Non-Etalon Atomic Emission Method
of Quantitative Element Analysis of Materials

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Abstract – The paper presents the results of investigation of the method of qualitative element analysis for the spectroanalytical complex ДФС-458С. The proposed method allows minimize factors (alternating value of arc current, change in location of a light spot with respect to input slot, etc. for arc excitation) influencing non-controlled change in intensity of spectral lines, used to calculate element concentration. Thus, the method permits use of etalon spectra atlases for qualitative research.

1. Introduction

Calculation of substance composition and control of its purity (dopant-free) are essential for production in various industrial branches. Spectral analysis is widely used to solve these tasks. Spectral analysis is a complex of techniques by means of which one can calculate quantitative content of particular elements in the investigated sample by measuring and analyzing atomic/molecular emission/absorption spectra of the sample.

Each spectral line in atomic spectrum is characterized by wave-length λ and emission intensity I. Emission intensity I is an integral value bound by a spectral line. Emission intensity at transition between the two energy states i and k (Fig. 1) depends on a number of emitting Ni atoms per 1 cm^3 and possibility of spontaneous emission A_{ik} according to the formula (1):

$$I_{ik} = N_i A_{ik} h \nu_{ik}, \qquad (1)$$

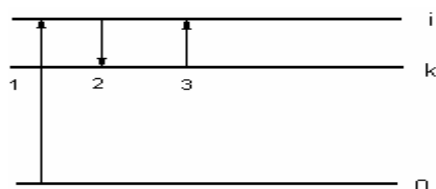where h – Plank constant; ν_{ik} – energy of emitted quantum.

Fig. 1. Schematic of transition of atomic states: 1 – excitation from normal state; 2 – spontaneous emission of quanta; 3 – absorption of quanta

If we want atoms to emit energy, we need to transfer them from normal state (with the least energy) to the highest excited state i. The transition is executed in various light sources (arc, spark, etc.), mostly under collision between electrons. Spontaneous emission of quanta results from recombination processes.

Decomposition of incident radiation into monochromatic components is possible if we use a dispersive element – prism or diffraction lattice, which deflect light beams with various wave-lengths.

2. Quantitative Spectral Analysis

Quantitative spectral analysis aims at calculation of dopant unknown concentration by measuring relative intensity of an analytical pair of lines.

Quantitative spectral analysis [1] implies monotonical increase in intensity of analytical lines with the increase in content of the calculated element in a sample.

Dependence of intensity on concentration is defined experimentally. For this purpose "etalons" or "standard samples" are used. Etalons are samples with content similar to that of analyzed samples with known content of the calculated element. If conditions of measurement of line intensities in etalon spectra are the same as conditions of investigation of analyzed samples, one can obtain corresponding intensities I for a number of values of concentrations C. Using the obtained data, one can draw an interpolate curve, otherwise termed graduate diagram or calibrated curve. With the help of the curve we can graphically calculate dopant concentrations. In order to draw the graduate diagram and make analysis on the basis of the measurements, we need accurate reproduction of excitation conditions and registration of etalon and sample spectra. The more precise analyses we need, the more difficult it is to achieve the required stability of spectra conditions.

3. Factors Influencing Intensity of Spectral Lines

When we make a spectral analysis under some particular situation, concentration values can be significantly influenced by systematic errors, which depend on:

1. Discrepancy in composition, structure and sizes between analyzed samples and used etalons.

2. Influence of structure, composition and size of a sample onto bias and change of the slope angle of graduate curves.

3. Intensity of spectral lines depends on excitation conditions in discharge plasma (discharge current power, inductance of the discharge contour, discharge power and duration, etc.), on illumination of the spectrograph slot, on exposure value. All these factors can variously influence not only single lines, but intensity of the spectrum on the whole.

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4. Method of Exclusion of Non-Controlled Factors Influencing Intensity of Spectral Lines

As it has already been mentioned above, intensity of the whole spectrum and that of single spectral lines will differ under different conditions of registration of the optical spectrum of the same sample.

We can avoid influence of factors onto intensity of spectral lines by using the method of normalization of spectrum intensity.

Normalization of an optical spectrum or single spectral lines means the following: a spectrum or spectral lines are integrated, then intensity $I(\lambda)$ is divided by integral S. As a result, we obtain spectrum $I_n(\lambda)$, where I_n is a normalized value of optical spectrum intensity.

