

Instytut Chemii UMCS
Zakład Chemii Nieorganicznej i Ogólnej

Janina WYSOCKA-LISEK, Zofia RZĄCZYŃSKA, Barbara PASZKOWSKA

Spectrographic Determination of Rare Earth Elements on Molybdenum Electrodes

Spektrograficzne oznaczanie pierwiastków ziem rzadkich na elektrodach molibdenowych

Спектрографическое определение редкоземельных элементов с применением молибденовых электродов

Exciting the rare earth elements emission spectra between graphite, cupric, aluminium, nickel and molybdenum electrodes a very distinct matrix effect has been observed [1-3]. In the case of C-, Cu-, Al- and Ni-electrodes the thermochemical reactions on their surfaces can be seen.

Esko Saari [4] investigated the thermochemical reactions of 15 rare earth oxides with graphite powder exciting them in d.c. arc, under conditions generally accepted in the spectrographic analysis of the rare earth elements. The formation of RC_2 (R - rare earth element) type carbides is dominant under given conditions. Only lutecium is found in part to be present in the form of Lu_2C_3 . Also Eu, Sm, Yb and Tm differ from the remaining rare earth elements in it that their reduction is characterized by the reaction which leads to formation of metal itself.

The investigation of rare earth elements thermochemical reactions excited on Cu-, Ni- and Al-electrodes [5] proved the formation of R_2CuO_4 , R_2NiO_4 as well as $RAIO_3$ (which are more stable for ceric group element) with the material of the electrodes. These observations agree with the literature data [6-12] for high temperature reactions of Cu, Ni and Al oxides with the rare earth oxides.

In the case of molybdenum electrodes, the formation of different compounds only among the excited rare earth elements has been observed [13]. It seems that the molybdenum electrodes do not take part in the thermochemical reactions with rare earth oxides under conditions of excitation.

The differences in the formation of carbides, R_2CuO_4 , R_2NiO_4 and $RAIO_3$ for different rare earth elements may give the additional matrix effect in their spectrographic determination. While using the molybdenum electrodes the matrix effect is expected to be due only to thermochemical reactions among the excited rare earth elements. For this

reason the molybdenum electrodes were used for spectrographic determination of rare earth mixtures in the present study.

EXPERIMENTAL

Spectrographic equipment. The grating spectrograph PSG-2 type in the second range spectrum was used. Spectra were excited in the intermittent a.c. arc of 4.6 or 6.6 Å with the aid of ABR-3 generator. Spectrograms were evaluated by photometric measurements on the W and D scales. All the instruments were produced by C. Zeiss.

As the auxiliary electrodes, for the interrupted feeding of a solution into radiation source, molybdenum rods 'specpure' (J. Matthey) were used, 20 mm in length and 5 mm in diameter, with planar and truncated cone ends. All spectra were photographed on the ORWO WO-3 spectral plates at 20 s time exposure.

To prepare the standard solutions the following substances were used: La_2O_3 , Pr_6O_{11} , Gd_2O_3 , Er_2O_3 prepared by rare earth mixtures separation in the Inorganic Chemistry Department, UMCS, Lublin; Nd_2O_3 , Sm_2O_3 , Dy_2O_3 puriss. (99.9%) made by Fluka AS, Buchs SG; Y_2O_3 prepared by rare earth mixture separation in the Rare Earth Elements Laboratory, UAM, Poznań; $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ *pro analysis* made by Riedel E. de Haën.

The choice of the analysis lines. As the rare earth elements spectra are very complex and of great number of lines, the choice of analysis lines for eight-component mixtures is very difficult because of the coincidence possibility. In the range of 360 to 450 nm, also molybdenum has its own rich spectrum, but PGS-2 spectrograph gives the possibility of the photometric measurements for two lines when the difference between their wavelength is not smaller than 0.015 nm. Using atlases [14, 15] and tables [16, 17] of different authors, coincidence probability and choice of the lines were carefully established.

In the case of the coincidence between intensive and weak lines of a rare earth element, the presence of other lines on the spectrogram with the same intensity of a coinciding element has been verified. In this way the lines of a high and moderate intensity were chosen for the photometric measurements and they are listed in Table 1.

