

The Past, Present and Future of Atomic Spectroscopy in Chemical Analyses

KAROL FLÓRIÁN and *JÜRGEN HASSLER

Department of Chemistry, Faculty of Metallurgy, Technical University of Košice,
SK-042 00 Košice, Letná 9; *Wacker Ceramics, D-87405 Kempten, P.O.BOX 1526

Abstract. The DC arc excitation has played an important role (as the well-known spectrographic analytical technique) in the analysis of solid samples, first of all in specific area of geochemical analyses, for a long period. Unfortunately, in this time all possibilities of the optimisation of photographically registered spectra were fully exploited and after the introduction of modern spectrometric techniques based on ICP excitation also in the field of solid sampling spectrometry the DC arc method lost its importance. The necessity of new, quick and simple methods has led to the comeback of the old DC arc spectroscopy. This situation was caused by some of their advantages, first of all the working temperature. The use of modern, computer-controlled equipment with exactly defined arc current/time programme gives a new design. On the other hand the connection of the spectrometer to the source by quartz-fibre optics is also a new instrumentation. In direct analysis of powder samples it is one of the successful ways for work without any additives in sample preparation. The electrothermal vaporization (ETV) is a well-known and powerful device for the sample introduction in optical emission spectroscopy. This timesaving, robust and precise method became more and more important in industrial laboratories as well as in science and research. In the meantime a nearly perfect commercial ETV-system is available and it represents in connection with an ICP-CID-spectrometer the future in the spectrochemical analysis of powders.

Key words: atomic emission spectroscopy, solid sample analysis, old-fashioned and modern methods, come back of DC-ARC, ETV-ICP-OES.

The past

The history of atomic spectroscopy goes back to the spectroscope (Fig.1), which has been used for first time by Bunsen and Kirchhoff in 1859 (Kirchhoff et al.,1860). For a long period of spectroscopic history the direct – current arc excitation has been the leading technique of direct analysis of powdered samples, first of all in specific area of geochemical analyses. This, first only semi-quantitative method, achieved after a long-year optimization and quantification (Zimmer et al.,1982) e. g. internal standard method, Lomakin-Scheibe equation, blackening-transformation procedures, etc. the position of a quick, wide used multi-element quantitative method. The last optimization in evaluation of photographically registered spectra using modern densitometers (Zimmer et al.,1982), have led to average precision of about 15 % with relatively low detection limits. Some modifications of the D.C.arc itself were also developed, at least the use of the stationary magnetic fields (Lummerzheim et al., 1969), inhomogeneous magnetic fields (Todorović et al., 1969), or the double-plasma method (Vukanović et al., 1977) should be mentioned. Also continuous sample introduction techniques (Fig. 2) were successfully evaluated and used in the practical analysis of powdered samples.

The intensive development of new excitation sources in atomic spectroscopy and commercial use of modern spectrometric techniques, which began in the half of the

last century, has stopped the whole evaluation of mentioned old spectrographic technique. The research was consequently directed towards the use of solution methods, connected with the most successful excitation source of this period, the ICP.

The present

The development of spectrochemical methods is mainly prompted by three aims (Broeckaert et al.,1987): the improvement of the limit of quantification, the increase of the reliability of analytical information and the cost reduction – economical aspects. In most typical analyses of solid samples the direct analysis (solid sampling – analysis) seems to be an advantageous alternative to the usually preferred methods using wet digestion in sample preparation. The advantages are obvious, they are summarized (Bendicho et al.,1991; Schrön et al.,1997) as follows:

- reduced sample pre-treatment and hence, an increase in the speed of the whole analytical procedure,
- low contamination risk, an essential requirement when trace levels of metals are to be determined,
- fewer possibilities of analyte losses during the sample pre-treatment or retention of insoluble residues,
- the use of corrosive and hazardous chemicals is avoided
- very small material consumption.