Normalization of the optical spectrum can be made in two ways:

1. Full normalization – analytical lines of each element are normalized by integral of the whole registered spectrum.

2. Partial normalization – analytical lines of each element are normalized by the total of intensities of element analytical lines.

5. Equipment and Experimental Methods

Research for this paper was done using the spectroanalytical complex ДФС-458, equipped with a photoelectric device.

The non-etalon method was tested using steel P6M5 etalon.

Registration of spectra was executed under the two regimes, which simulated changes in optical emission excitement conditions.

We used alternating current arc with arc current of 5 A for the method of emission excitation for the both regimes.

1. Exposure time was 50 ms, number of frames – 10, time of arc burning without registration of spectrum – 1 s, distance between the electrodes – 2 mm;

2. Exposure time was 30 ms, number of frames – 10, time of arc burning without registration of spectrum – 1 s, distance between the electrodes – 4 mm.

Exposure time is time interval at which photodetectors, used in systems with photoelectric registration of spectra, register incident radiation. Exposure time of photodetectors is not more than several seconds.

A frame is a complex of the following actions: clearing of the photodetector, registration of emission, record of a signal from the photodetector.

Time of arc burning without registration of spectrum is time gap between switching on of arc and start of spectrum registration.

Registration of spectral characteristics was done in the wave-length range of 228–352 nm.

In order to calculate the results of the above-mentioned methods of normalization, we chose three analytical lines for each element. The elements and wave-lengths of analytical lines are given in Table.

Table. Wave-lengths of analytical lines

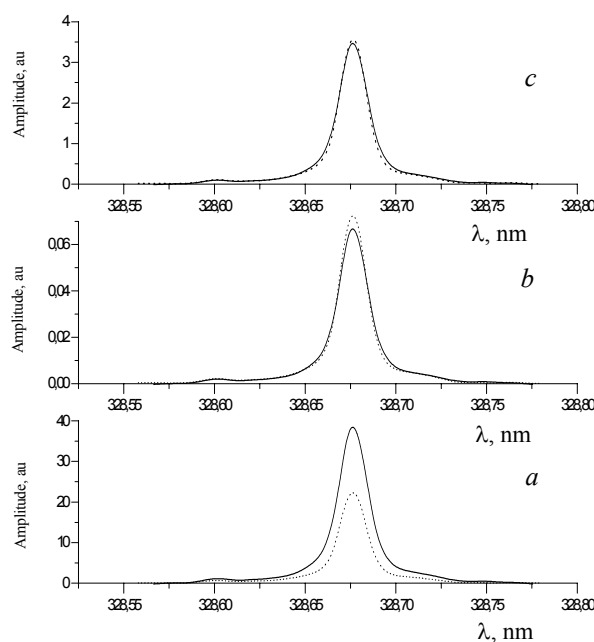| Element	Cr	Fe	Ni	Mo	Mn	Si	V	W
Wavelength, nm	267.716	239.562	336.957	283.144	241.057	252.851	268.796	241.116
	286.092	258.500	341.477	290.306	293.306	252.412	289.331	247.780
	286.257	328.675	349.296	297.114	294.921	288.158	305.633	284.157

Fig. 2. Analytical line for Fe, $\lambda = 328.675$ nm. *a* – non-normalized; *b* – full normalization; *c* – partial normalization.
—— First method of excitation. ······ Second method of excitation

6. Discussion

Figure 2 shows spectral line for Fe $\lambda = 328.675$ nm. Fig. 2, *a* shows that line intensity I_1, registered using the first method is more than intensity of the line I_2, registered by the second method. The obtained ratio is $I_1/I_2 = 1.85$. Using the method of exclusion of non-controlled factors influencing intensity of spectral lines we obtained $I_1 = I_2$ (Fig. 1, *b*, *c*).

7. Conclusion

It was found out that the proposed method of exclusion of non-controlled factors influencing intensity of spectral lines allows use of etalon spectra registered by other devices. However, conditions of spectra excitation for investigation of samples should be similar to excitation conditions of etalon spectra registration, since intensity of spectral lines depends on excitation conditions in discharge plasma (discharge current power, inductance of discharge contour, discharge power and duration, distance between electrodes, etc.). All these factors can influence intensity of single lines, thus use of etalons is essential.

References

[1] *Methods of spectral analysis*, Ed. by V.L. Levshin, Moscow, Publ. by the Moscow University, 1962, 510 pp.