Table 1. Set of spectral lines chosen for photometric measurements for rare earth after [16] and for manganese after [17]

Element	λ nm	IA	IS	J
Yttrium	417.414	5	3	I
Yttrium	371.030	10	20	II
Lanthanum	388.636	6	7	II
Praseodymium	410.074	9	10	II
Praseodymium	398.206	9	6	II
Neodymium	401.225	10	10	II
Samarium	425.639	6	7	II
Gadolinium	376.839	10	10	II
Dysprosium	404.599	10	5	I
Dysprosium	421.175	10	8	I
Erbium	390.634	5	6	II
Manganese	379.022	30		I
Manganese	370.607	24		I

Sampling and solution preparation. For measurements there were prepared eight-component standard samples of rare earth chloride mixtures. Y, La, Pr, Nd, Sm, Gd, Er and Dy were in turn a matrix element, and seven others were additional elements. The concentration of the matrix element increased from 16, 30, 51, 72 to 86 per cent of oxide, and the concentration of the seven additional elements decreased from 12, 10, 7, 4 to 2 per cent for the oxide of each element. Manganese chloride added both to the standard and analysed solutions was used as the internal standard.

The thin salt layers obtained by drying the solution transferred on the surface of the molybdenum electrodes, were excited in the intermittent a.c. arc. Each reference solution was transferred on 5 electrodes, and hence the results of the photometric measurements are the arithmetical mean value of 5 parallel excitation data.

In order to transform the photometric measurements of the photographed spectral line blackening, the calibration curves of the spectral plates were plotted on the basis of the multiplet of the iron lines in the range of 375 to 383 nm [18]. The gamma coefficients of spectral plate emulsion were in the range of 0.76 to 0.83.

For all chosen analytical spectral lines of rare earth elements, analytical curves were plotted by means of the pairs of values: $\log c$ and $\Delta W_{R/Mn}$ pertaining to the reference samples. Some analytical curves were also plotted by means of $\log c$ and I after the plate calibration.

Photometric measurements. In order to verify the use of manganese as the internal standard its spectral lines were photometred on D scale. On D scale the lines of all rare earth elements in the standard samples were also measured in order to estimate the differences of line intensities versus the increasing concentration of the element. All the measurements were carried out by simultaneously taking into account the blackening of emulsion close to the measured lines.

Then analogous measurements were carried out on scale W in order to select the analytical curves. The results of the photometric measurements are presented on the diagrams showing the course of manganese line intensity and that of the analysed rare earth element lines.

Quantitative determination of rare earth element concentration in the mixtures was accomplished by recording the standard (with corresponding matrix element) and analysed mixtures on the same plate. The results of quantitative analytical determination are shown in Table 2.

RESULTS

Using the Czakow and Steciak [19] formula the a values corresponding to relative line intensity were calculated taking into account the background close to the line,

$$a = \frac{D_t}{D_{l+t}} - 1$$

where D_t – transparency of background, and D_{l+t} – transparency of line with the background.

Table 2. Comparison of the determination results for: Y, La, Pr, Nd, Gd from analytical curves drawn on coordinates ΔW and I versus $\log c$

Determined oxide	Anal. curve kind	Oxide % and samples number						Matrix compon.
		1	2	3	4	5	6	
Y ₂ O ₃	ΔW	0.6	1.9	0.8	0.7	-----	1.0	Pr ₆ O ₁₁
	I	1.8	2.0	0.6	0.5	-----	1.2	
Y ₂ O ₃	ΔW	17.8	-----	1.2	1.0	10.0	6.6	Nd ₂ O ₃
	I	20.0	-----	1.8	1.6	12.5	7.9	
La ₂ O ₃	ΔW	-----	-----	-----	31.6	-----	27.5	Pr ₆ O ₁₁
	I	-----	-----	-----	32.3	-----	28.2	
La ₂ O ₃	ΔW	1.8	-----	1.7	39.8	32.4	-----	Nd ₂ O ₃
	I	1.6	-----	1.6	34.9	34.7	-----	
Pr ₆ O ₁₁	ΔW	-----	15.1	8.1	14.5	9.8	-----	La ₂ O ₃
	I	-----	15.1	7.9	14.8	10.2	-----	
Nd ₂ O ₃	ΔW	9.5	9.5	16.6	34.6	23.4	-----	La ₂ O ₃
	I	9.5	9.8	17.7	33.8	22.4	-----	
Gd ₂ O ₃	ΔW	1.6	2.1	16.6	2.4	-----	15.4	Nd ₂ O ₃
	I	1.3	1.5	14.8	2.5	-----	15.5	

