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Abstract

Full Text

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CHEMISTRY

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A Reference-Free Quantitative Method for the Spectral Determination of Small Amounts of Impurities of Rare-Earth Elements

(Presented by Academician A. P. Vinogradov, 19 III 1960)

The well-known difficulties associated with the preparation of standards in the development and application of various methods of quantitative spectral analysis^(1,2) are especially acute because of the lack of the necessary amounts of pure preparations when developing various methods for the analysis of rare-earth elements⁽³⁾. The proposed method makes it possible to determine small amounts of impurities of rare-earth elements in pure preparations of these elements without the use of standards. The idea of the method consists in using two comparison lines. It can be applied to the development of reference-free methods for the analysis of other elements.

The ratio of the intensity of an analytical line to a comparison line for neutral atoms has the form (1):

$$\frac{I_{\ell}}{I_{\text{cp}}} = \frac{\alpha_{\ell}}{\alpha_{\text{cp}}} \frac{N_{\ell}}{N_{\text{cp}}} \frac{A_{\ell}}{A_{\text{cp}}} e^{-\frac{E_{\ell} - E'_{\text{cp}}}{kT}} \frac{h\nu_{\ell}}{h\nu_{\text{cp}}} C^b, \quad (1)$$

where E_{ℓ}, E'_{cp} are the excitation potentials, respectively, of the analytical line and the comparison line; K is Boltzmann's constant; T is the absolute temperature of the plasma; C is the content of the element in the sample; b is a coefficient characterizing self-absorption of the line and equal to unity at small C ; $\alpha_{\ell}, \alpha_{\text{cp}}$ are coefficients depending on the type of light source, the spectral apparatus, the method of introducing the sample into the arc gap, the processes occurring during the transition of the sample into vapor, etc.; $\nu_{\ell}, \nu_{\text{cp}}$ are the frequencies of the emitted lines; h is Planck's constant; A_{ℓ}, A_{cp} are the transition probabilities; N_{ℓ}, N_{cp} are the total numbers of unexcited atoms of the given elements in the arc plasma.

Equation (1) is the analytical expression of the calibration curve. As is evident, at an unchanged content of the element the relative intensity of the lines de-

depends substantially on the arc temperature, except for the rarely encountered practical case when $E_\ell = E'_{cp}$. Changes in current strength and in the values of the arc and discharge gaps lead to a substantial change in the arc temperature and, consequently, to a change in the relative intensities. This dependence is a difficult-to-control source of analytical errors and makes quantitative determination of elements without the use of standards impossible.

To take the temperature change into account, let us take one more comparison line, I''_{cp} , also belonging to the comparison element. Then

$$\frac{I''_{cp}}{I'_{cp}} = \frac{A''_{cp}}{A'_{cp}} \cdot e^{-\frac{E''_{cp} - E'_{cp}}{kT}}. \quad (2)$$

Eliminating the temperature from equations (1) and (2), we obtain

$$\lg C = \lg \frac{I_1}{I'_{cp}} + A \lg \frac{I''_{cp}}{I'_{cp}} + B, \quad (3)$$

where

$$A = -\frac{E_1 - E'_{cp}}{E''_{cp} - E'_{cp}},$$

$$B = A \lg \frac{A''_{cp}}{A'_{cp}} - \lg \left(\frac{\alpha_1}{\alpha_{cp}} \frac{N_1}{N_{cp}} \frac{A_1}{A_{cp}} \frac{h\nu_1}{h\nu_{cp}} \right).$$

The right-hand side of this equation does not depend on the arc temperature. Consequently, having once determined the coefficients A and B for a given instrument, the parameters of which are unchanged, one can subsequently determine the content of elements by means of formula (3) without using standards. The coefficients A and B are determined by solving a system of two equations for two values of the concentration C . The aim of the present investigation was the experimental proof that the right-hand side of equation (3) is independent of changes in the parameters determining the operating conditions of the light source.