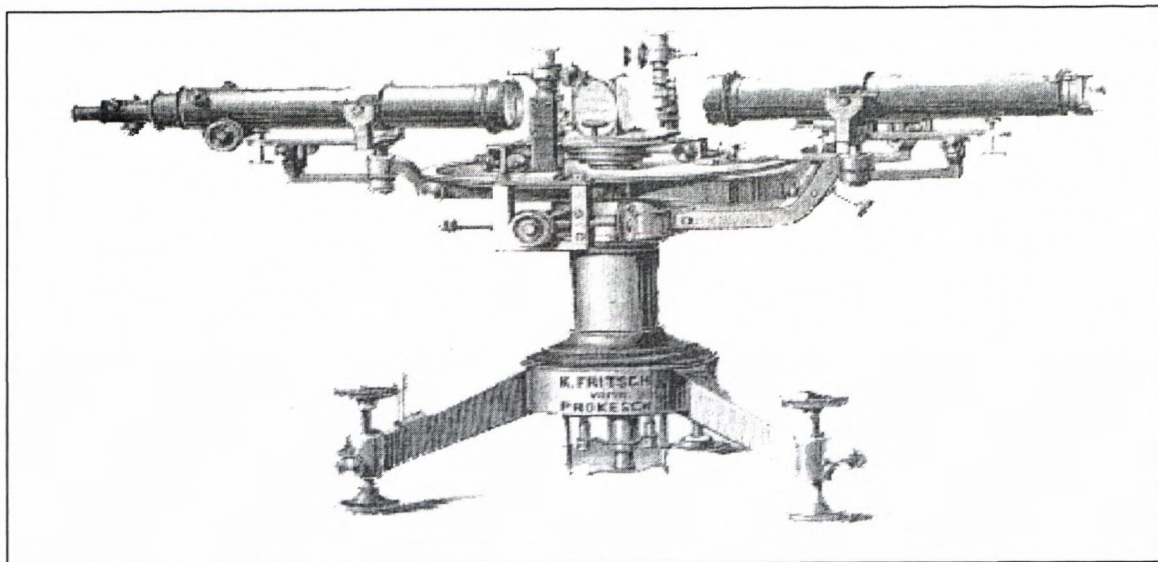


Fig. 1 The old-fashioned spektroscope

On the other hand, there are many of disadvantages to mention, just the most important (Schrön et al., 1997; Pauwels et al., 1991) of these:

- small range of the suitable reference materials (CRM-s),
- dosage problems caused by low sample weight (inhomogeneity),
- difficulty of independent and absolute calibration,
- difficulty connected with the direct-weighing method (inability to dilute samples, having analyte concentrations greater as the working range).

In the development of modern spectrometric methods of direct analysis of solids the attention was logically focused on the most successful excitation source in optical emission spectrometry (OES), the inductively coupled plasma (ICP). Besides the methods of direct sample introduction (Fig. 3): DSI-ICP (Blain et al., 1992) and slurry technique (Dočekal et al., 1992), the main attention was paid to the electrothermal vaporization systems (ETV), similarly to the technique applied in atomic absorption spectrometry (AAS), where many of alternative systems have been described and discussed in recent years (Kurfürst, 1998; Matusziewicz, 1986; Kántor et al., 1992; Golloch et al., 1995). It was stated, that because of the maximum temperature level of ETV at about 2900°C either the use of modifiers (Broeckert et al., 1989; Nickel et al., 1995), or special working gas mixtures (Verrept et al., 1993; Kántor et al., 1992) is needed for the successful analyses of such typical materials, as advanced ceramic powders (e. g. SiC, B₄C, Si₃N₄, etc.) or other materials containing refractory elements.

On the other hand, the once successful solid-sampling technique – the D.C. arc evaporation and excitation source with higher evaporation and excitation temperature