On the basis of calculated a_{Mn} values the diagrams (Fig. 1) were made in order to investigate possible changes of manganese spectral line intensity versus the concentration and kind of matrix element.

The diagrams (Fig. 1) show that intensity variations of the main component affect slightly the a_{Mn} and they are within the limits of the measurement error.

If samarium or gadolinium are the main components, the spectral line intensity of manganese linearly decreases with an increase of the concentration of the main component, and, thus, it is possible to use the manganese lines to draw analytical curves $\Delta W_{R/Mn}$ versus $\log c$.

Distinct variations of manganese line intensity depend on the kind of a main component. The a_{Mn} value is the lowest in the presence of praseodymium and dysprosium, and the highest one in the presence of neodymium.

The manganese spectral line intensities calculated from the calibration curves of the spectral plates (Fig. 2) confirm the application of manganese lines as the internal standard lines in the multi-component rare earth mixtures. A relationship of the a values of several rare earth elements to their concentration, as the additional components including the main components, is shown in Figs. 3 and 4.

A comparison of spectral line intensity and element concentration changes show sufficiently considerable differentiation of the spectral line sensitivity depending on the kind of the main component.

Independently from the matrix component only samarium shows the weakest sensitivity during the excitation in the molybdenum arc. The praseodymium spectral lines are

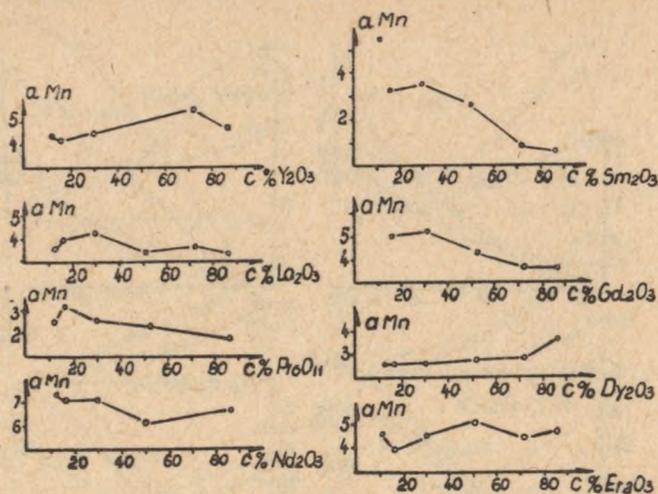


Fig. 1. a values of manganese spectral line versus concentration of a matrix component in the mixtures

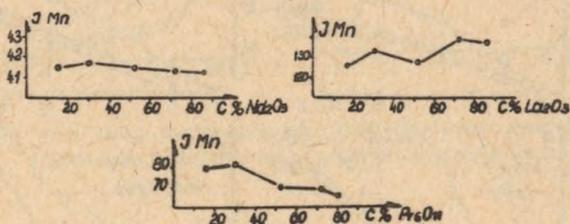


Fig. 2. J_{Mn} values versus concentration of praseodymium and neodymium as the matrix components in the mixtures

of similar sensitivity as those of samarium when erbium is the main mixture component. In other cases their sensitivity is higher. The lines of dysprosium have low sensitivity in the presence of high concentrations of lanthanum, neodymium, gadolinium and erbium. One can observe high sensitivity of lanthanum and erbium lines in the presence of samarium, gadolinium, yttrium and neodymium as the matrix elements.

