

Study of correction possibilities of the temperature and electron pressure influence on the spectral line intensity

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The influence of the discharge temperature and of the electron pressure on the spectral line intensity of selected elements was studied. Both parameters were calculated using spectral lines of iron. It was determined that the mathematical correction of the influence of the temperature and of the ionization on the intensity of spectral lines yields satisfactory results only for spectral lines of iron. In the case of other elements a satisfactory correction of the followed parameters cannot be obtained in consequence of different spatial distribution of corresponding atoms.

Изучалось влияние температуры разряда и давления электронов на интенсивность спектральных линий избранных элементов. Оба параметра находились с использованием спектральных линий железа. Было найдено, что расчетная поправка на влияние температуры и ионизации дает удовлетворительные результаты только в случае спектральных линий железа, но в случае остальных элементов коррекция становится недостаточной вследствие разного пространственного расположения соответствующих атомов.

The quantitative spectrochemical analysis consists in determining concentration of elements in a sample using intensity values of their spectral lines [1, 2]. The intensity of spectral line is not only a function of concentration of the corresponding element, but it depends on many other factors, too. Among them the dependence of the concentration of the investigated element in the discharge plasma on its original concentration in the sample, the discharge temperature, the degree of ionization, as well as the coefficient of self-absorption have to be taken into account. Several of these parameters show a spatial distribution. The present paper analyzes the possibilities of correction of the temperature and electron pressure influence on the intensity of spectral lines. The influences manifest in the given procedure are also studied. To ensure accurate spectrochemical results the temperature and electron pressure can be maintained on a constant level either by

using calibration standards corresponding in their composition as closely as possible to the composition of the sample, or by addition of an appropriate spectrochemical additive. Several papers [3—6] were devoted to the question of choice and use of spectrochemical buffers, but it has not been satisfactorily solved till now. The survey of efficiency of various buffers as well as the necessary amounts of the additive is given by *Holdt* [7]. Apart from these procedures the given problem can be solved by the mathematical correction of the influence of temperature and ionization on the intensity of spectral lines. In this direction mainly works by *Frisque, Dennen* and *Sankaran* [8, 9] and recently by *Decker* and *Eve* [10, 11] are known. The latter authors have made correction only for conventionally chosen conditions of temperature and electron pressure. In the present work the possibility of correction of ΔY values on the average temperature and average electron pressure is investigated. The effectiveness of the correction is followed by the comparison of the uncorrected with the corrected values in dependence on the temperature. The temperature values characterizing the discharge as a whole were calculated by means of intensities of two Fe spectral lines of known transition probabilities and corresponding to the same species. The degree of ionization was determined by means of intensity values of one Fe ion and one Fe atom line. In the calculation the partition functions and the transition probabilities for the used ion and atom line were taken into account. The necessary numerical values were gained from graphical plots according to *Boumans* [12]. Using the calculated temperature and degree of ionization a formula for the number of particles of the investigated element in dependence on the intensity of its atom, *viz.* ion line was derived. The found number of particles is thus directly connected with the concentration of the given element.

Experimental

Different discharge temperatures were obtained by using Ba, Sn, Ca, Zn, Si, and Mg (all in appropriate compounds) in the quality of spectroscopic buffers, mixed with carbon powder SU-602 (Elektrokarbon, Topoľčany) in the ratio 1 : 1. The elements were selected according to different ionization potentials and different volatilities. The evaporation of Ti, Sb, Ni, Co, Cd, and Fe from the mixture of their compounds, each contained in 1% concentration in the carbon powder SU-602 was investigated under the application of the above-mentioned buffers. To avoid the occurrence of different chemical reactions between the investigated elements and buffer in the electrode, as well as the eventual preferred evaporation of the buffer, the evaporation from a specially constructed electrode was investigated. The electrode was made of graphite rods Elektrokarbon, Topoľčany SU-106 and SU-101 shaped according to Fig. 1.

The inner electrode was filled with a mixture of the investigated elements. The space around it and above it was filled with the buffer. The spectra were taken under the

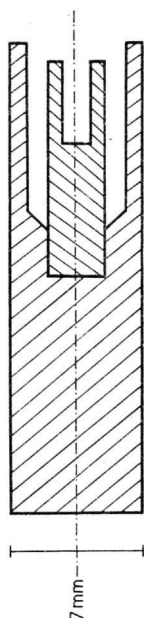


Fig. 1. Shape of the used electrode.