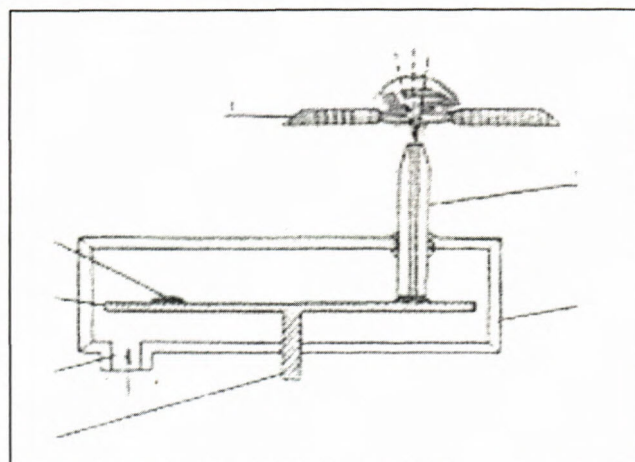
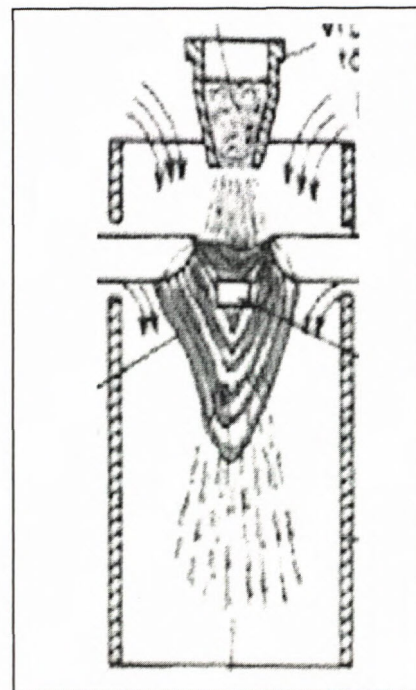


Fig. 2 Two typical continuous introduction systems of powdered samples

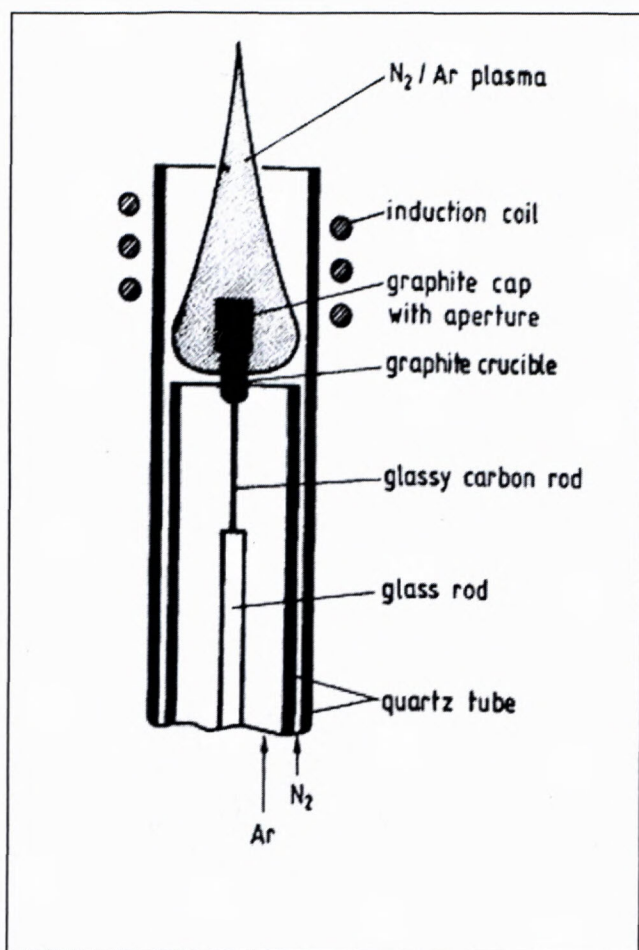


Fig. 3 Direct sample introduction system into ICP excitation source

(about 4000°C) was totally forgotten, first of all because of poor precision of old-fashioned spectrographic technique with photographic registration of spectra. In order to avoid the disadvantages of the old-fashioned DC-arc spectrography a new, electronically controlled DC arc was connected with the quartz-fibre optics to a multi-channel spectrometer (Fig. 4 – an overview on electrode profile and the double-optics signal processing system) as an alternative method to the ETV-ICP and/or SS-ETV-AAS techniques in the routine analysis (Flórián et al., 1996).

The precision, reproducibility and long-time stability of the DC-ARC-OES method in SiC analysis should illustrate the data (Hassler, 2001) in the Table 1.

