Accounting for the effects of third elements in the emission spectral analysis and construction of global analytical techniques

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Abstract. The paper discusses the method of processing the metals and alloys spectra, which were obtained using emission spectrometers with spark excitation spectra. The proposed technique makes it possible to build a global method for analyzing any alloys, taking into account the so-called “third elements effects”.

1. Introduction

During the determination of the elemental composition of substances by the method of emission spectral analysis, the so-called problem of “accounting for the influence of third elements” often arises [1–6]. Its essence is as follows. As is known, in order to implement this method using a specific instrument (emission spectrometer), it is necessary to calibrate it using working reference samples (WRS), i.e. samples of this type of substance with different (but known) content of elements to be determined. Calibration graphs are built on a set of WRS for each element separately and represent a smooth curve, which, as a rule, is approximated by a polynomial of some degree (usually no more than four). The calibration curve obtained in this way is the dependence of the concentration of the element being determined, on the intensity of its analytical spectral line. When examining a sample of unknown composition, the concentration of the impurity element is determined from the measured intensity of the analytical line using a calibration curve.

2. Materials and methods

However, when constructing calibration graphs in some types of samples, the dependence of the concentration of an element on the intensity of its analytical line is not monotonous. That is, WRS with a greater concentration of this element gives a lower intensity of the analytical line or vice versa. The reason is that the intensity of the analytical line of a certain element can be influenced by the fact that there is another impurity element in the WRS. Especially this effect is significant in the analysis of alloys using a low-voltage spark, which is the most common method for determining the elemental composition of metals [7–10]. It also manifests itself in the analysis of powder samples by the method of fractional evaporation from the crater of a graphite electrode. The simplest example is that if there are alkali metals in the powder sample as an impurity, the intensities of the analytical lines of all the elements being determined are significantly reduced (compared to the same sample without an alkali...
metal). This occurs, in particular, due to a decrease in the plasma temperature and, as a consequence, a
decrease in the rate of excitation of the corresponding atomic (and ionic) levels. Thus, the results of
the analysis for the content of a certain impurity in a sample by emission methods depend on the
content of other impurities in this sample. This fact must be taken into account when analyzing
samples with an unknown composition. This is the essence of the problem of the "third element
influences".

The above factors are the reason that, for example, when analyzing metals and alloys, it is
necessary to analyze different alloys on one basis under different conditions [11–12]: the parameters
of the spectrum excitation source, the recording system, sample preparation, the set of analytical lines
and reference lines. The examples include carbon and high speed steels, various types of bronzes, and
the like. The above parameters in the analysis using the emission spectrometer are the so-called
analytical methods, the choice of which in the software of a modern spectrometer is carried out by the
operator manually. Each technique has individual calibration curves for the impurity elements to be
determined, which allow to analyze only a specific type of alloy.

Thus, for accurate quantitative analysis, it is necessary to know the grade of alloy being analyzed,
in order to relate it to a specific type, and select the appropriate analytical method. When the grade of
the alloy is unknown, the quantitative analysis of the sample is substantially difficult if not impossible.
The reason for this is the influence of the third elements in alloys of various types.

Thus, the methods of constructing so-called “global techniques” are relevant, in which, using
uniform calibration graphs, it is possible to determine the content of impurity elements in any (or at
least in large quantities) different types of substance on one basis, for example, in any alloys based on
Fe by taking into account the influence of third elements. In addition, even within the same type of
alloys, taking into account this phenomenon can significantly reduce the systematic errors in
measuring the concentrations of impurity elements.

3. Discussion
In the software of modern Russian emission spectrometers, the influence of the third elements is taken
into account according to a linear empirical theory, which does not allow building global methods
covering a large number of types of substances with the same basis. The situation is somewhat better
with imported devices, where even quadratic, but also empirical approximation formulas are used.

We are developing a general methodology for taking into account the influence of third elements
from first principles, which is applicable to all types of substances. This technique was preliminarily
tested by us on the Russian emission spectrometer SPAS-02, intended for the analysis of metals and
alloys. SPAS-02 is a desktop instrument with average technical characteristics. Testing has shown that
it is possible to build global methods for analyzing alloys, the systematic error in determining the
composition of which does not exceed that in the method for analyzing one type of alloys. That is, for
example, the determination of the concentration of an impurity element in the method of analysis of
carbon low and medium alloyed steels is the same as in the global method of analysis of Fe-based
alloys (high-speed steels, high-alloyed and high temperature steels, bleached cast iron, tool steels,
etc.).

Some results of this testing are given below. Fig. 1 shows the dependence of calculated and
passport concentrations of copper in WRS. The influence on the definition of Cu of the following
elements was taken into account: Ni, W, Cr, V, since the high-speed steels contain high concentrations
of W, V, and high-alloyed ones contain Ni, Cr. It can be seen that the general theory significantly
reduces the error in determining the concentration of copper steels. The average standard deviation of
the calculated concentration from the passport is reduced by 2.4 times – from 14.1 % to a value of
5.8 %. At the same time, the standard deviation for the set of low and moderately alloyed steels (where
the influence of the third elements is not observed) is 5.6 %, that is, as noted, they are almost equal.
Влияние Ni, W, Cr и V на определение Cu в сталях (низко и среднелегированные быстро режущие и хромоникелевые) по одному градуировочному графику:

- $C_{calc}$ (специф. конц.), %
- $C_{spec}$.
- $C_{calc}$.
- $C_{calc}^1$.
- $C_{calc}^2$.

**Figure 1.** Results of the developed theory application for determining the copper content (high-speed steel, high-alloyed and high temperature steels, bleached cast iron, tool steels, etc.) in a single graph. The standard deviation in the global method (5.8 %) is almost equal to the same value but for the determination method in low- and medium-alloy steels (5.6 %). $C_{calc}$ - calculation of the content without taking into account influences; $C_{calc}^1$ - calculation using linear theory; $C_{calc}^2$ - calculation using the general theory; $C_{spec}$ – specified concentration.

**4. Conclusion**

The proposed theory in this particular case almost ideally takes into account the influence of the third elements. It should be noted that the average standard deviation of the calculated concentration from the nameplate, taking into account the influence of the same elements according to the empirical theory, is 11 %, that is, twice the corresponding value for the general theory.

It is interesting to note that the range of concentrations of Cu using the results of taking into account the effects of third elements on the definition of copper according to the general theory, as can be seen from Fig. 1 – $0.007$–$8$ % – more than three orders of magnitude.

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