EFFECT OF THE DISCHARGE TEMPERATURE ON THE EVAPORATION OF SAMPLES FOR SPECTROCHEMICAL ANALYSIS

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Dedicated to Professor S. Stankoviansky on the occasion of his 70th birthday.

The time sequence of evaporation of sample components of different volatilities from an electrode crater was investigated by employing normalized evaporation relation curves. A d.c. arc was used for the evaporation and for the excitation of the optical atomic spectra; the temperature of the arc was adjusted by using buffers containing elements of different ionization potentials. An increase of temperature was found to improve the time uniformity of evaporation of components of different volatilities.

Evaporation of samples from an electrode crater into the plasma of the electric arc belongs to the most commonly used techniques of excitation of optical atomic spectra for analytical purposes. Since such a source of radiation exhibits a rather low time stability, the intensity of the analytical spectral line must be related to that of a reference line and their ratio is employed as the analytical signal in almost all cases[1]. Essential changes in the ratios of the contents of the elements examined can occur during the arc burning owing to the fractionated evaporation of the various sample components of different volatilities, which results in changes in the ratios of the corresponding spectral lines even if all the other parameters remain constant. This leads to systematic errors particularly during the application of the current procedures using incomplete sample evaporation. Accurate analytical results can be therefore obtained only if the evaporation of the sample components is ensured to proceed as uniformly as possible, *i.e.* so that the mutual component ratios in the plasma approach closely those in the original sample.

The sample evaporation is affected by many variables, as we pointed out during the investigation of the effect of the crater depth[2]. During that study we observed an appreciable influence of the discharge temperature on the uniformity of evaporation of the sample components. In the present work we deal with this problem in detail.

EXPERIMENTAL

The temperature of a freely burning electric d.c. arc, with a constant electrode gap-length and a constant current, can be varied within a relatively wide range by changing the effective ionization potential of the discharge medium[3]. We prepared therefore three sets of samples containing

differently volatile elements, each in 0·1 mol% concentration (highly volatile: Ga, In; medium volatile: Co, Ni; low-volatile: Ti, Sc). The elements were added as oxides to carbon powder matrices containing 41·67 wt.% one of the following spectrochemical buffers: Li_2CO_3 (ionization potential of Li is $E_{ionLi} = 5·363$ eV), MgO ($E_{ionMg} = 7·61$ eV), Sb_2O_3($E_{ionSb} = 8·5$ eV). The emission optical spectra of the samples were excited and recorded in the following conditions: Spectrograph PGS-2 (Zeiss, Jena), grating 650 lines/mm, blaze 300 nm, first order, single passage of the beam; spectral region 210—390 nm; a three-lense illumination system with intermediate imaging, diaphragm 3·2 mm, slit width 0·020 mm. Electrode material: graphite SU-104 (Elektro-karbon, Topol'čany). Carrier electrode: outer diam. 3·5 mm, inner diam. 2·0 mm, depth 1·5, 3, 6, 10·5 mm; counter-electrode with a cylindrical jut, diam. 1·6 mm, length 6 mm; electrode gap--length 4 mm. Photographic material ORWO WU-3, developer ORWO R-09 (dilution 1 : 20), 5 minutes, 20°C. Excitation: d.c. arc, anodic polarization of the analytical electrode; 220 V, 6 A. Exposure: the plate is moved forward in 10 s intervals during the whole sample burning-off. The spectral lines measured are listed in Table I.

In each case the mean discharge temperature was obtained by measuring the intensity ratio of the lines Ni I 338·05 nm ($E_{exc} = 3·09$ eV) (I_1) and Ni I 336·95 nm ($E_{exc} = 3·67$ eV) (I_2), applying the formula

$$T = 2116·8/[0·462 - \log(I_1/I_2)] .\qquad (1)$$

The respective transition probabilities were taken from[4]. The temperatures found are given in Table II.

In addition to the discharge temperatures, the electrode temperatures were measured, too, by means of a micropyrometer Pyromet (Metra, Blansko). The electrode temperatures were measured 3 mm below the head of the sample-bearing electrode. The measurements were carried out 20 s after the start of arcing, when the steady temperature conditions could be assumed to be established. The results are given in Table II. The temperatures measured involved considerable errors and can therefore serve only for a rough orientation. Further details concerning the electrode temperature measurements will be published later.