Table 1

Experimental conditions

Spectrograph	PGS-2 (Zeiss, Jena)
Grating	651 lines/mm
Order	$m = 1$
Imaging	3 lenses with intermediate stop
Intermediate stop	3.2 mm
Filter	3 step
Slit width	0.020 mm
Electrode separation	4 mm
Exposure	5 min
Wavelength range	235—360 nm
Carrier electrode	see Fig. 1
Counter electrodes	SU-104, Elektrokarbon, Topolčany, conic
Excitation	D.C. arc, 6 A
Photographic emulsion	ORWO WU-3
Developing	ORWO R 09, 1:20, 5 min

conditions given in Table 1. In comparison with currently used electrodes the described shape of the electrode enables to achieve practically linear dependence of ΔY values on ionization potentials of the buffering elements and also on the discharge average temperature.

Results and discussion

The following equations were used for the analysis of possibilities to correct the influence of temperature and electron pressure on the spectral lines intensities. Boltzmann's distribution law

$$n_m = \frac{g_m}{Z_a} n_a e^{-E_m/kT} \quad (1)$$

and Saha's equation

$$\frac{n_i n_e}{n_a} = \frac{x}{1-x} p_e = \frac{Z_i}{Z_a} 2 \frac{(2\pi m_e)^{3/2} (kT)^{5/2}}{h^3} e^{-E_i/kT} \quad (2)$$

The temperature was calculated according to the relation given for these conditions by *Sobolev* [13]

$$T = \frac{5200}{0.42 - \log I_1/I_2} \quad \begin{array}{l} I_1 - \text{Fe II } 256.2 \text{ nm} \\ I_2 - \text{Fe II } 258.5 \text{ nm} \end{array} \quad (3)$$

The calculated values characterize the discharge as a whole.

The degree of ionization can be determined by measuring the intensity of the ion and atom line of an element. Various authors recommend different lines [12]. In the present work the lines of the same element — iron — were used both for thermometric and manometric measurements, to ensure these measurements to be made at the same distribution of particles in the discharge. The degree of ionization of the investigated element was obtained using the following relations.

Intensity of atom spectral line

$$I_a = A_a g_a h \nu_a N_a \frac{1}{Z_a} e^{-E_a/kT} \quad (4)$$

Intensity of ion spectral line

$$I_i = A_i g_i h \nu_i N_i \frac{1}{Z_i} e^{-E_i/kT} \quad (5)$$

If higher ionization states are energetically considerably remote

$$\frac{N_i}{N_a} = \frac{x}{1-x} \Rightarrow \frac{x}{1-x} = \frac{I_i}{I_a} A \frac{Z_i}{Z_a} e^{(E_i - E_a)/kT} \quad (6)$$

where

$$A = \frac{A_a g_a \nu_a}{A_i g_i \nu_i} \quad (7)$$

For the calculated temperature the Z_a and Z_i values were taken from graphical representations of the dependence of $\log I$ upon $5040/T$ plotted according to *Boumans* [12]. Reliable numerical values of transition probabilities for ion and atom lines are tabulated only for some spectral lines. *Boumans* presents those values for the spectral lines Mg I 277.98 nm and Mg II 279.55 nm. The corresponding constants for spectral lines Fe II 273.9 nm and Fe I 275.0 nm used by *Turko* [14], in whose work the partition functions had not been taken into account, had to be determined experimentally.

The relation of transition probabilities for the Fe spectral lines used by *Turko* [14] was calculated from the intensities of the Mg and Fe spectral lines measured in spectrograms taken using a mixture of MgO and Fe₂O₃ in CaCO₃ matrix. The obtained value equals $\log A = 2.34$.

In the case when the temperature and degree of ionization is known the number of particles N can be theoretically calculated. Its value is in a direct connection with the concentration of the element in question. The calculation can be performed as follows:

The number of nonionized particles N_a is related to the number of all particles N of the given element by the equation

$$N_a = (1 - x)N \quad (8)$$

The degree of ionization of one element can be calculated from the determined degree of ionization for another element

$$\frac{x_2}{1 - x_2} = \frac{x_1}{1 - x_1} \frac{Z_{i2} Z_{a1}}{Z_{i1} Z_{a2}} e^{-(V_2 - V_1)/kT} \quad (9)$$

if

$$\frac{x_2}{1 - x_2} = k \Rightarrow (1 - x_2) = \frac{1}{1 + k} \quad (10)$$

At a known temperature and intensity relation of atom to ion lines, with regard to the relation (6), it can be written

$$k = A \frac{I_{i1}}{I_{a1}} \frac{Z_{i1}}{Z_{a2}} e^{(E_{i1} - E_{a1}) - (V_2 - V_1)/kT} \quad (11)$$

