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Application of ^{241}Am EDXRF to the determination of rare earth samples of solvent extraction processes

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Abstract

A rapid energy dispersive X-ray fluorescence spectroscopy (EDXRF) analysis system is established to determine rare earth concentrations. The characteristic K-shell series X-rays of rare earths were excited by a 1.1×10^9 Bq ^{241}Am radioisotope source. The spectra were recorded and analyzed using a multi-channel analyzer, employing a high-purity Ge detector. In this method, the Compton scattering peak, absorption of elements, and specific simplification are considered. Samples of light, middle and heavy rare earths during separation processes in both hydrochloride solution and rare earth loaded organic phases were analyzed off-line. Some comparative results measured by ICP are also given. The results show that the method can be used for a wide range of rare earth concentrations (0.1–300 g l^{-1} rare earth oxide). Being rapid, effective, precise and non-destructive, the method can be applied to on-line analysis to determine rare earth concentrations during separation by solvent extraction.

Keywords: ^{241}Am; Energy dispersive X-ray fluorescence spectroscopy; Rare earths

1. Introduction

Analytical methods for determining rare earths have been widely developed in recent years. Among these methods, energy dispersive X-ray fluorescence spectrometry (EDXRF) is frequently used for various kinds of rapid multi-element analyses. Because of the rare earth characteristic L series overlapping with the transition element K series peaks or the high brehmsstrahlung-produced background, rare earths are difficult to detect with X-ray tube excitation. Replacement with radioisotopes as excitation source is convenient because of the simple spectrum. From the many radioisotopes available, a ^{241}Am source with a photon energy of 59.6 keV and 458 year half-life makes it suitable for analyzing rare earths [1–5].

In this work, an ^{241}Am EDXRF fast rare earth analysis system is established to calculate the compositions of solutions of rare earth mixtures. Here, counts in the Kα_1 peak maximum of individual elements instead of the peak area, which was selected as the intensity, reduces the overlapping of Kα and Kβ to the smallest extent. Furthermore, two main factors, how to correct the absorption and how to deal with the background of the Compton scattering peak, are considered. Generally, the Compton scattering peak can be chosen as an inner standard to correct the absorption in light rare earth determination, but the overlapping of Kβ and the Compton limits the analysis to middle and heavy rare earths. Introducing an absorption function expands the intensity correction suitable for the measurement of light to heavy rare earths. In addition, strong Kα and Kβ can be used as analytical lines in heavy rare earth determinations.

2. Experimental

2.1. Devices

A block diagram of the ^{241}Am EDXRF system is shown in Fig. 1. The ^{241}Am source has an activity of 1.1×10^9 Bq (30 mCi). The active diameter of the high-purity Ge planar detector is 16 mm, the sensitive depth 10 mm, the detector-to-window distance 7 mm, and the resolution 190 eV at

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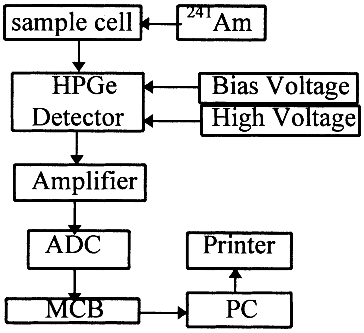

Fig. 1. Block diagram of the ^{241}Am EDXRF system.

5.9 keV. The arrangement of the detector is shown in Fig. 2.

2.2. Procedure

Both aqueous and the most common loaded organic phase solutions used in industry for individual lanthanides and mixtures were prepared. Solution (5.00 ml) was placed in a sampling cell and the data collected by an EG&G Ortec multi-channel analyzer controlled by a personal computer. The live time was preset to 300 s, and the remaining parameters were as follows: bias voltage, −1500 V; amplifier, coarse gain 20, fine gain 1.5; base line reduce, automatic pile zero; shaping time, 3 μs; input, norm.; uni shaping, Gaussian.

The unloaded organic phase and 0.5 M HCl are measured as reference solutions under the same conditions. The spectrum was recorded in a multi-channel buffer and transferred to a file to be treated. Typical spectra of light, middle and heavy rare earths are shown in Figs. 3–5, respectively.

2.3. Analysis method

The method of analysis can be described as follows: running the MCA software; recalling the spectrum of the sample against the blank; smoothing once; reading the counts in the channels which is the Kα_1 peak maximum of the lanthanides. For each individual lanthanide, we assume

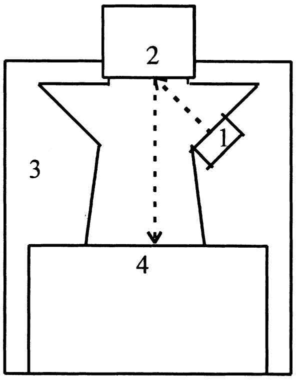

Fig. 2. Detector arrangement. (1) ^{241}Am source; (2) sampling cell; (3) Pb shielding; (4) HP Ge detector with Be window.