Neodymium has lines of rather high sensitivity in the presence of yttrium, praseodymium, gadolinium and dysprosium. Gadolinium has also lines of high sensitivity in the presence of samarium, yttrium and neodymium. The spectral lines of other elements have medium sensitivity in the presence of different matrix elements.

The above mentioned measurements of a values were preliminary in estimating the possibility of analytical curve construction. The diagrams of Figs. 5 and 6 give the set of analytical curves for standard mixtures of different matrix components.

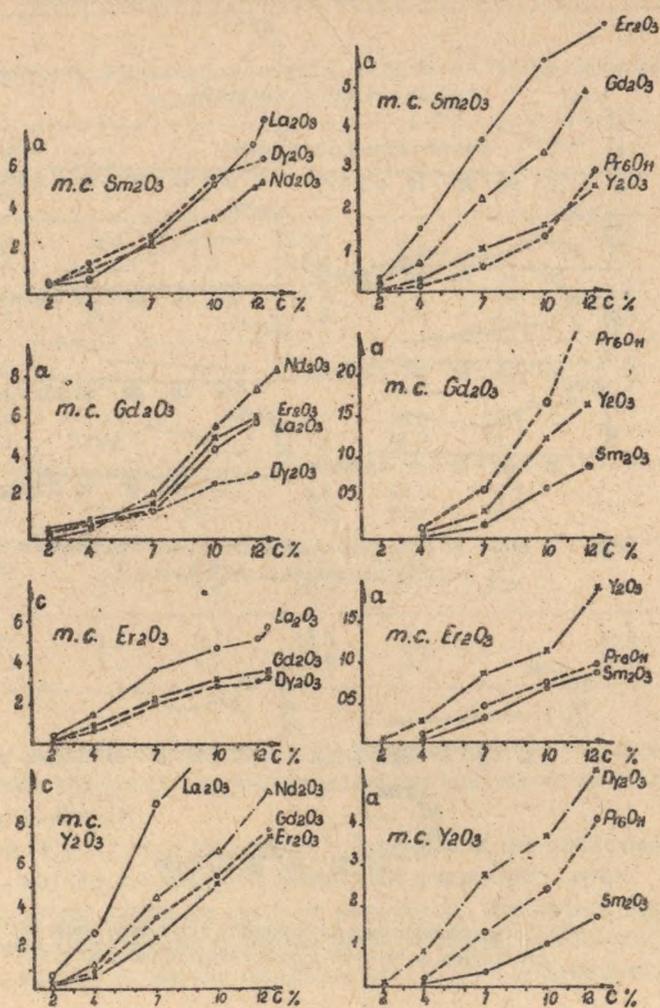


Fig. 3. *a* values inconstancy of additional element spectral line intensities in dependence of a matrix component (m.c.)

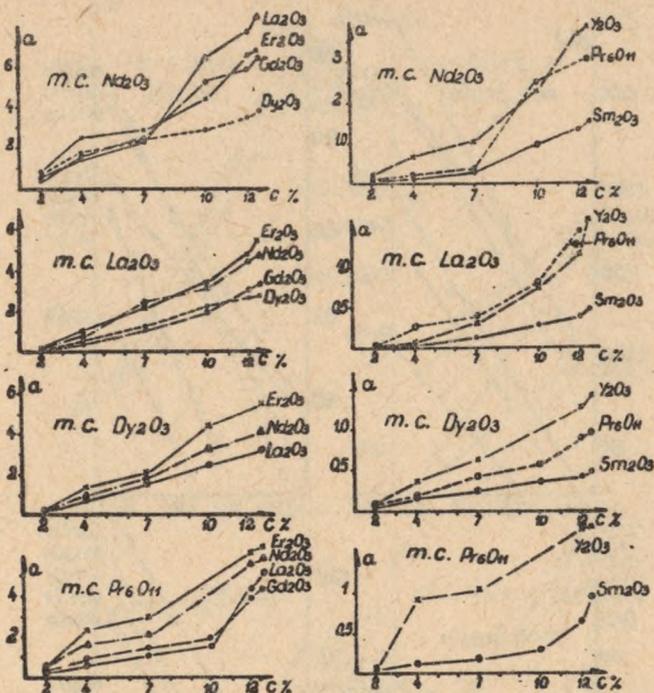


Fig. 4. a values inconstancy of additional element spectral line intensities in dependence of a matrix component (m.c.)

