Evaporation of the Chosen Elements from Auxiliary DC Arc Discharge and their Excitation in the Marinković Source*

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Marinković plasma source has been connected with a vessel for production of vapours of solid samples by DC arc discharge. Efficiency of that method was studied by the determination of the half ($t_{50\%}$) and total ($t_{100\%}$) time evaporation of the studied elements with different spectrochemical character. The vapours of the studied elements have been homogenized in the vessel for production of aerosol. The created vapours have been injected into the Marinković source. This problem was not studied in the spectroscopic literature till now because the combination of auxiliary DC arc source with Marinković burner is a novel technique of the authors.

The direct analysis of solid powder samples in the plasma source of Marinković [1] is determined by the method of injection of the analyte into the plasma. It is not efficient to inject the powder sample immediately into the plasma, which is in the U-shape, because the contamination of equipment presents considerable, hardly eliminable "memory effects". Therefore, it was necessary to separate the evaporation process from the excitation process [2, 3]. It was achieved by the separation of the evaporation in DC arc (Ist source) in the silicon vessel and so created vapours were injected into the Marinković burner. This one was attached to the DC arc (IInd source).

EXPERIMENTAL

Conditions of the experiments and character of used equipment are summarized in Table 1. The spectral lines of the studied analytical elements and their parameters are shown in Table 2. Basic experiments have been carried out with the model mixtures consisting of oxides of elements (B, Be, Ca, Cr, Cu, Ni, Pb, Si, V, and Zr) and graphite powder. The spectpure J. Mathey, London chemicals were exlusively used. The content of oxides was 0.1 % in graphite powder and the oxidation stages are given in Table 2. Argon was used as optimal transport gas. The method of preliminary evaporation of a powder sample in auxiliary DC arc discharge [2, 3] and the injection by this manner enriched transport gas with evaporated components has been tested. This method requires, however, application of intensive auxiliary DC arc in order to reach evaporation similar to total evaporation. The scheme of the applied equipment is described in [2].

Table 1. Experimental Conditions

Spectrometer	Polyvac BV 953, Hilger
Grating	1800 lines per 1 mm
Usable range	174—448 nm
Reciprocal linear dispersion	0.54 nm per 1 mm
Plasma	U-shaped DC arc by Marinković
Source I	Evaporation DC arc, 10 A
Source II	Excitation DC arc, 10 A
Ar flow in evaporation vessel	1 dm^3 min^{-1}
Ar flow in Marinković burner	2 dm^3 min^{-1}
Carrier electrodes	SU-302 Elektrokarbon
Counter electrodes	SU-202 Elektrokarbon
Distance of electrodes	4 mm
Amount of sample	10 mg
Total exposure time	120 s
Bunch of the partial exposure time	5 s

This experimental process has been evaluated by the method of exposure time splinted spectrogram which shows the dependence of variable intensities of radiation of spectral lines of analytical elements (X) on time (t). It was found that observation of changes of brutto intensities $I(\mathrm{X})_{\mathrm{L+B}}$ is not suitable and therefore it was necessary to use netto intensities $I(\mathrm{X})_{\mathrm{L}}$ and so to carry out the correction of background intensity $I(\mathrm{X})_{\mathrm{B}}$. Comparing graphical representations of time course of netto intensities values $I(\mathrm{X})_{\mathrm{L}}$ and their background intensities $I(\mathrm{X})_{\mathrm{B}}$, the values of blank ex-

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Table 2. Parameters of the Studied Elements

Element	Oxidation form	λ/nm	E_i/eV
B	B_2O_3	249.777	8.30
Be	BeO	313.042	9.32
Ca	CaO	393.367	6.11
Cr	Cr_2O_3	425.433	6.76
Cu	CuO	327.396	7.72
Ni	NiO	352.454	7.63
Pb	PbO	405.782	7.42
Si	SiO_2	251.611	7.15
V	V_2O_5	437.924	6.74
Zr	ZrO_2	339.198	6.84

λ – wavelength, E_i – excitation energy.

periment showed the time intercepts when evaporation was still intensive and when the process was finished. From the courses of normed [4] dependences $\Sigma I(\mathrm{X})_\mathrm{L} = \mathrm{f}(t)$ the half-time ($t_{50\%}$) of evaporation [5] and the time of total evaporation ($t(\mathrm{X})_{100\%}$) have been determined. Finally, the radial distribution of the intensity of background $I(\mathrm{X})_\mathrm{B}$ and its fluctuation has been found.