The N value can be then calculated from the equation for the intensity of spectral line using calculated k value and the expression $(1 - x_2)$. For the atom spectral line

$$I_a = A (1 - x)N \frac{1}{Z_a} e^{-E_a/kT} \quad (12)$$

For the ion spectral line

$$I_i = AxN \frac{1}{Z_i} e^{-E_i/kT} \quad (13)$$

The expression of the number of particles N from the eqns (12) and (13) is evident.

The number of particles expressed in this way should for a given concentration depend no more on the temperature and the electron pressure. The influence of such a correction of spectral line intensities was followed using graphical dependences of the ΔY values for different Fe atom — or ion — spectral lines upon the ionization potential of the applied spectrochemical buffers, *i.e.* upon the temperature. The courses of uncorrected ΔY values are shown in Fig. 2. The corresponding courses of ΔY values corrected using eqns (12) and (13) are shown in Fig. 3.

According to the theoretical presumption the uncorrected courses have an ascending tendency. It means that the ΔY values depend under the given conditions on the temperature the more the greater is the difference of the excitation potentials of the two used spectral lines. After the correction, values proportional to the number of Fe particles are obtained. As expected, the

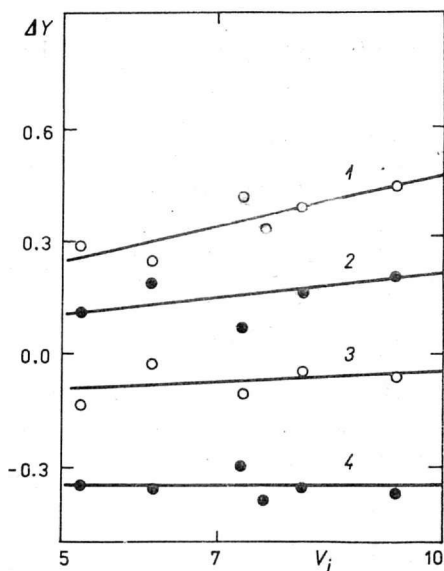


Fig. 2. Dependence of the ΔY value on the ionization energy [eV] of the used buffering elements.

1. Fe II 273.95 nm/Fe II 258.58 nm, $\Delta E = +0.72$ eV; 2. Fe I 309.99 nm/Fe I 275.0 nm, $\Delta E = +0.45$ eV; 3. Fe II 256.2 nm/Fe II 273.95 nm, $\Delta E = +0.31$ eV; 4. Fe I 309.99 nm/Fe I 310.03 nm, $\Delta E = +0.02$ eV.

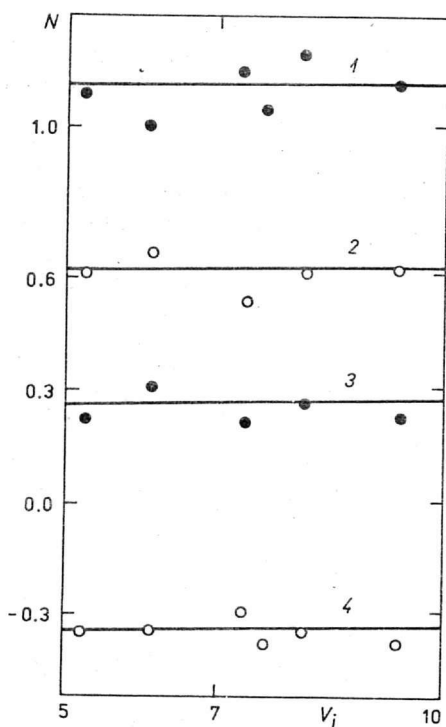


Fig. 3. Dependence of the relative number of particles on the ionization energy of the buffering elements.

1—4 as in Fig. 2.

corresponding value of the logarithm of the relation of relative Fe particle concentrations calculated by means of intensity of the first and the second line does not change with the ionization potential of the used buffer. All the corrected curves are parallel to the abscissa. The dependences of ΔY values on the temperature can be followed in a similar way also for the pairs of Fe spectral lines formed from one ion and one atom spectral line. The results are in Fig. 4.