TABLE I

The Spectral Lines Measured

Element	Wavelength, nm	Excitation energy, eV
Ga I	294·36	4·31
In I	293·26	4·49
Co I	304·40	4·07
Ni I	305·08	4·09
Sc I	327·36	3·81
Ti I	319·99	3·92

TABLE II

Temperatures of the Arc and the Electrode

Buffer	Temperature, K	
	arc	electrode
Li_2CO_3	5 414	1 300
MgO	5 880	1 700
Sb_2O_3	6 880	2 150

RESULTS AND DISCUSSION

For various combinations of highly, medium, and low volatile elements the norma-
lized integral evaporation relation curves were plotted[5]. The curves for the pair
of elements of the most different volatilities, *viz.* Ga/Sc, are shown in Figs 1—3.
The temperature of both the arc and the electrodes increase in the order Li—Mg—Sb
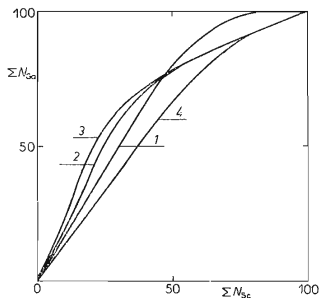

FIG. 1

Normalized Evaporation Relation Curves
for the Ga/Sc Combination and the Li_2CO_3
Buffer

   Crater depth: *1* 1·5 mm, *2* 3 mm, *3* 6 mm,
4 10·5 mm. $\sum N_{Ga}$, $\sum N_{Sc}$ normalized integral
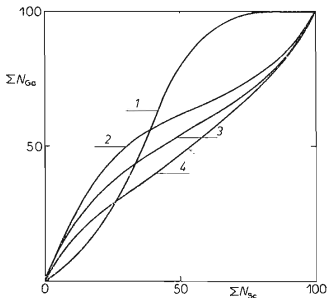intensities of the Ga and Sc lines, respectively.

FIG. 2

Normalized Evaporation Relation Curves for
the Ga/Sc Combination and the MgO Buffer

   Crater depth: *1* 1·5 mm, *2* 3 mm, *3* 6 mm,
4 10·5 mm. $\sum N_{Ga}$, $\sum N_{Sc}$ normalized inte-
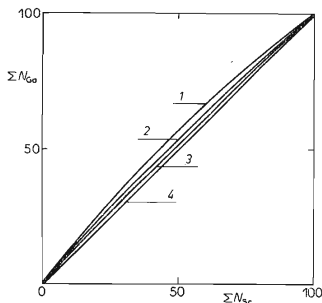gral intensities of the Ga and Sc lines, res-
pectively.

FIG. 3

Normalized Evaporation Relation Curves for
the Ga/Sc Combination and the Sb_2O_3
Buffer

   Crater depth: *1* 1·5 mm, *2* 3 mm, *3* 6 mm,
4 10·5 mm. $\sum N_{Ga}$, $\sum N_{Sc}$ normalized inte-
gral intensities of the Ga and Sc lines,
respectively.

(Table II). As can be seen from the figures, an increase of the discharge temperature brings about an improvement of the linearity of the evaporation relation curves, corresponding to uniform evaporation.

While an appreciable preference of evaporation of Ga to that of the low-volatile Sc is observed during the application of the lowest discharge temperature (Fig. 1), in the case of the highest temperature (Fig. 3) both elements evaporate evenly virtually during the whole evaporation process despite the high difference between their volatilities. The deepening of the crater contributes to the uniformity of the evaporation for reasons dealt with in the paper[2]. In the case of the other, less extreme combinations of elements, similar dependences are obtained, the evaporation being uniform at lower temperatures than for the combination mentioned.

The behaviour of the evaporating components as observed can be explained as follows:

A lower temperature implies a lower electric power supplied to the carrier electrode; the electrode heats and burns off rather slowly. The fractional evaporation of the various sample components can then occur, in accordance with their volatilities. If higher temperatures are applied, the electrode heats and burns off more rapidly and the whole evaporation process runs faster. The various components tend to evaporate simultaneously and the role of the different volatilities diminishes.

The results obtained indicate that additions of the current spectrochemical buffers, which stabilize the discharge temperature by lowering it, affect infavourably the uniformity of evaporation of differently volatile components of the sample. If highly even evaporation of the various sample components is desired, for the ratio of the components in the plasma to equal that in the original sample, an arc discharge of temperature as high as possible should be used.

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