A new method of the construction of evaporation relation curves in spectrochemical analysis

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A simplified method for obtaining the evaporation relation curves which is more rapid than the method hitherto used has been proposed for a quantitative evaluation of the evaporation of elements. Instead of obtaining the values of integral intensities ΣI by addition, using particular spectra obtained by means of the cassette movement, the integral intensities can be found directly by gradually cutting down the slit height of a spectrograph. This reduction is carried out by inserting a six-step diaphragm placed inside the slit fitting of the spectrograph. The integral intensities obtained by either way are proportional to each other as it was demonstrated by concrete examples. Furthermore, this method enables us to take a record repeatedly in quick succession on the same place of photographic plate what is not always possible if the plate cassette moves.

The sequence in which the individual evaporated components of an investigated sample, the internal reference element, and the components of spectrochemical admixtures enter the discharge space plays an important role in the development of spectrochemical analytical methods. According to the character of the solved problem the evaporation of individual components is then either promoted in a convenient way or suppressed [1].

The succession in which the individual elements enter the discharge is most conveniently followed by measuring the course of the intensities in time of the corresponding spectral times. In the case of photographic record the continuous recording of intensity in time is replaced by measurements in certain intervals. From the technical point of view, it is taking of spectra by means of a moving cassette which may be graphically expressed in the form of intensity — time curves [2]. The intensity — time curves which enable us to evaluate qualitatively the process of evaporation have been presented for different materials by *Rusanov* [3]. Because of a relative simplicity of construction this method is still used for the description of the evaporation of components from investigated systems.

A quantitative evaluation of the relative evaporation of two components important from the point of view of the evaluation of the properties for the purpose of the selection of internal reference element was, however, not possible before evaporation relation curves had come into use [4]. In spite of a relatively complicated construction which necessitates the calculation of intensities in different time intervals during the evaporation process the use of relation curves widely spread because of their obviousness and quantitative character; the evaporation relation curves became a good aid for the elaboration of new spectrochemical procedures [5—13].

In this paper we present a simplified procedure for the construction of evaporation

relation curves. This method utilizes the integrating ability of photographic material for a direct recording of the integral intensities obtained in the course of evaporation process.

Experimental

The spectra were taken under the conditions given in Table 1. The individual elements were put into the carbon matrix in the form of suitable compounds. The content of individual investigated elements in the matrix was 0.02%.

Table 1

Spectrograph	PGS-2, VEB Zeiss, Jena
Grating	651 rulings per mm, blaze 3000 Å
Order	1
Recorded region	2350—3600 Å
Electrodes	SU 104 (Elektrokarbon, Topoľčany) shape in Fig. 1
Electrode gap	4 mm
Excitation	d.c. arc, 6 A, terminal voltage 220 V
Illumination	three-lens, intermediate diaphragm 3.2 mm
Slit width	0.020 mm
Photographic material	ORWO WU-3
Development	ORWO R 09; 1 : 20; 5 minutes
Spectral lines measured	Nb 2927.8 Å; Au 2675.95 Å; B 2497.73 Å; Si 2519.21 Å

In the first case the plate cassette was shifted by 1 mm after 15 seconds arc discharge; the height of slit was also 1 mm. In the second case the height of illuminated slit was cut down by inserting a reducing six-step diaphragm placed inside the slit fitting of spectrograph. The exposure times were so chosen that the density of measured lines did not exceed $S \approx 1.5$.

The blackenings of individual spectral lines were measured microphotometrically and transformed into the intensities by means of the calibration curve of emulsion.

Results and discussion

As obvious from Fig. 2, six differently exposed spectra are obtained one below the other if the slit of spectrograph is gradually cut down by inserting the reducing diaphragm. *Boumans* [14] made use of an analogous principle for a qualitative evaluation of evaporation by using a gradual diaphragm of special form. In our case, spectrum 1 corresponds to the exposure time from 0 to 15 seconds, spectrum 2 to the exposure time from 0 to 30 seconds and so on up to spectrum 6 which corresponds to the integral radiation within the whole exposure time from 0 to 90 seconds. From this fact it follows that the intensities of spectral lines found in spectra correspond to the integral intensities as postulated in paper [4] and may be immediately used for the construction of evaporation relation curves.