In the case of the lines Fe II 258.58 nm/Fe I 309.99 nm a clear growing course of the ΔY value is obtained also in spite of the fact that $\Delta E = -0.22$ eV. This is caused by the faster generation of ions than the lowering corresponding to the negative difference of the excitation energies. With the lines Fe II 256.2 nm/Fe I 310.03 nm, for which $\Delta E = +0.83$ eV, the run with a high slope is obtained. In this case the relative excitation as well as the ionization grows with the temperature. The procedure for the correction has been proved as accurate also in these cases, in spite of the overcorrection of the second line pair at higher ionization potentials.

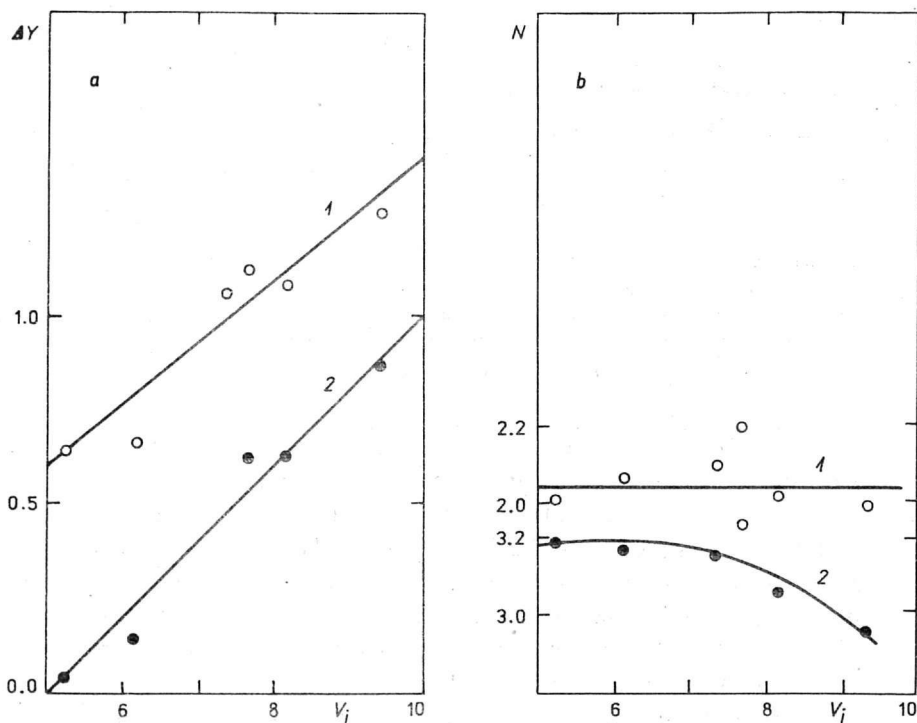


Fig. 4. Dependence of the ΔY value (a) and of the relative number of particles (b) on the ionization energy of the used buffering elements.