The analytical curves drawn in the coordinates $\Delta W_{R/Mn}$ and $\log c$ have mainly similar slopes and are often parallel. Some deviations are observed in the curves of the spectral lines of praseodymium, dysprosium and lanthanum in the presence of dysprosium, gadolinium and samarium, respectively.

In order to verify the correctness of analytical curves, plotted on the coordinates $\Delta W_{R/Mn}$ and $\log c$, after the plate calibration, they are drawn on the coordinates I and $\log c$. Some of them are given in Fig. 7. Partial rectilinearity of these analytical curves confirms the usefulness of the molybdenum electrodes in the analyses of the mixtures of rare earth compounds.

The results of a quantitative determination of some rare elements in the mixtures with lanthanum, praseodymium and neodymium as the matrix elements are given in Table 2. The table includes the comparison of the results obtained with both kinds of the analytical curves. The deviations between the values of praseodymium and neodymium, in the five mixtures with lanthanum as the matrix element, show a good agreement.

In Y, La and Gd determinations, the deviations of the results may be higher, particularly with an increase of the analysed concentration.

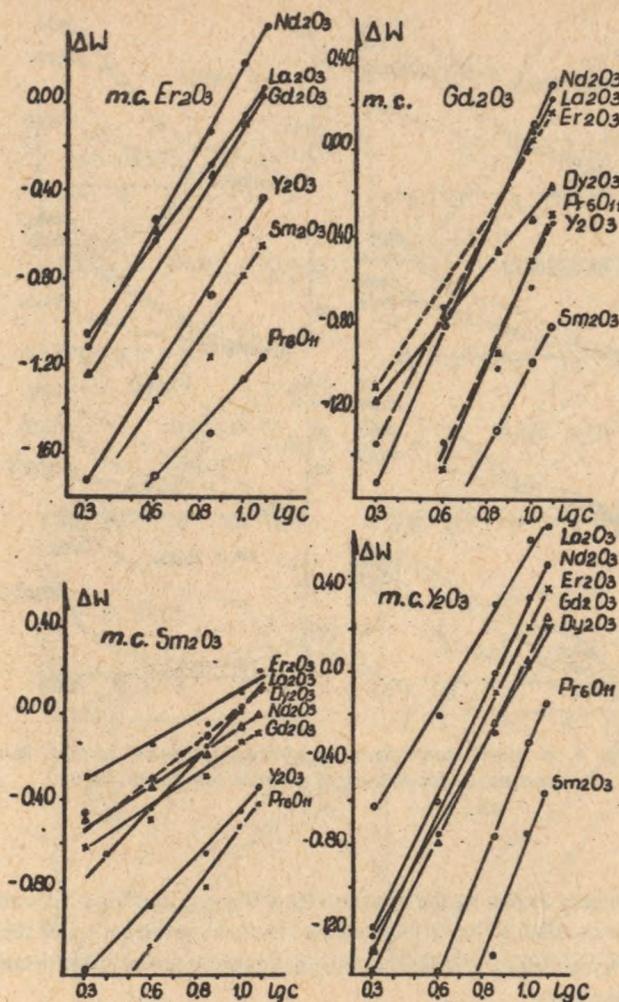


Fig. 5. Analytical curves plotted on coordinates $\Delta W/R/Mn$ and $\log c$ for Y, La, Pr, Nd, Sm, Gd, Er and Dy in the presence of erbium, gadolinium, samarium and yttrium as the matrix components