RESULTS AND DISCUSSION

The final results of the evaporation process of the studied elements from the graphite matrix are shown in Table 3. During the evaporation of the elements from the studied tandem source by Marinković neither Ahrens' sequence [6] nor Rusanov's sequence [7] were confirmed. This fact is determined by set of specific factors of this source. Production of carbides [8] is accelerated namely at given temperature (4000 K) on the top of the carrier electrode [9]. The carbides expressively affect the process of evaporation and change this process in comparison with evaporation of the oxides of studied elements. From these results it is evident that Ni and Cr reached time of the half evaporation $t_{50\%}$ at the beginning, then V, Si, Ca were evaporated in the time period from 10 s to 12 s and Pb, Cu,

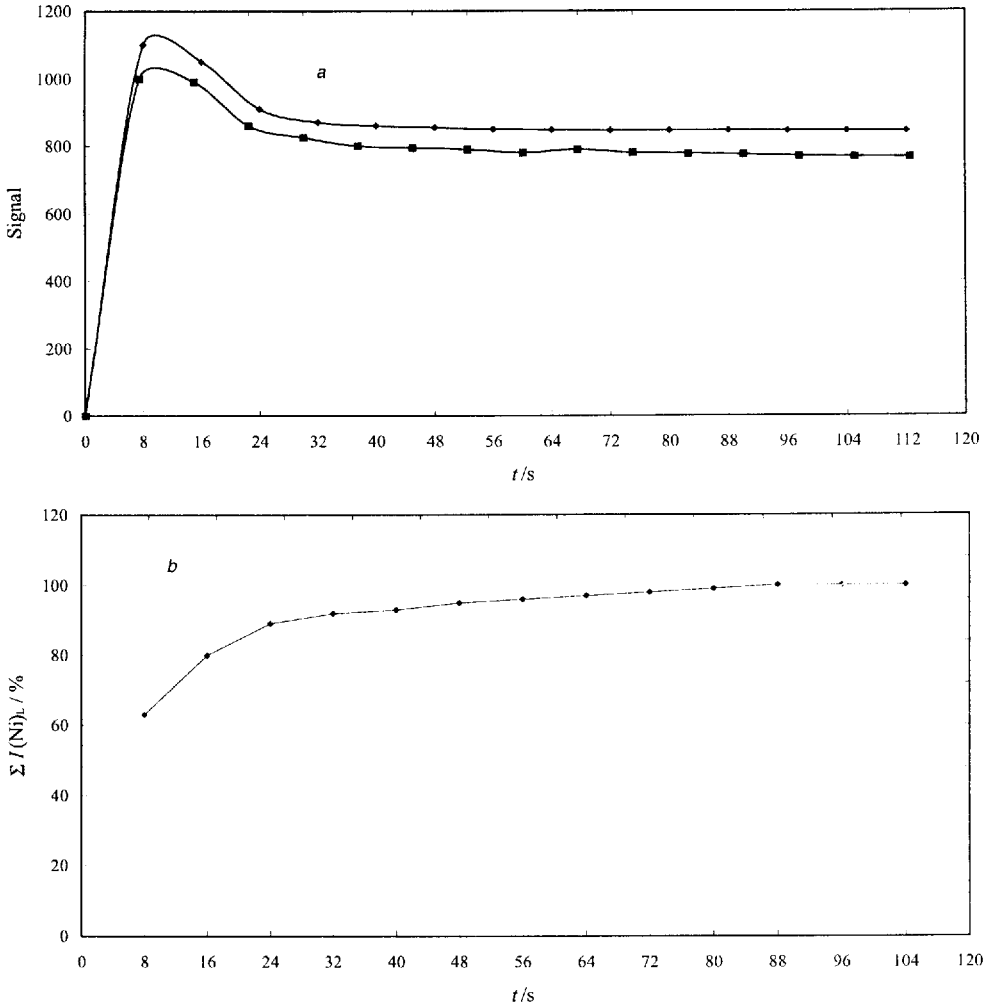

Fig. 1. Evaporation curves of the element Ni. *a*) Time dependence of the Ni signal; *b*) time dependence of the normed Ni signal. ■ $I(\mathrm{Ni})_\mathrm{B}$, ♦ $I(\mathrm{Ni})_\mathrm{L}$.

Table 3. The Evaporation Halftime $t_{50\%}$ and the Total Evaporation Time $t_{100\%}$ of the Tested Analytical Elements

Element	$t_{50\%}$/s	Element	$t_{100\%}$/s
Ni	5.7	V	16.5
Cr	6.3	Zr	64.0
Zr	9.7	Ca	87.7
V	11.0	Cr	88.0
Si	11.6	Ni	88.0
Ca	12.4	Pb	93.1
Pb	18.5	B	96.0
Cu	18.9	Be	93.0
B	19.1	Si	104.6
Be	19.7	Cu	120.0

B, Be were evaporated from 18 s to 20 s.

Concerning the total evaporation $t_{100\%}$ totally different sequence has been reached. V was totally evaporated already in 16 s and Zr was unexpectedly evaporated till 64 s. Ca, Cr, Ni, Pb, B, and Be reached the effect of total evaporation from 88 s to 93 s. The slow evaporation of the element Pb is unpredictable. Si and Cu reached the total evaporation after 105 s and 120 s, respectively. Considerable homogenization of composition of the evaporated products has been reached by application of the vessel for production of vapours.