The future

Since many years a lot of effort has been taken to introduce solid samples directly into an ICP without dilution. Electrothermal vaporisation of powdered samples in a graphite tube and graphite boat and transfer of the aerosol via a tube connection to the plasma is one of the most interesting methods because of its precision and good reproducibility, its robustness and its easy and fast handling. It should be mentioned, that the idea of such sample evaporation, separated from the excitation process

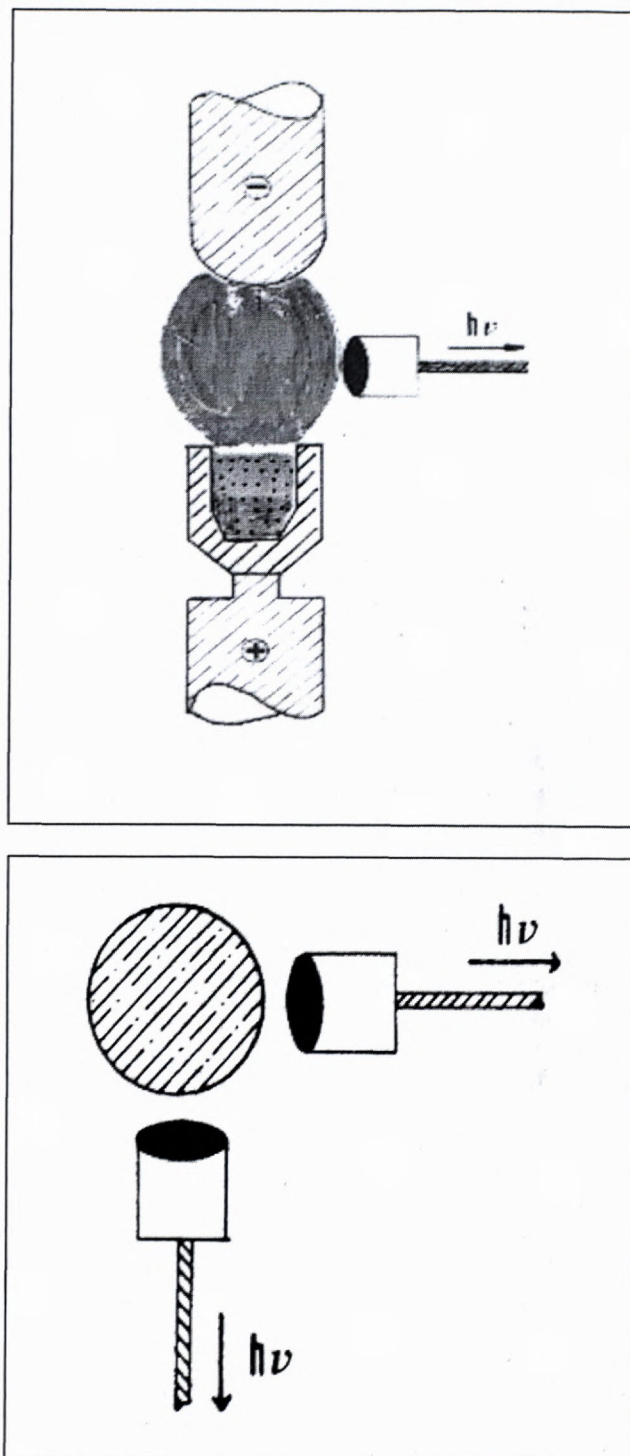


Fig. 4 The double optics signal processing system in connection with modernized DC-arc source

(Fig.5) goes back to the 40-ties of last century (Preuss, 1940). Following several laboratory concepts and own inputs a commercial state-of-the-art instrument has been developed (Hassler et al., 2002). Meanwhile its has become an important tool in a lot of industrial and research laboratories in both, routine analyses and research work. An integrated autosampler (Fig.6) with micro balance allows to work with excellent efficiency especially in industrial applications. For the ETV furnace a special gas-

