

## Laboratorní a výpočetní technika

### USE OF THE GRIMM DISCHARGE LAMP IN SPECTROCHEMICAL ANALYSIS OF MAGNESITE REFRACTORIES

KLÁRA SEBÁTOROVÁ, EDUARD PLŠKO

*Refractories Research Institute, Februárového víťazstva 71, 898 11 Bratislava*

*Geological Institute, Faculty of Natural Sciences*

*Geological Institute, Faculty of Natural Sciences, Komenius University, Zadunajská 15  
811 00 Bratislava*

Received 15. 12. 1976

*Electrically non-conductive materials can be analyzed spectrochemically by means of the Grimm discharge lamp after being ground and mixed with a conductive material (e.g. copper powder) and pressed into pellets. Si, Fe, Ca, Al were determined in this way in magnesia-based refractory materials. The influence of the matrix was found to be completely suppressed.*

#### INTRODUCTION

The continuing advances in the production of refractory materials bring requirements for more rapid and economical analytical determination of their composition.

In the case of magnesia-based refractories accurate and rapid determination of  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$  in raw materials, semi-finished products as well as the final ones is of utmost significance for the manufacturer.

At present, classical analytical methods [1], [2], [3], atomic absorption spectroscopy [4], [5] and methods based on X-ray fluorescence [6] and their combinations are mostly employed for this purpose. Considerable attention is also paid to emission spectrochemical analysis using conventional sources of excitation [7].

The economic factors and the investigation of the reliability of the results obtained were the reasons why the present authors decided to study possible application of emission spectrochemical analysis using spectra excitation in the Grimm discharge lamp [8], [9] in the determination of the respective components in magnesites, sintered magnesia and magnesia bricks. Information in literature [10], [11], [12], [13], [14], [15] concerning the high excitation stability and the practically completely suppressed influence of the matrix served as a stimulus for experimental evaluation of this type of excitation in spectrochemical analysis of magnesia-based refractories.

#### EXPERIMENTAL

Spectra of electrically non-conductive materials can be excited in the glow discharge lamp only when the material has been homogenized with an electrically conductive additive and the mixture pelletized. Pulverized electrolytical copper is usually employed as the conductive additive which is introduced

in various proportions [13], [14]. The possibility of utilizing pure graphite powder or a mixture of copper and graphite powder has also been described [15], [16], [17]. On the basis of preliminary experiments concerned with various types of conductive additives, the additive-sample ratio in the mixture and the pelletizing technique, the following conditions were chosen to ensure the optimum analytical results. The sample was mixed in a 1 : 19 ratio with pulverized electrolytical copper having a grain size up to 40  $\mu\text{m}$ . After thorough homogenization (manual grinding in an agate mortar being fully satisfactory) the mixture was pelletized into dia. 20 mm pellets approximately 1.5 mm in thickness under a pressure of 980 MPa. The pellets were smooth glossy and planparallel. If the difference in thickness at the edges exceeds 0.06 mm spectra of inferior quality are obtained. Before measurement the pellets were washed with ethyl alcohol and dried in order to remove possible impurities.

The spectra were obtained by means of the HKG 2 glow discharge lamp fed by the HVG 4 voltage source (both manufactured by Messrs. RSV Hechendorf am Pilsensee).

The pellets were fixed in a special water-cooled holder by underpressure.

The experimental conditions are listed in Table I.

Table I

Experimental conditions	
Spectrograph:	ISP 28 of medium dispersion (USSR)
Slit illumination:	direct distance of the lamp from the slit 25 cm
Slit width:	0.025 mm
Photographic mat.:	ORWO-WU-2
Argon:	3N5 (Moravské chem. záv. n. p. Ostrava) composition: Ar min. 99.65 O <sub>2</sub> max. 10 ppm CH <sub>4</sub> max. 15 ppm N <sub>2</sub> max. 400 ppm
Excitation conditions:	I. Discharge tube evacuation 90 s II. Rising with argon 90 s III. Pre-discharge 180 s IV. Exposure 240 s
Mode:	Pulsed, 1,200 V; 150 mA obtained by adjustment of argon pressure

Table II

Analytical line	The spectral line pairs used		Reference line
Wavelength [nm]	Excitation energy [eV]	Wavelength [nm]	Excitation energy [eV]
Si I 288.16	5.08	Cu I 299.74	5.78
Fe I 302.06	4.10	Cu I 299.74	5.78
Ca II 317.93	7.05	Cu I 319.41	5.52
Al I 396.15	3.14	Cu I 402.27	6.87

The spectral line blackening was transformed into the logarithm of intensity with the use of emulsion standard curves constructed by means of a preliminary curve [18] for the respective wavelength ranges. The Respectra instrument manufactured by Aristo Hamburg was used for the evaluation.

According to the concentration range to be covered by the analysis, the most convenient spectral line pairs were selected using copper as the internal reference element. The values of the pairs are listed in Table II.