1. Fe II 258.58 nm/Fe I 309.99 nm, $\Delta E = -0.22$ eV; 2. Fe II 256.2 nm/Fe I 310.03 nm, $\Delta E = +0.83$ eV.

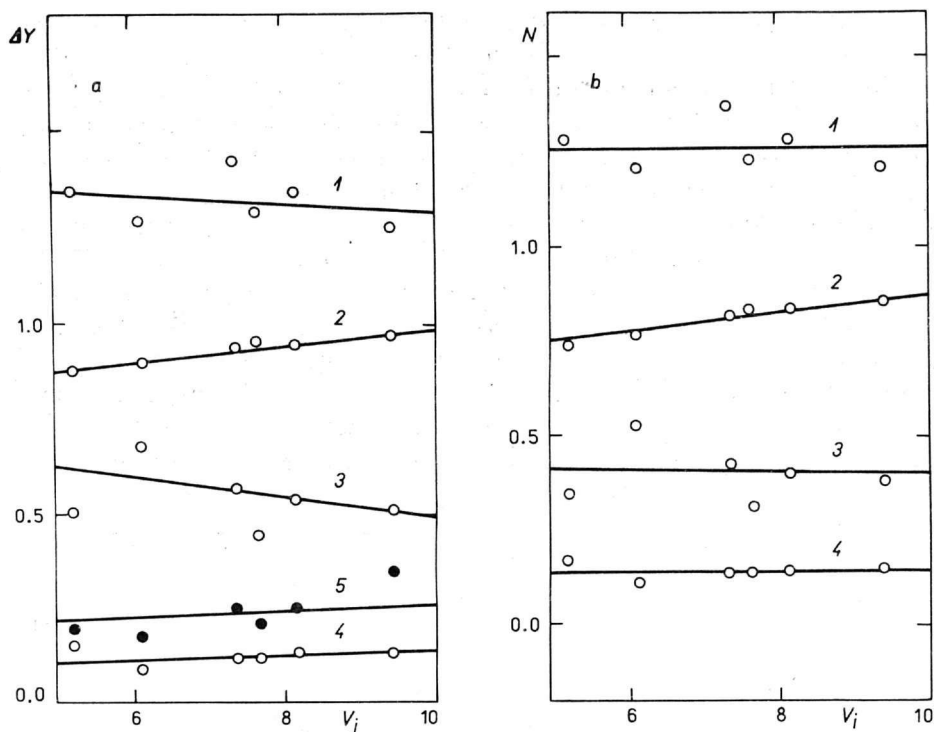


Fig. 5. Dependence of the ΔY value (a) and of the relative number of particles (b) on the ionization energy of the used buffering elements.

1. Ni I 310.16 nm/Ni I 309.91 nm, $\Delta E = -0.06$ eV; 2. Co II 237.86 nm/Co II 236.37 nm, $\Delta E = -0.12$ eV; 3. Ci I 304.4 nm/Co I 346.28 nm, $\Delta E = -0.14$ eV; 4. Ti I 264.42 nm/Ti I 264.1 nm, $\Delta E = +0.02$ eV; 5. Cd I 346.6 nm/Cd I 340.3 nm, $\Delta E = 0$ eV.

Similar dependences were obtained also for spectral lines of the other investigated elements when the lines of the same element had been compared. As a matter of fact the evaporation rates do not play any role under the mentioned conditions. The dependences corresponding to the lines of Ni, Cd, Ti, and Co are in Fig. 5.

The runs of ΔY values for spectral lines corresponding each to another element, as it occurs in practical analysis, are presented in Figs. 6—8. Iron which serves for the determination of both the temperature and degree of ionization, was used as a reference element. The character of all the presented runs agrees with the expected one, considering the influence of the temperature and of the electron pressure.

Apart from the presented explainable and more or less corrigible runs, also runs contradictory to the theoretical presumptions were obtained. The examples are in Fig. 9. The dependences had an experimentally determined growing character also

in spite of the negative ΔE value and the negligible difference in the ionization potentials of the investigated two elements.

A similar disagreement in experimental results exists also in the following measured line pairs: Co I 304.4 nm/Fe I 275.0 nm ($\Delta E = -0.49$ eV), Ti I 264.42 nm/Fe I 275.0 nm ($\Delta E = +0.15$ eV).

The causes of these disagreements can be different. Apart from the differences in volatilities, chemical reactions in the discharge can play a role. Their occurrence can hardly be influenced. Chemical reactions between the investigated elements and the buffer in the electrode cannot practically occur thanks to the used special electrode shape. Apart from the temperature and the electron pressure, the differences in the distribution of species in the discharge influence the intensity of spectral line, too. It can be proved by the fact that in the case of Fe all corrected as well as uncorrected runs of the dependence of ΔY on the ionization potentials of buffers are in agreement with the theoretical expectations. The temperature and the degree of ionization were calculated using only Fe spectral lines intensities, so the distribution of species in the discharge was the same in all cases. Disagreement and anomalies occur in the dependences of ΔY for other elements related to Fe, where a different distribution of species occurs.

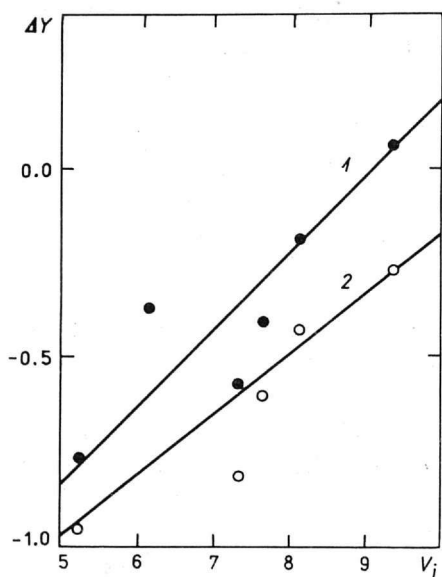


Fig. 6. Dependence of the ΔY value on the ionization energy [eV] of the used buffering elements.