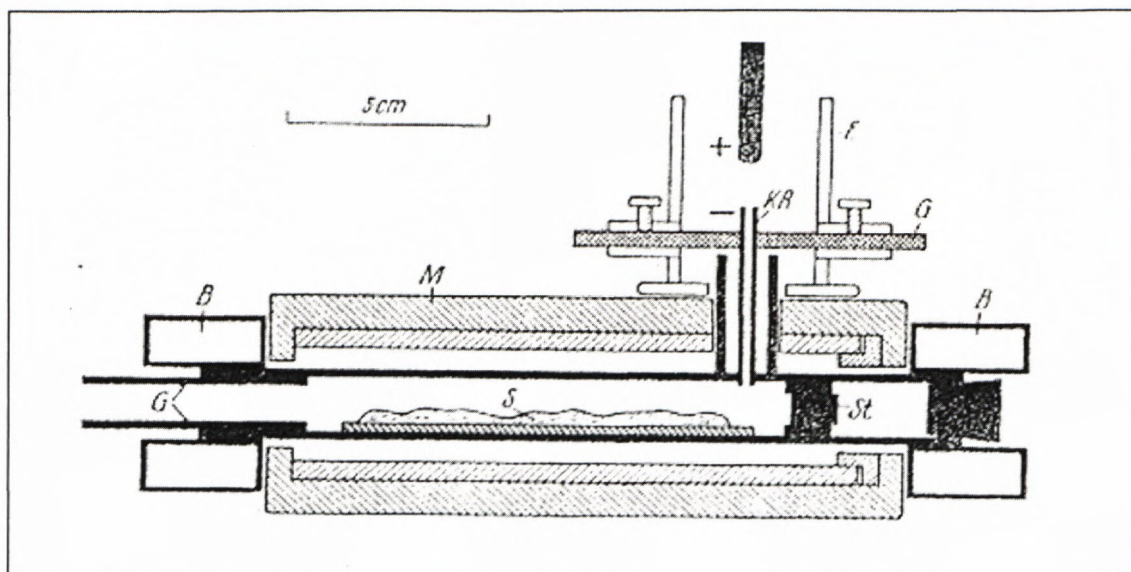


Fig. 5: The old-fashioned solid-sample evaporation and excitation system, proposed by Preuss

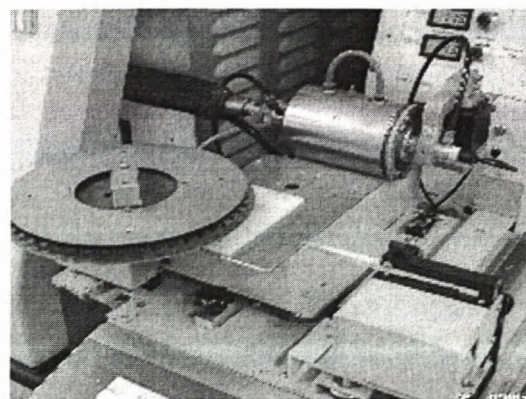
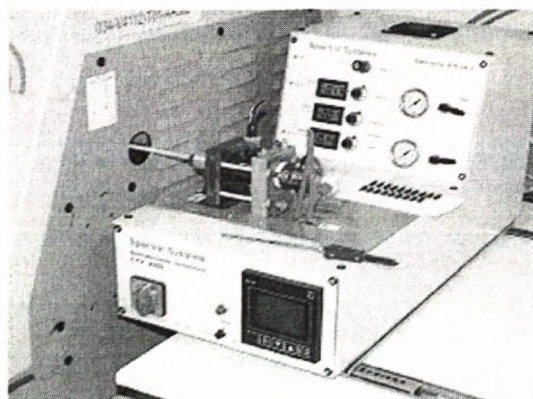


Fig. 6 The modern automatized ETV instrumentation

guide was developed which allows very high transport efficiencies and minimum memory effects. This is – among the robust, compact design and engineering – one of the main advantages against former concepts. Furthermore, the sample can be halogenised by a small amount of reaction gas in order to transform also the refractory elements into volatile halogenides. This lowers the vapourisation temperature and suppresses the formation of carbides. An integrated online-pyrometer measures and controls the boat temperature, which allows the use of individual temperature programmes via microprocessor control.

Some results (Hassler, 2001) of SiC analysis using the above described ETV-ICP technique and their comparison with results of solution ICP analysis as well as DC-ARC-OES analysis are summarized in the Table 2.

The common problem of all solid sampling spectrochemical methods is the adequate calibration. Mostly only a limited number of adequate certified reference materials (CRM-s), or laboratory reference materials

(LRM-s) is available. Therefore besides the use of solution standards some other calibration procedures were proposed as the so called one-standard method. Here the change of independent variable – concentration is achieved by applying different weights of one standard. The comparison of the efficiency of both above mentioned calibration methods enable the validation characteristics of DC-ARC-OES analysis of BN and B₄C (Flórián et al., 2003) summarized in the Table 3.