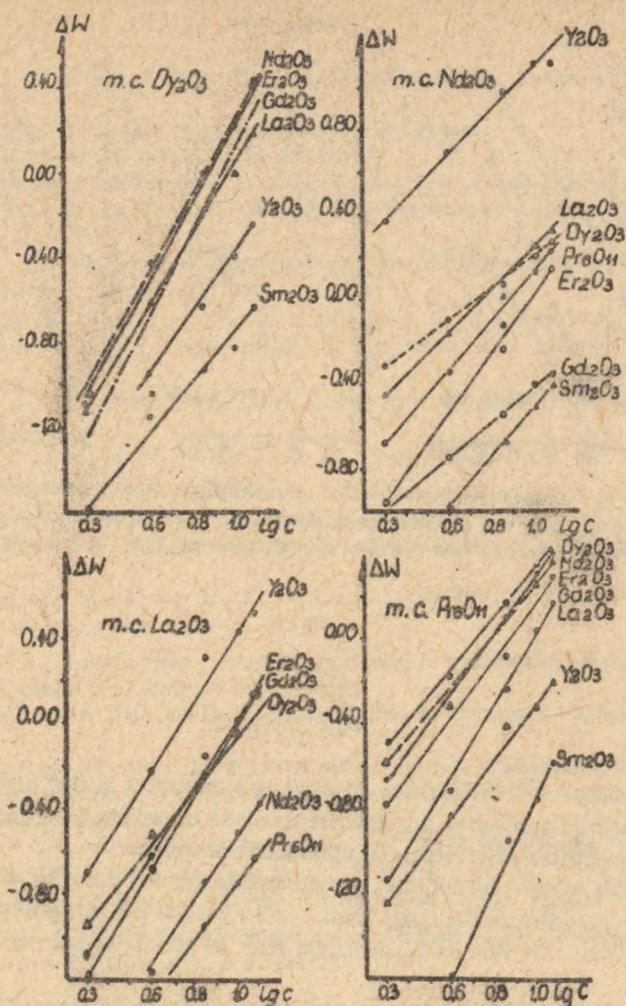


Fig. 6. Analytical curves plotted on coordinates $\Delta W/R/Mn$ and $\log c$ for Y, La, Pr, Nd, Sm, Gd, Er and Dy in the presence of lanthanum, praseodymium, neodymium and dysprosium as the matrix components

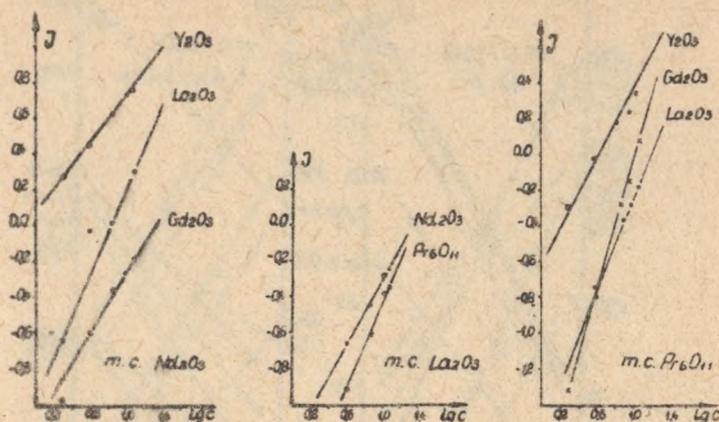


Fig. 7. Analytical curves plotted on coordinates J and $\log c$ for Y, La, Gd, in the presence of neodymium; for Pr, Nd in the presence of lanthanum; for Y, La, Gd in the presence of praseodymium as the matrix components

CONCLUSIONS

As the deviation of manganese spectral line intensity is not high (Figs. 1 and 2), manganese may be applied as the internal standard in the spectrographic analyses of rare earth multicomponent mixtures on molybdenum electrodes.

On the basis of the photometric measurements (partial linearity of analytical curves) one may conclude that in the range from 2 to 15% oxide concentration, and even in higher concentrations, the rare earth elements may be estimated on the molybdenum electrodes.

However, if the number of additional components is different in the standard and analysed substances, the results of the estimation of some elements (for example yttrium in the praseodymium-rich mixtures) may be erroneous because of the matrix effect. Just for that reason it is necessary to use appropriately analogous standard samples for different analysed mixtures.