The condition of a correct course of the relation curves constructed on the basis of gradual reduction of the slit height during the evaporation process and integrating ability of photographic recording is a uniform illumination of the slit of spectrograph along its whole length used. For this purpose a careful adjustment of the external illuminating system into the optical axis of spectrograph is necessary. This aim can be achieved by

illuminating the spectrograph with an adjustment lamp in the direction opposite to the usual path of the rays after a convenient wavelength of the visible spectrum or achromatic maximum of zero order has been adjusted.
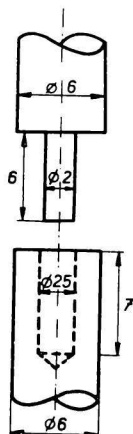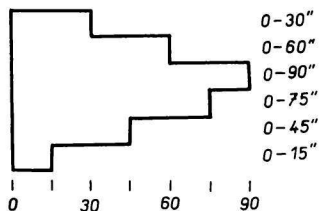

Fig. 1. Shape of the electrodes.

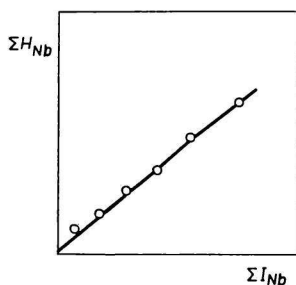*Fig. 2.* Diagram of the six-step diaphragm.

Fig. 3. Evaporation relation curve for Nb I 2927.8 Å.

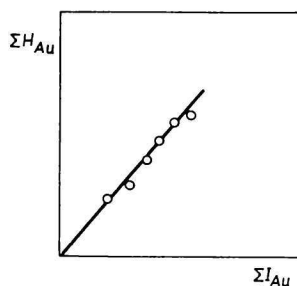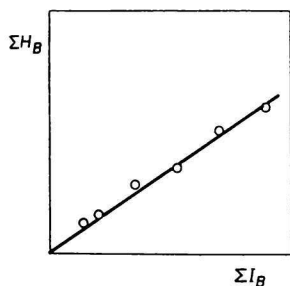*Fig. 4.* Evaporation relation curve for Au I 2675.95 Å.

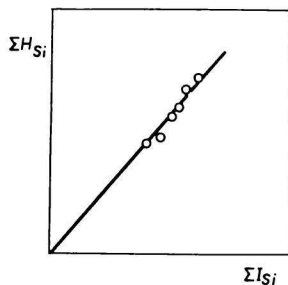*Fig.* Evaporation relation curve for B I 2497.73 Å.

Fig. 6. Evaporation relation curve for Si I 2519.21 Å.

Another possible incorrectness of the evaporation relation curves thus constructed might be due to the Schwarzschild effect. For the photographic material and conditions used this effect is, however, negligible, especially with respect to the fact that these curves are used for the evaluation of a relatively steady evaporation of the analytical and the reference element. Since the exposure times in practical spectrochemical analysis are mostly in the period from 1 to 2 minutes, the new method enables us to obtain the relation curves which describe the evaporation process even more accurately than the relation curves obtained by a numerical integration within short periods of time.

In order to judge the possibilities of the direct estimation of integral intensities by cutting down the slit height with a diaphragm (ΣH) we plotted the values thus obtained against the values of integral intensities (ΣI) found by the addition of the values measured in the particular spectra which were obtained by means of a cassette movement. All the plots thus obtained are of linear character as evident from the examples given for Nb,
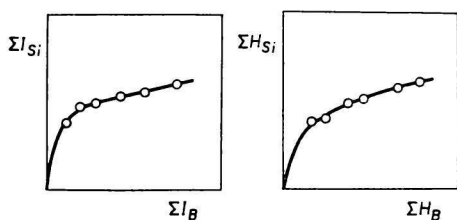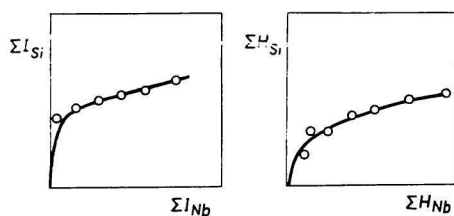

Fig. Evaporation relation curves for Si and B.

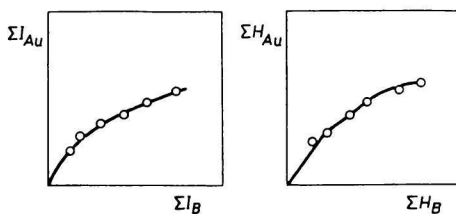*Fig. 8.* Evaporation relation curves for Si and Nb.

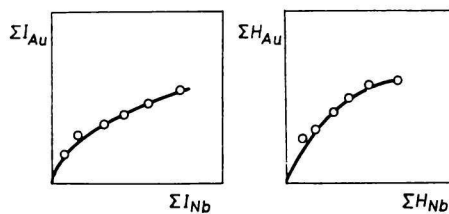*Fig. 9.* Evaporation relation curves for Au and B.
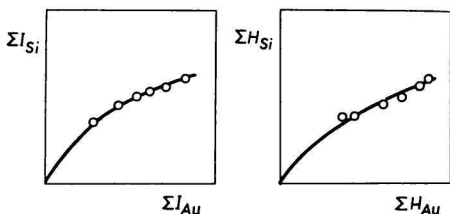

Fig. 10. Evaporation relation curves for Au and Nb.