1. Cd I 346.62 nm/Fe I 275 nm; 2. Cd I 340.36 nm/Fe I 275 nm.

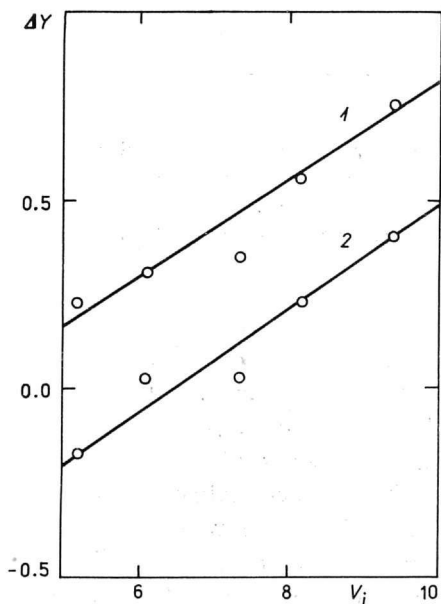


Fig. 7. Dependence of the ΔY value on the ionization energy [eV] of the used buffering elements.

1. Sb I 287.79 nm/Fe I 275 nm; 2. Sb I 276.99 nm/Fe I 275 nm.

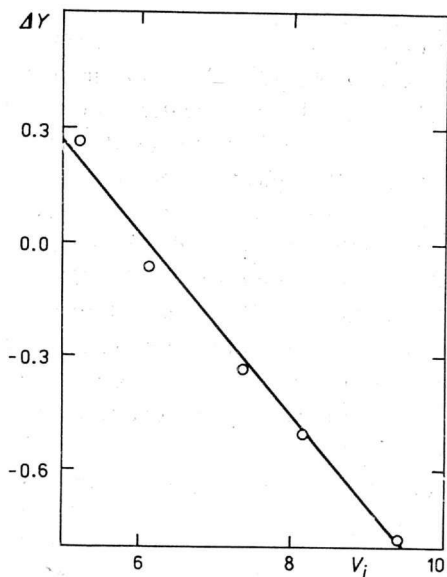


Fig. 8. Dependence of the ΔY value on the ionization energy [eV] of the used buffering elements.

Ti I 264.42 nm/Sb I 276.99 nm.

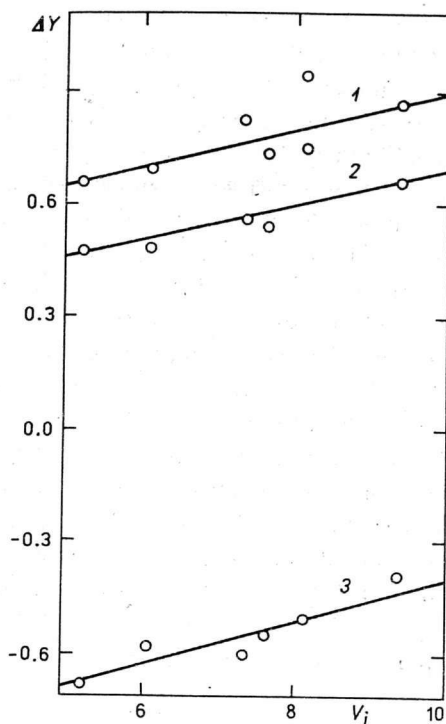


Fig. 9. Dependence of the ΔY value on the ionization energy [eV] of the used buffering elements.

1. Ni I 310.16 nm/Fe I 275 nm; 2. Ni I 310.18 nm/Fe I 275 nm; 3. Ni I 309.91 nm/Fe I 275 nm.

The self-absorption, the wandering of the discharge, eventual incorrect tabulated E values, measurement of the blackening, coinciding lines, etc. can represent additional sources of errors of this correction.

In a deeper study of the mentioned factors, the presented mathematical correction of spectral line intensities on the influence of the temperature and of the degree of ionization with the aim to eliminate the influence of the matrix leads to a significant improvement of the accuracy of spectrochemical analytical results. From above it follows that the applicability of the results of the work is not universal and a corresponding study of the given analyzed system must be performed before the application.

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