Change dependences of corrected intensities on their backgrounds and also those of the backgrounds on time in Figs. 1 and 2 have confirmed time stability of evaporation. Fig. 1 represents the less advantageous and Fig. 2 the most advantageous evaporation. From the presented dependences it is evident that intensities of the lines of evaporated analytical elements and also intensities of backgrounds have been stabilized on constant values after the first 20 s of exposition.

CONCLUSION

The evaporation of the studied elements (B, Be, Ca, Cr, Cu, Ni, Pb, Si, V, and Zr) from the high-energy

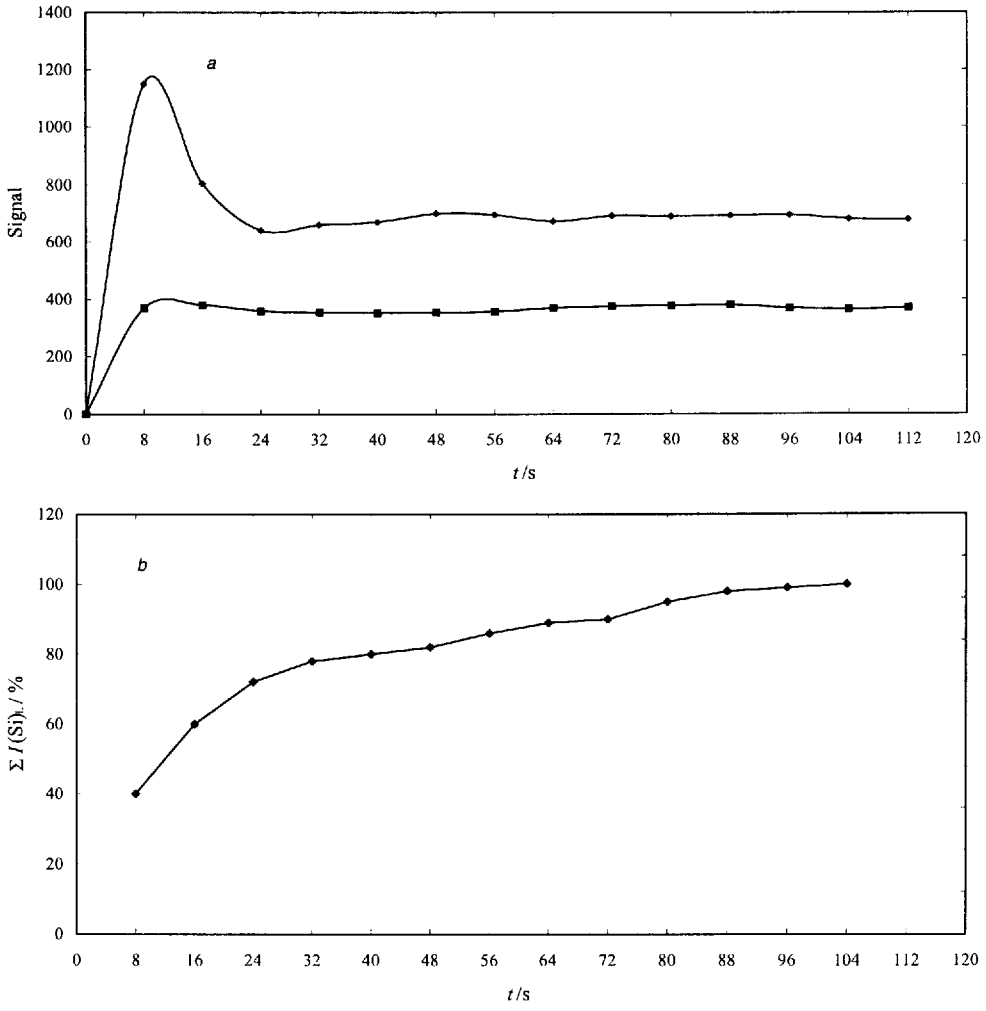

Fig. 2. Evaporation curves of the element Si. *a*) Time dependence of the Si signal; *b*) time dependence of the normed Si signal. ■ $I(\mathrm{Si})_B$, ♦ $I(\mathrm{Si})_L$.

DC arc has different behaviour than expected by the Ahrens classification. The courses of evaporation have been observed for a consideration of integrated intensity $\Sigma I(\mathrm{X})$ curves. The time of the evaporation of the half amount ($t_{50\%}$) of samples corresponds only partially with the time of total evaporation ($t_{100\%}$). Remarkable is the fact that the elements V and Zr were totally evaporated after about 60 s. It has been shown that at the beginning of the exposition the vapours are homogenized only partially. The behaviour of the element Zr has been in our concrete case a leverage.

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