REFERENCES

1. Wysocka-Lisek J., Mazur J.: Ann. Univ. M. Curie-Skłodowska, Lublin, sectio AA 28, 229 (1973).
2. Wysocka-Lisek J., Kosmala F.: *ibid.* 26/27, 159 (1971/72).
3. Wysocka-Lisek J.: *ibid.* 28, 267, 273, 284, 293 (1973).
4. Esko Saari: Ann. Acad. Sci. Fennicae Ser. A, II, *Chemica*, 174, (37 pp), Helsinki 1974.
5. Wysocka-Lisek J., Sroka T.: Ann. Univ. M. Curie-Skłodowska, Lublin, sectio AA 33, 123 (1978).
6. Леонов А. И.: Высокотемпературная химия кислородных соединений церия. Изд. „Наука”, Ленинград 1970.
7. Торопов Н. А., Бондар И. А., Лазарев А. Н., Смолин Ю. И.: Силликаты редкоземельных элементов и их аналогии. Изд. „Наука”, Ленинград 1971.
8. Kenjo T., Yajima S.: Bull. Chem. Soc. Jap. 46, 2619 (1973) — Реф. жур. хим. 6 В 538 (1974).
9. Савченко В. Ф., Рубинчик И. С., Павлюченко М. М.: Изв. АН ВССР, сер. хим. нау. № 6, 11 (1973).
10. Longo J. M., Raccach P. M.: J. Solid State Chem. 6, 526 (1973).
11. Goudenough M. M. J. V., Démazeau G., Pouchard M., Hagemüller P.: J. Solid State Chem. 8, 325 (1973).
12. Arjomand M., Machin D. J.: J. Chem. Soc. Dalton Trans., No 11, 1055, 1081 (1975) — Р. жур. хим. 24 В 19, 20 (1975).
13. Wysocka-Lisek J.: Badanie efektu matrycowego w analizie spektrograficznej pierwiastków ziem rzadkich, UMCS, Lublin 1977 (docent's dissertation).
14. Gatterer A., Junkes J.: Atlas der Restlinien, Italia, Specola Vaticana, Bd II, Spektren der Selten Erden, 1945.
15. Idzikowski A., Gądek S., Mleczko W.: Atlas widm łukowych 70 pierwiastków do spektrografu dyfrakcyjnego. Prace Nauk. Inst. Chemii Nieorganicznej i Metalurgii Pierwiastków Rzadkich Pol. Wrocławskiej, Ser. Monografie No. 3, 1973.
16. Wysocka-Lisek J.: Spectrum Lines of Rare Earths Arranged by Wavelengths. PWN, Łódź 1970.
17. Сеидель А. Н., Прокофьев В. К., Райски С. М., Славный В. А., Шрейдер Е. И.: Таблицы спектральных линий. Изд. „Наука”, Москва 1977.
18. Mika J., Török T.: Analytical Emission Spectroscopy. Akademiai Kiado, Budapest 1973.
19. Czakow J., Steciak T.: Chem. Anal. 2, 426 (1957).

STRESZCZENIE

W pracy opisano ilościowe spektrograficzne oznaczanie pierwiastków ziem rzadkich przy zastosowaniu elektrod molibdenowych. Oznaczano pierwiastki ziem rzadkich w wieloskładnikowych mieszaninach z różnymi składnikami matrycowymi (La, Nd, Pr), wzbudzając chlorki w przerywanym łuku prądu zmiennego. Rejestrację widm przeprowadzono za pomocą spektrografu siatkowego PGS-2 na płytach spektralnych ORWO WO-3. Jako standard wewnętrzny stosowano linie manganu.

РЕЗЮМЕ

В работе описывается спектрографическое количественное определение редкоземельных элементов с применением молибденовых электродов. Определяли редкоземельные элементы в многокомпонентных смесях с различными матричными компонентами (La, Nd, Pr), возбуждая хлориды в прерывистой дуге переменного тока. Регистрацию спектров вели при помощи дифракционного спектрографа PGS-2 на спектральных пластинках ORWO WO-3. Внутренним стандартом были линии марганца.