Table 1

Dependence of the terms of equation (3) on the parameters of the light source

	Thulium in er- bium, λ_{Tu}	Thulium in er- bium, λ_{Tu}	Thulium in er- bium, λ_{Tu}	Thulium in er- bium, λ_{Tu}	Europium in gadolin- ium, λ_{Eu}	Europium in gadolin- ium, λ_{Eu}	Europium in gadolin- ium, λ_{Eu}	Europium in gadolin- ium, λ_{Eu}
Parameters of the alternating current arc	$3362,6;$ λ'_{Er} $3369,2;$ λ''_{Er} $3368,0;$ $lg \frac{I_{Tu}}{I'_{Er}}$ $A lg \frac{I''_{Er}}{I'_{Er}}$	$3362,6;$ λ'_{Er} $3369,2;$ λ''_{Er} $3368,0;$ $lg \frac{I_{Tu}}{I'_{Er}} +$ $A lg \frac{I''_{Er}}{I'_{Er}}$	$3362,6;$ λ'_{Er} $3369,2;$ λ''_{Er} $3368,0;$ $lg \frac{I_{Tu}}{I'_{Er}} +$ $A lg \frac{I''_{Er}}{I'_{Er}}$	$3362,6;$ λ'_{Er} $3369,2;$ λ''_{Er} $3368,0;$ B	$4435,5;$ λ'_{Gd} $4437,4;$ λ''_{Gd} $4431,4;$ $lg \frac{I_{Eu}}{I'_{Gd}}$ $A lg \frac{I''_{Gd}}{I'_{Gd}}$	$4435,5;$ λ'_{Gd} $4437,4;$ λ''_{Gd} $4431,4;$ $lg \frac{I_{Eu}}{I'_{Gd}}$ $A lg \frac{I''_{Gd}}{I'_{Gd}}$	$4435,5;$ λ'_{Gd} $4437,4;$ λ''_{Gd} $4431,4;$ $lg \frac{I_{Eu}}{I'_{Gd}} +$ $A lg \frac{I''_{Gd}}{I'_{Gd}}$	$4435,5;$ λ'_{Gd} $4437,4;$ λ''_{Gd} $4431,4;$ B
$I_1 =$	$0,05 \pm$	$0,18 \pm$	$0,23 \pm$	$-1,77 \pm$	$0,08 \pm$	$0,23 \pm$	$0,31 \pm$	$-1,69 \pm$
5 a	$0,02$	$0,02$	$0,05$	$0,05$	$0,02$	$0,02$	$0,04$	$0,04$
$I_2 =$	$0,09 \pm$	$0,13 \pm$	$0,22 \pm$	$-1,78 \pm$	$0,12 \pm$	$0,20 \pm$	$0,32 \pm$	$-1,68 \pm$
14 a	$0,02$	$0,02$	$0,04$	$0,04$	$0,02$	$0,02$	$0,04$	$0,04$
$l_1 =$	$0,10 \pm$	$0,13 \pm$	$0,23 \pm$	$-1,77 \pm$	$0,14 \pm$	$0,18 \pm$	$0,32 \pm$	$-1,68 \pm$
3,5 mm	$0,02$	$0,02$	$0,04$	$0,04$	$0,02$	$0,02$	$0,04$	$0,04$
$l_2 =$	$0,21 \pm$	$0,04 \pm$	$0,25 \pm$	$-1,75 \pm$	$0,26 \pm$	$0,06 \pm$	$0,32 \pm$	$-1,68 \pm$
8 mm	$0,02$	$0,01$	$0,03$	$0,04$	$0,02$	$0,02$	$0,04$	$0,04$
$d_1 =$	$0,23 \pm$	$0,02 \pm$	$0,25 \pm$	$-1,75 \pm$	$0,28 \pm$	$0,05 \pm$	$0,35 \pm$	$-1,65 \pm$
0,5 mm	$0,02$	$0,01$	$0,03$	$0,04$	$0,02$	$0,02$	$0,04$	$0,04$
$d_2 =$	$0,09 \pm$	$0,15 \pm$	$0,24 \pm$	$-1,76 \pm$	$0,12 \pm$	$0,19 \pm$	$0,31 \pm$	$-1,69 \pm$
0,1 mm	$0,01$	$0,02$	$0,03$	$0,04$	$0,02$	$0,02$	$0,04$	$0,04$

Note. I_1, I_2 are the current strength; l_1, l_2 are the interelectrode distance; d_1, d_2 are the discharge gap of the activator.

Table 1 gives experimental data for cases of determining small amounts of thulium in erbium and europium in gadolinium (the apparatus and preparation of samples for analysis are analogous to those described in (3)). As can be seen, the first two terms of the right-hand side of equation (3) each undergo substantial changes when passing from one mode of operation of the source to another, whereas the sum of these terms and the coefficient B remain unchanged within the measurement error. This circumstance made it possible to use—

Table 2

Comparison of the results of analysis of rare-earth elements by the standardless method

Introduced Tu in Er, %	Found by the stan- dardless method, %	Deviation	Introduced Eu in Gd, %	Found by the stan- dardless method, %	Deviation
0,010	0,011	+0,001	0,010	0,009	-0,001
0,015	0,014	-0,001	0,015	0,014	-0,001
0,01	0,10	0	0,10	0,11	+0,01

use the coefficient values found for further analysis without the use of standards. The studies showed that the root-mean-square error of a single determination, by the standardless method, of small amounts of rare-earth-element impurities in pure preparations of these elements is $\pm 15\text{--}20\%$.

Table 2 gives, for comparison, the results of determining thulium in erbium and europium in gadolinium by the standardless method. As can be seen from the table, within the limits of error the analytical data agree with the amounts introduced.

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CITED LITERATURE

1. S. L. Mandelstam, *Introduction to Spectral Analysis*, Moscow, 1946.
2. L. S. Lomonosova, O. B. Falkova, *Spectral Analysis*, Moscow, 1958.
3. T. I. Grishina, *ZhAKh*, **14**, No. 4 (1959); in: *Rare-Earth Elements*, Publishing House of the Academy of Sciences of the USSR, 1958, p. 256.

Note: Figure translations are in progress. See original paper for figures.

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