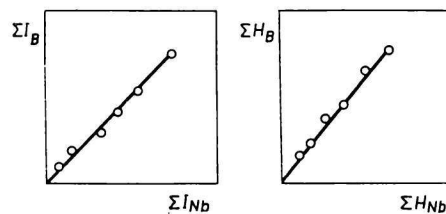*Fig. 11.* Evaporation relation curves for Si and Au.

Fig. 12. Evaporation relation curves for B and Nb.

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Au, B, and Si in Figs. 3—6. A relatively precise linear course indicates that the integral intensities obtained by either procedure are proportional to each other so that it makes no difference which method has been used to construct the relation curves. That is also confirmed by the relation curves constructed for the pairs of integral intensities of spectral lines of the investigated elements some examples of which are presented in Figs. 7—12. These examples demonstrate a full similarity between both plots obtained for a given pair of lines irrespective of the method of construction. Besides the justification for the construction of relation curves by the above simple and rapid method, the plots obtained enable us to draw further conclusions about the spectrochemical behaviour of the selected four elements during the process of evaporation.
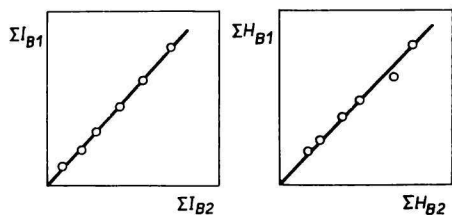

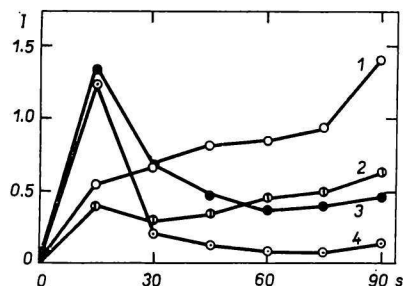*Fig. 13.* Evaporation relation curves for B_1 2497.73 Å and B_2 2496.78 Å.

Fig. 14. Intensity—time curves for *1.* Nb I 2927.8 Å; *2.* B I 2497.73 Å; *3.* Au I 2675.95 Å; *4.* Si I 2519.21 Å.

Fig. 13 shows the evaporation relation curves constructed by means of two different spectral lines of the same element (B 2497.73 and 2496.78 Å) when the equality of evaporation is ensured. It is obvious that both relation curves are linear.

While the classical intensity—time curves presented in Fig. 14 for the investigated elements can show at the most that Au and Si evaporate preferentially before Nb and B, it is possible to demonstrate by means of the evaporation relation curves that both gold and silicon evaporate preferentially before boron and niobium (Figs. 7—10). For silicon (Figs. 7, 8) the relation curves are more curved from which it may be inferred that the fractional evaporation is more intensive when compared with gold (Figs. 9, 10). This fact is also confirmed by the course of the relation curve Si/Au (Fig. 11) which indicates that Si really evaporates in preference before Au though both these elements arrive into the discharge space with constant rate ratio during further evaporation as obvious from the linear character of graphically interpolated section of the corresponding relation curves (Fig. 11). The relation curves referred to B and Nb manifest almost equal character for Si as well as Au which indicates the similarity in the evaporation of Nb and B. The linearity of their relation curves may serve for the evidence of the above statement (Fig. 12). That means that Nb and B evaporate with a constant relative rate under given experimental conditions. This analysis of the relation curves constructed for the evaporation of selected model elements demonstrates a good applicability of this technique to the spectrochemical determination of the relations occurring during the evaporation of substances from the cavities in electrodes.

We conclude that the evaporation relation curves describing graphically the relative ⁃ vaporation of two elements by measuring the increase in integral intensity of the corres-

ponding spectral lines during the evaporation process may by constructed with advantage by the method described in this paper in addition to the method hitherto used [4]. The intensity of spectral lines in the particular steps of spectrum corresponding to the gradual reduction in the slit height corresponds then directly to integral intensities. This method thus renders a more rapid and simple construction of evaporation relation curves possible without impairing their accuracy.

Another advantage of the proposed method of the construction of evaporation relation curves consists in the fact that the record may be taken repeatedly on the same place of photographic plate on account of which the intensity of the investigated spectral lines increases. Considerable difficulties occurring often in the method with moving cassette because of relatively short exposure times may thus be avoided. If the cassette shifts, a repeated photographing on the same place is practically impossible owing to the imperfect control of the cassette movement.

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Translated by R. Domanský