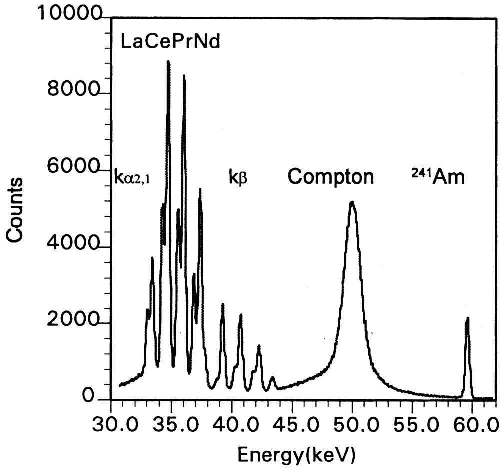

Fig. 3. Typical X-ray spectrum of light rare earths.

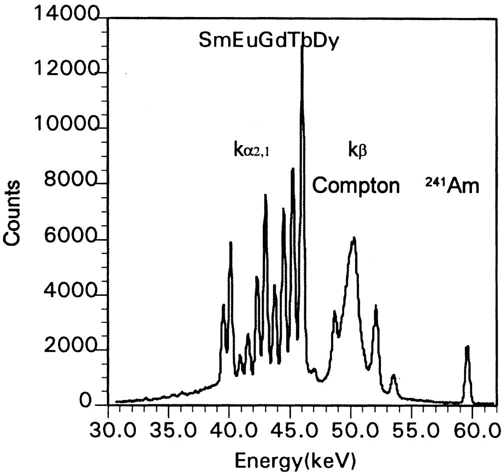

Fig. 4. Typical X-ray spectrum of middle rare earths.

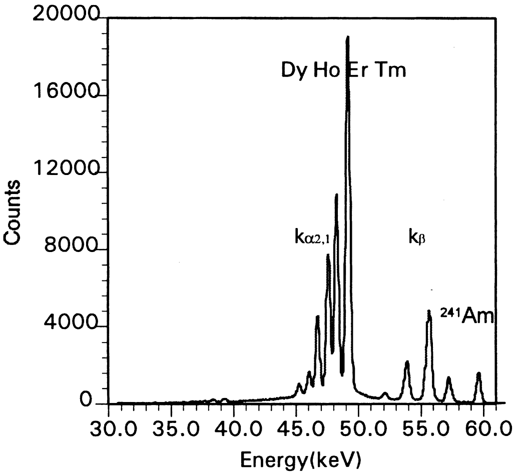

Fig. 5. Typical X-ray spectrum of heavy rare earths.

Table 1
Prepared and calculated concentrations of La

Counts	c_a (g l^{-1})	c_b (g l^{-1})	$(c_b - c_a)/c_a$
709	1.10	1.092	−0.73%
1098	1.75	1.702	−2.74%
2099	3.54	3.312	−6.44%
3920	6.60	6.393	−3.14%
6417	11.03	10.97	−0.54%
8686	15.81	15.52	−1.83%
12834	24.36	25.02	2.71%
16081	33.88	33.75	−0.38%
20138	46.51	46.73	0.47%
22798	56.83	56.85	0.04%
25172	67.56	67.24	−0.47%

c_a, prepared concentration; c_b, calculated concentration.

that the counts and the concentration obey the following equation:

$$y = \frac{(b + cx)}{(1 + ax)} \qquad (1)$$

where x and y are the lanthanide concentration and counts, respectively, and a, b and c are parameters to be optimized; $1/(1 + ax)$ is the absorption factor. The absorption corrected counts, Y, are linearly proportional to the rare earth concentration. That is:

$$Y = y(1 + ax) = b + cx \qquad (2)$$

For each lanthanide, the parameters are optimized by fitting the Kα_1 intensity and the corresponding rare earth concentration to Eq. (1). Assuming that the Kα_1 intensities of the other lanthanides also obey Eq. (1), the background is composed of the intensities. Therefore, a set of equations for each element can be obtained.