## RESULTS

Natural standard samples and materials of reliably defined composition determined by repeated analyses were used as calibration standards. The natural standards were based on magnesite or magnesia. The synthetic standards were prepared by adding the respective amounts of  $\text{SiO}_2$ ,  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$  to pure  $\text{MgO}$  obtained by calcinating  $\text{Mg}(\text{OH})_2$ , and by homogenizing the mixture thoroughly. The compositions of the individual calibration standards are listed in Tables III and IV.

Table III

Composition of the natural standards [%]

	$\text{SiO}_2$	$\text{CaO}$	$\text{Al}_2\text{O}_3$	$\text{FeO}_3$
1.	0.593	0.581	0.414	2.434
2.	1.64	3.56	0.21	4.22
3.	1.41	0.84	0.48	3.72
4.	0.81	2.55	0.41	7.50
5.	1.59	2.65	0.62	7.35
6.	3.55	1.75	0.97	3.55

1, 2, 3 Magnesite, 4, 5, 6 Magnesia.

Table IV

Composition of the synthetic standards [%]

	$\text{SiO}_2$	$\text{CaO}$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$
1.	0.1	0.2	0.3	0.1
2.	0.1	0.1	0.2	0.2
3.	0.3	0.3	0.5	0.5
4.	0.5	0.5	0.1	0.3
5.	0.7	0.7	1.0	1.0
6.	1.0	1.0	2.0	0.7
7.	2.0	2.0	0.7	4.0
8.	4.0	10.0	4.0	0
9.	7.0	7.0	0	2.0
10.	10.0	4.0	0	6.0

The analytical standard curves were constructed in the  $\Delta Y/\log c$  coordinates. The relationships obtained were virtually linear within the given concentration ranges and the points corresponding to the natural standards, as well as those based on magnesites, magnesia and the synthetic standards, formed a single straight line. This indicates that in agreement with the results mentioned in literature the influence of the matrix does not interfere significantly with spectra excitation in the glow discharge lamp.

The accuracy of the procedure was determined by estimating the relative standard deviation based on 15-fold taking of the spectrum of the Kutná Hora standard magnesite. The relative standard deviations for the mean value of two parallel measurements are listed in Table V together with the concentration range in which the analytical calibration standard curve was constructed.

*Table V*  
The concentration range of the determined elements  
and the relative standard deviation

Concentration range in %		$\delta_{cr}$
SiO <sub>2</sub>	0.1—10	0.044
Fe <sub>2</sub> O <sub>3</sub>	0.5—12	0.045
CaO	0.1—10	0.045
Al <sub>2</sub> O <sub>3</sub>	0.1—4	0.066

The given concentration ranges cover fully the requirements corresponding to the basic materials encountered in the magnesite refractory industry. The determination accuracy depends to a considerable degree on the precision of the photographic detection technique employed.

The accuracy of the procedure described was verified by comparison of the results of spectrochemical analyses with the results of chemical analyses of more than 20 samples, and with the recommended compositions of standard reference samples.

The correlation between the results of chemical analyses and those of the spectrochemical method was evaluated by two-dimensional regression analysis as both groups of results necessarily involve certain errors. Orthogonal regression coefficients were calculated as well as correlation coefficients for the dependence of the results of chemical analysis on those of spectrochemical analysis, and as the difference of their mean values. The respective numerical data for the components are given in Table VI.

In spite of the fact that the distribution of the results cannot be fully described by normal distribution, the results of regression analysis offer the best picture of the accuracy of the method.

The values of the orthogonal regression coefficient characterizing the course of the relationship between the spectrochemical results and the chemical ones are very close to unity. The differences between the two groups of results are small when compared to the mean content values. This proves a satisfactory agreement of the independent results of chemical analysis with those of spectro-

## Use of the Grimm Discharge Lamp ...

Table VI

Orthogonal regression coefficients, correlation coefficients and the difference of mean values

Element	$w$	$r$	$a$	$n$
SiO <sub>2</sub>	1.052	0.985	0.018	22
Fe <sub>2</sub> O <sub>3</sub>	1.028	0.989	0.050	20
CaO	0.982	0.997	0.022	21
Al <sub>2</sub> O <sub>3</sub>	0.848	0.943	0.151	20

$n$  = the number of compared pairs of results.

chemical analysis and thus also a high reliability of the procedure described above. A deviation has been observed only in the determination of aluminium, and this can be explained by the unsatisfactory reliability of the standard chemical methods in the given concentration range. The accuracy of the spectrochemical results obtained has also been verified by a highly satisfactory correlation with the results of chemical analysis.

### CONCLUSION

Spectrochemical analysis of magnesia-based refractories by means of the Grimm glow discharge lamp is described. The pulverized samples were homogenized with copper powder and pressed into pellets. The relative standard deviations of the determination results were calculated. The results obtained were evaluated by means of the regression analysis.

### Acknowledgement

The authors wish to express their gratitude to Ing. K. Florián, CSc., from the Technical University at Košice for the execution of the regression analysis.