The comparison of both studied calibration procedures shows their matrix dependence. While the results of BN matrix illustrate a good agreement in calibration parameters (a, b, r), in matrix B₄C are these quite different, in some cases more as one order of magnitude. Some further experiments with various matrices, more analytes and variable excitation conditions (to avoid the influence of excitation process) are needed. At least it is possible to declare the one-standard method as a possible alternative of calibration if none other ways are disposable.

Table 1: The RSD (%) – values of 6 repeated measurements of 5 analytes in 4 SiC standards and 12 repeated series

Element	Standard	Series											
		1	2	3	4	5	6	7	8	9	10	11	12
Al	1	4.5	4.5	6.6	6.0	5.1	5.2	5.8	7.5	4.6	8.4	4.1	5.4
	2	3.9	7.7	6.3	5.1	2.9	7.9	10.8	9.1	4.8	6.1	7.7	6.6
	3	5.0	4.8	3.9	5.7	5.0	5.8	6.2	7.4	3.5	7.5	5.7	5.7
	4	8.3	6.3	3.9	4.0	7.6	8.0	9.7	10.1	8.3	7.4	4.8	7.4
Fe	1	2.5	2.0	4.8	4.0	4.4	4.2	4.2	5.6	3.5	7.5	5.0	5.1
	2	2.7	4.6	2.4	3.2	1.5	4.3	4.8	8.6	1.5	3.7	3.0	4.0
	3	2.7	3.6	2.4	7.0	2.6	3.4	6.4	2.9	3.2	3.6	6.0	2.8
	4	5.3	5.8	6.4	5.2	3.9	2.4	5.7	11.4	7.2	6.5	6.6	4.3
Ni	1	4.7	2.5	10.8	6.1	6.4	5.4	6.4	8.1	8.5	13.2	7.7	7.9
	2	3.5	4.8	2.8	4.8	2.6	5.5	7.4	11.8	2.7	6.4	5.3	7.4
	3	4.6	3.2	5.6	8.4	4.6	4.5	9.1	6.6	2.6	6.4	8.2	5.6
	4	8.8	10.1	11.1	9.5	9.7	6.8	9.3	17.9	12.0	10.3	6.5	8.4
Ti	1	4.4	5.4	6.9	5.5	6.4	9.5	5.5	5.0	5.1	8.6	7.0	4.8
	2	4.8	6.7	6.2	8.3	4.5	8.7	6.6	10.7	4.5	8.4	6.0	9.1
	3	3.5	7.9	6.6	8.0	6.5	10.6	7.6	9.2	8.9	8.8	7.6	4.0
	4	8.6	9.6	7.8	9.8	7.8	4.7	10.2	11.9	8.5	6.9	6.9	5.7
V	1	5.0	5.7	7.3	10.1	7.1	8.1	6.3	10.1	6.5	8.9	4.0	6.4
	2	5.5	9.6	7.0	8.9	5.1	10.9	8.7	6.7	8.0	9.1	7.4	8.0
	3	7.8	7.8	8.8	9.1	7.0	10.1	6.3	7.5	10.9	10.4	7.2	9.7
	4	8.1	10.4	8.4	10.1	9.2	5.9	10.2	15.0	10.9	8.2	6.0	6.8

Table 2: Comparison of main validation characteristics of some analytes in SiC obtained using 3 different methods of spectrochemical analysis

Method	RSD / %					Recovery / %				
	Al	Fe	Ti	V	Zr	Al	Fe	Ti	V	Zr
solution ICP-OES	3.4	7.4	6.3	7.8	8.9	100	107	100	96	112
DC-ARC-OES	2.0	2.8	4.6	9.2		107	105	101	78	
ETV-ICP-OES	3.4	1.9	3.0	11.5	3.4	107	100	119	101	99

Table 3/a : The main characteristics of calibration functions ($y = a + b \cdot c$) of Ca and Si in BN