In a mixture sample, each Kα_1 intensity is the total contribution of the individual element in the mixture. The denominator in the absorption factor uses the total rare earth concentration C_T. The group equations can be set up by combining them for individual ones. The calculation can easily be realized in the program according to the following procedure: read out the intensity of each peak from the spectrum of the sample; calculate the initial concentration with the equation for the individual element; correct the concentration using the iteration method until the absolute deviation for each element concentration is less than 0.005 g l^{-1}.

3. Results and discussion

By applying the above method, both individual lanthanides and mixtures of light, middle and heavy rare earths in different media can be determined. Some results are summarized in Tables 1 and 2.

Table 1 shows that the absorption function can best be fit with the experimental data for La due to less interference. In producing pure lanthanide, the above described method is accurate for obtaining the element concentration. Table 2 suggests that increasing the absolute rare earth concentration improves the accuracy. The ICP results for the mixture samples are listed in Table 3. The precision is a bit lower than found in the present study. In our method, only one standard solution set was needed for determining

Table 2
Prepared and calculated concentrations of Sm–Dy

No.	c_{Sm} (g l^{-1})		c_{Eu} (g l^{-1})		c_{Gd} (g l^{-1})		c_{Tb} (g l^{-1})		c_{Dy} (g l^{-1})		c_T (g l^{-1})	
	a	b	a	b	a	b	a	b	a	b	a	b
1	11.85	11.71	4.09	4.03	20.06	19.2	39.88	38.65	4.15	4.12	80.03	77.71
2	11.96	11.66	3.97	3.86	16.32	15.89	28.15	28.62	20.36	20.04	80.76	80.07
3	11.96	11.92	3.97	3.85	16.32	15.82	15.84	15.71	31.63	30.92	79.72	78.22
4	11.96	11.77	3.97	3.92	16.32	15.62	19.94	19.90	28.49	28.05	80.68	79.26
5	0	0.10	0	−0.10	8.16	7.95	16.42	16.62	55.17	56.11	79.75	80.68
6	0	0.02	0	−0.02	4.08	3.97	11.73	12.26	63.43	64.12	79.24	80.35
7	0	0.01	0	−0.05	0	−0.12	8.21	8.13	71.46	72.14	79.67	80.11

a, prepared concentration; b, calculated concentration; $c_T = c_{Sm} + c_{Eu} + c_{Gd} + c_{Tb} + c_{Dy}$.

Table 3
ICP results for Sm–Dy

No.	c_{Sm} (g l^{-1})	c_{Eu} (g l^{-1})	c_{Gd} (g l^{-1})	c_{Tb} (g l^{-1})	c_{Dy} (g l^{-1})	c_T (g l^{-1})
1	13.30	3.98	18.20	36.70	8.44	80.62
2	13.10	3.91	15.00	27.30	22.20	81.51
3	12.90	3.87	15.30	16.00	31.40	79.47
4	13.80	3.85	14.4	20.20	30.40	82.65
5	3.01	0.26	7.68	16.60	54.70	82.25
6	2.96	0.24	4.27	12.20	61.80	81.47
7	2.83	0.23	0.73	8.94	68.70	81.43

$c_T = c_{Sm} + c_{Eu} + c_{Gd} + c_{Tb} + c_{Dy}$.

the composition of the mixture. If the percentage difference between two tested elements is too large, the accuracy in measuring the concentration of the smaller one will be lower. The component number in the system is another important factor affecting the precision of the calculation. Counts in the specific channels chosen as the intensity instead of peak area can greatly reduce the overlap of different elements. Calibrating the peak position with a known rare earth element can also simplify the procedure. Being rapid, non-destructive, etc., the method can be applied to the on-line analysis of lanthanides in industrial separation processes.

4. Conclusions

In the above analysis method, because the X-ray absorption of light element-containing media is quite weak, it is applicable for both aqueous and non-aqueous solutions. Therefore, some of the sample preparation steps can be omitted, and the speed of analysis can be accelerated. The $K\alpha_1$ energy of light rare earths is lower than that of the Compton scattering peak, thus Compton interference can be neglected. Besides the self-absorption correction of rare earths, the Compton peak intensity can also correct the absorption in the analysis. Using a ^{241}Am radioisotope source, the characteristic K series X-rays of the rare earths from La to Tm, including Y, can be effectively excited. Because the $K\alpha_1$ peaks of heavy rare earths overlap with the Compton scattering peak, measuring the $K\beta$ instead of the $K\alpha_1$ peak is more suitable. Rare earth (except for Sc, Yb and Lu) concentrations can be analyzed from their spectra. Two main influences in the analysis procedure are considered and overcome. By introducing absorption and background functions to correct the absorption, elemental interference has been solved. The results meet the requirements of rare earth on-line analysis.

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