agreed with those of INAA and ICP.

References:

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Table 1. The concentration of some rare-earth elements in SRM IGS-36 by INAA and ICP- AES.

Elements	SRM IGS-36		
	INAA (%)	ICP-AES (%)	Reported (%)
CeO_2	24.60 ± 0.68	25.46 ± 0.09	24.92
La_2O_3	11.63 ± 0.36	11.99 ± 0.21	11.93
Pr_6O_{11}	2.85 ± 0.16	2.61 ± 0.14	2.795
Nd_2O_3	10.26 ± 0.54	10.56 ± 0.13	10.505
Sm_2O_3	1.48 ± 0.07	2.09 ± 0.03	1.54
Eu_2O_3	339 ± 22 (ppm)	431 ± 2.25 (ppm)	349 (ppm)
Gd_2O_3	0.776 ± 0.05	1.07 ± 0.03	0.77
Tb_4O_7	0.105 ± 0.015	n.a	0.11
Dy_2O_3	0.30 ± 0.02	0.33 ± 0.001	0.31
Ho_2O_3	366 ± 19 (ppm)	n.a	397 (ppm)
Yb_2O_3	305 ± 9.6 (ppm)	353 ± 2.06 (ppm)	295 (ppm)

Table 2. The average concentration of some rare-earth elements in Thai monazite sample by INAA, ICP-AES and XRF*.

Elements	Thai monazite No.475		
	INAA(%)	ICP-AES(%)	XRF(%)
CeO_2	25.46	25.95 ± 0.594	26.0
La_2O_3	10.80	12.20 ± 0.019	11.7
Nd_2O_3	10.73	10.26 ± 0.012	10.3
Y_2O_3	n.a.	2.59 ± 0.003	3.28
Pr_6O_{11}	n.a.	2.88 ± 0.006	2.91
Sm_2O_3	1.48	2.74 ± 0.004	2.58
Gd_2O_3	n.a.	1.48 ± 0.003	1.70
Dy_2O_3	0.541	0.64 ± 0.027	0.68
Er_2O_3	n.a.	n.a.	0.25
Yb_2O_3	n.a.	0.17 ± 0.007	0.23
Elements	Thai monazite No.476		
	INAA(%)	ICP-AES(%)	XRF(%)
CeO_2	25.89	23.70 ± 1.451	26.2
La_2O_3	11.26	11.97 ± 0.115	10.8
Nd_2O_3	9.91	9.13 ± 0.651	10.0
Y_2O_3	n.a.	2.66 ± 0.043	3.16
Pr_6O_{11}	n.a.	2.57 ± 0.114	2.91
Sm_2O_3	1.76	2.34 ± 0.232	2.12
Gd_2O_3	n.a.	1.36 ± 0.07	1.47
Dy_2O_3	0.527	0.65 ± 0.003	0.66
Er_2O_3	n.a.	n.a.	n.a.
Yb_2O_3	n.a.	0.15 ± 0.011	0.20

* Measured by Mr. Karl Mauser, Brucker Company, Germany
n.a = not available