Calibration parameter	Element			
	Ca		Si	
	5 LRM	single measur. n = 25	5 LRM	single measur. n = 25
concentration range / $\mu\text{g}\cdot\text{g}^{-1}$	20 - 295	7 - 355	18 - 75	3 - 88
r	0.998	0.999	0.999	0.983
RSD _{method} / %	4.8	8.5	3.7	9.7
a	6.44 ± 0.950	6.71 ± 0.896	5.55 ± 0.180	5.63 ± 0.299
b	0.166 ± 0.0056	0.163 ± 0.0056	0.220 ± 0.0051	0.213 ± 0.0080

Table 3/b : The main characteristics of calibration functions ($y = a + b \cdot c$) of Al and Fe in B₄C

Calibration parameter	Element			
	Al		Fe	
	4 LRM	single measur. n = 15	4 LRM	single measur. n = 15
concentration range / $\mu\text{g}\cdot\text{g}^{-1}$	35 - 100	6.8 - 100	580 - 1200	108 - 1500
r	0.994	0.929	0.999	0.971
RSD _{method} / %	5.7	17.8	1.3	14.3
a	6.36 ± 0.372	7.59 ± 0.512	37.7 ± 0.167	19.2 ± 2.98
b	0.074 ± 0.0047	0.140 ± 0.0115	0.023 ± 0.0005	0.055 ± 0.0036

References

- Kirchhoff, G. & Bunsen, R.: *Spectralbeobachtungen*. C. A. Lenoir, Wien (1860).
- Zimmer, K., Flórián, K. & Heltai, Gy.: *Progr. analyt. atom. Spectrosc.*, 1982, **5**, 341 (and references cited therein).
- Lummerzheim, D. & Nickel, H.: *Z. anal. Chem.*, 1969, **245**, 267.
- Todorović, M., Vukanović, V. & Georgijević, V.: *Spectrochim. Acta* 1969, **24 B**, 571.
- Vukanović, D., Simić, V., Vukanović, V., Nickel, H. & Mazurkiewicz M.: *Spectrochim. Acta* 1977, **32 B**, 305.
- Broekaert, J. A. C. & Tölg, G.: *Fres. Z. Anal. Chem.* **326** (1987), p. 495-509.
- Bendicho, C. & de Loos-Vollebrecht, M. T. C.: *J. Anal. Atom. Spectrom.* **6** (1991), p. 353-374.
- Schrön, W., Nimmerfall, G., Dressler, B. & Danzer, K.: *Proceedings of XXX. CSI Melbourne* (1997).
- Pauwels, J., De Angelis, L. & Grobecker, K. H.: *Pure & Appl. Chem.* **63** (1991), p. 1199-1204.
- Blain, L. & Salin, E. D.: *Spectrochim Acta* **47 B** (1992), p. 205-217.
- Dočekal, B., Broekaert, J. A. C., Graule, T., Tschöpel, P. & Tölg, G.: *Fresenius J. Anal. Chem.* **342** (1992), p. 113-117.
- Kurfürst, U. (ed.): *Solid Sample Analysis*. Springer Verlag Berlin-Heidelberg (1998).
- Matusiewicz, H.: *J. Anal. Atom. Spectrom.* **1**, (1986), p. 171-184.
- Broekaert, J. A. C., et al.: *Fresenius J. Anal. Chem.* **332** (1989), p. 825-838.
- Verrept, P., Galbács, G., Moens, L. & Dams, R.: *Spectrochim Acta* **48 B** (1993), p. 671-689.
- Nickel, H. & Zadgorska, Z.: *Spectrochim Acta* **50 B** (1995), p. 527-535.
- Kántor, T., Záray, Gy.: *Fresenius J. Anal. Chem.* **342** (1992), p. 927-932.
- Gollock, A., Haveresch-Kock, M., Platnikow-Vossstätter, F.: *Spectrochim Acta* **50 B** (1995), p. 501-516.
- Flórián, K., Hassler, J. & Schrön, W.: *Fresenius J. Anal. Chem.* **355** (1996), p. 601-605.
- Preuss, E.: *Z. angew. Mineral.* **1941**, 3, 8-20.
- Hassler, J., Detcheva, A., Förster, O., Perzl, P. K. & Flórián, K.: *Annali di Chimica* **89** (1999), p. 827-836.
- Hassler, J.: PhD-Theses, TU Košice (2001).
- Flórián, K., Hassler, J., Rutarová, P. & Záray, Gy.: *Chem. Papers* **57**, 151-154 (2003).