### References

- [1] Czechoslovak Standard ČSN 72 6116 (1965).
- [2] Bennett H., Reed R. A.: *Analyst* 96, 1146, 640 (1971).
- [3] Schmidt L., Tonind. *Ztg.* 97, 2, 38 (1973).
- [4] Debras-Guedon I., Boix A., Daignaud M.: *Bull. Soc. Franc. Chem.* 96, 11 (1972).
- [5] Rusňáková A.: Annual Research Report F-55-124-002-17, (1972). Refractories Research Institute Bratislava.
- [6] Matherny M.: *Proceedings Col. Spectr. Int. XVII. Grenoble (1975)* G.A.M.S. Paris, 289.
- [7] Herkelová M.: *Chem. zvesti* (in press).
- [8] Grimm W.: *Naturw.* 22, 586 (1967).
- [9] Grimm W.: *Spectrochim. Acta* 22B, 7, 443 (1968).
- [10] Dogan M.: Dissertation Thesis, Ruhr Univ. Bochum (1970).
- [11] Dogan M., Laqua K.: Massmann, H., *Spectrochim. Acta* 26B, 10, 631 (1971).
- [12] Dogan M., Laqua K.: Massmann, H., *Ibid* 27B, 2, 65 (1972).
- [13] El Alfy S., Laqua K.: Massmann, H., *Z. Anal. Chem.* 263, 1 (1973).
- [14] Moal Y. J., Brossier G.: *Proceedings Coll. Spectr. Int. XVI. Heidelberg*, II, 219.

- [15] Ropert M. E.: *Ibid* II. 160.  
[16] Czakov J.: *Chemia Analytyczna* 18, 891 (1973).  
[17] Ropert M. E.: Private communication.  
[18] Plško E.: *Chemické zvesti* 23, 150 (1969).

POUŽITIE TLEJIVEJ VÝBOJKY NA SPEKTROCHEMICKÚ  
ANALÝZU ŽIARUVZDORNÝCH MATERIÁLOV —  
NA BÁZE MgO

Klára Serátorová, Eduard Plško\*)

*Výskumný ústav hutnickej keramiky, Bratislava*  
*Geologický ústav Prírodovedeckej fakulty, Bratislava\*)*

Nevodivé, práškové vzorky možno analyzovať spektrochemicky za použitia Grimmovej výbojky ako budiaceho zdroja po homogenizácii s vodivou prísadou a lisovaní zmesi na tabletky. V predkladanej práci sa ako vodivá prísada použila prášková elektrolytická meď. Na kalibráciu sa používali prírodné aj syntetické štandardy. V súhlase s doteraz publikovanými údajmi sa experimentálne potvrdilo, že vplyv matrix je prakticky úplne potlačený. Analyzovali sa magnezity a magnézie použitím jednej kalibračnej krivky. Vypočítali sa relatívne štandardné odchýlky. Na zistenie správnosti stanovených výsledkov sa tieto zrovnávali s výsledkami chemickej analýzy. Vzťahy medzi výsledkami chemických metód a metódy spektrochemickej sa hodnotili pomocou dvojrozmernej regresnej analýzy, keďže oboje výsledky sú zatažené určitými chybami. Vypočítali sa ortogonálne regresné koeficienty ( $w$ ), korelačné koeficienty ( $r$ ) pre závislosti výsledkov analýzy chemickej od výsledkov spektrochemických, ako aj rozdiel ich stredných hodnôt ( $a$ ) (Tab. VI).

ПРИМЕНЕНИЕ ТЛЕЮЩЕЙ ЛАМПЫ ДЛЯ  
СПЕКТРОХИМИЧЕСКОГО АНАЛИЗА ОГНЕУПОРОВ —  
МАГНЕЗИТОВ

Клара Сераторова, Эдуард Плшко

*Научно-исследовательский институт огнеупоровое, Bratislava*  
*Геологический институт факультета естественных наук, Bratislava*

Непроводимые, порошковые образцы можно подвергать спектрохимическому анализу с применением лампы Гримма в качестве источника возбуждения после гомогенизации с проводимой добавкой и формования в таблетки. В предлагаемой работе в качестве проводимой добавки применяли порошковую электролитическую медь. Для калибровки пользовались как природными, так и синтетическими стандартами. Было доказано, в полном согласии с до сих пор опубликованными данными, что влияние матриц практически вполне исключается. Анализ подвергали магnezиты и одожтенную магnezитно с применением одной калибрационной кривой. Рассчитывали относительные стандартные отклонения. Для того, чтобы проверить правильность полученных результатов, сопоставляли их с результатами химического анализа. Отношения между результатами химических методов и спектрохимическим методом обрабатывали с помощью двухразмерного регрессного анализа, нoгомучто оба вида результатов содержат определенные погрешности. Были рассчитаны ортогональные регрессные коэффициенты ( $w$ ), коэффициенты корреляции ( $r$ ) для зависимостей результатов химического анализа от результатов спектрохимических анализов; кроме того было рассчитано различие их средних величин ( $a$ ) (Табл. VI).