Simultaneous spectrophotometric determination of chromium(VI) and iron (III) by H-point standard addition method

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Abstract. In this work the possibility of simultaneous spectrophotometric determination of chromium (VI) and iron (III) in alloys with help of the mixed organic reagent (diphenylcarbazide and 1,10-phenanthroline) is studied. We have applied H-point standard addition method to determine concentrations of chromium (VI) and iron (III) from the mixture. The pure signals of complexes of chromium (VI) with diphenylcarbazide and iron (III) with the 1,10-phenanthroline and their calibration plots are previously carried out. We established the possibility of simultaneous determination of chromium (VI) and iron (III) in the different concentration ranges by H-point standard addition method. Correctness of determination of concentration by means of the offered technique is proved by "added-found" method for a series of mixtures with different ratios of concentration of chromium (VI) and iron (III). It is founded that the error of determination of concentration doesn't exceed 33 %.

1. Introduction

Many common alloys consist of chromium and iron [1]. A quantity of iron in alloys is determined by ICP-AES [2], flame atomic absorption spectrometry [3], spectrophotometry [4], X-ray fluorescence spectrometry [5], voltammetry [6, 7]. Chromium can be analyzed by ICP-AES [8], sequential injection analysis [9], spectrophotometry [10], X-ray fluorescence spectrometry [11]. Simultaneous determination of chromium and iron can be realized by ICP-AES [12]. Analysis methods of chromium and iron often require additional stages of sample preparation, the chemical pretreatment stages, unconventional and high-cost equipments. Moreover for properties characterization of alloys it often requires to know the speciation of elements. It gives reasons for the development of simple and accessible techniques of simultaneous determination of Cr (VI) and Fe (III) in alloys.

In the industrial analysis the spectrophotometric determination of chromium (VI) with diphenylcarbazide (λ_{max} = 540 nm) and iron (III) with 1,10-phenanthroline (λ_{max} = 510 nm) are widely applied [13]. Spectrophotometric techniques of chromium (VI) and iron (III) determination are rather sensitive and selective. The problem of simultaneous determination of Cr (VI) and Fe (III) can be solved with use of the chromogenic and mixed organic reagents [14–20]. However in this case absorption spectra of chromium (VI) and iron (III) complexes overlaps therefore direct determination of concentration of the studied substances is impossible. To separate individual signals from epy overlapped absorption spectrum the different mathematical approaches, such as H-point method [16],

PLS regression [17], principal component analysis [16], artificial neural networks [18] and curve fitting [19, 20] were applied.
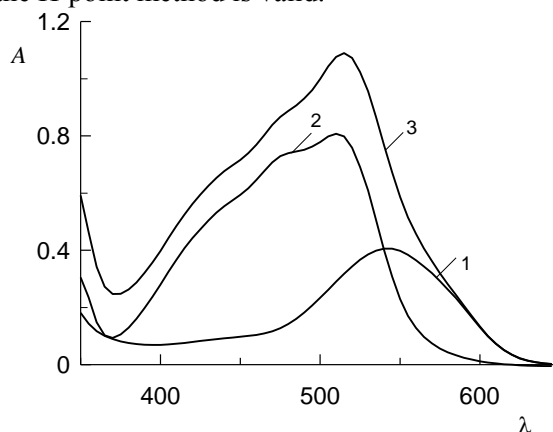
In this work we used the H-point standard addition method to determine concentrations of chromium (VI) and iron (III) from the overlapped absorption spectrum. The H-point method does not require application of the complicated procedure of resolution methods and have a sufficient accuracy provided additivity of overlapped signals and verification of the Beer's law.

Methodology of the H-point method was thoroughly described in the previous work [16]. The H-point standard addition method is a modification of the standard addition method. In this method a set of spectrophotometric signals of mixture of two components with the successive standard addition of second component is obtained. The method bases on the plotting of the calibration plots at two wavelengths. Two straight lines are obtained that have a common point with coordinates H($-C_H$, A_H), where $-C_H$ is the unknown concentration of the second component and A_H the analytical signal due to the first component.

Thus our goal is to study the possibility of simultaneous spectrophotometric determination of Cr (VI) and Fe (III) with mixed organic reagent (diphenylcarbazide and 1,10-phenanthroline) via the H-point method. For detection of absorption spectra we used UV Cary 60 Agilent Technology spectrophotometer in the range of wave length from 200 to 800 nm with cell length equal to 10 and 50 mm.
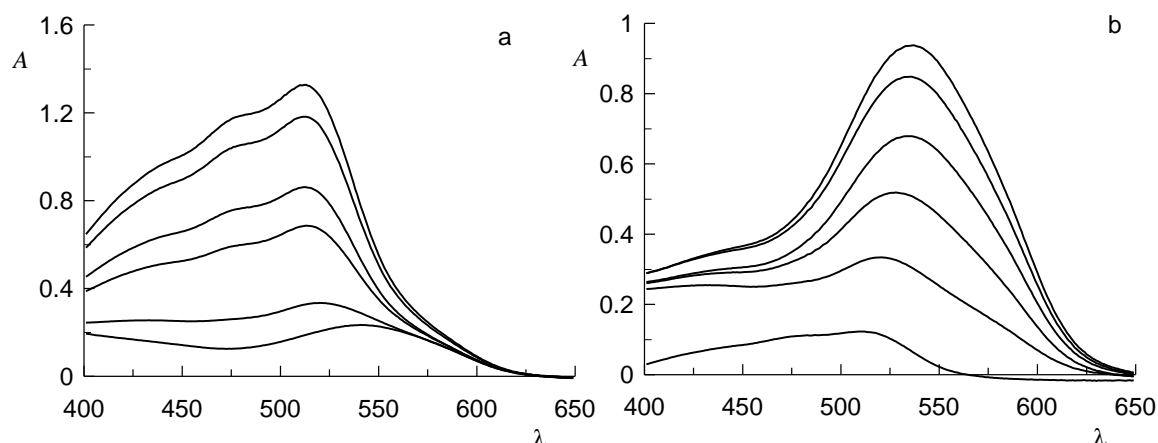
2. Results and discussion

We obtained the individual spectra of Cr (VI) with diphenylcarbazide and Fe (III) with 1,10-phenanthroline and their sum spectrum with mixed organic reagent (diphenylcarbazide and 1,10-phenanthroline). Figure 1 shows the received signals. As shown in figure 1, spectra of Cr (VI) and Fe (III) complexes are closely overlapped. Direct measurement of signals sizes and determination of concentration of Cr (VI) and Fe (III) from overlapped spectrum is impossible. As the signals are additive the application of the H-point method is valid.
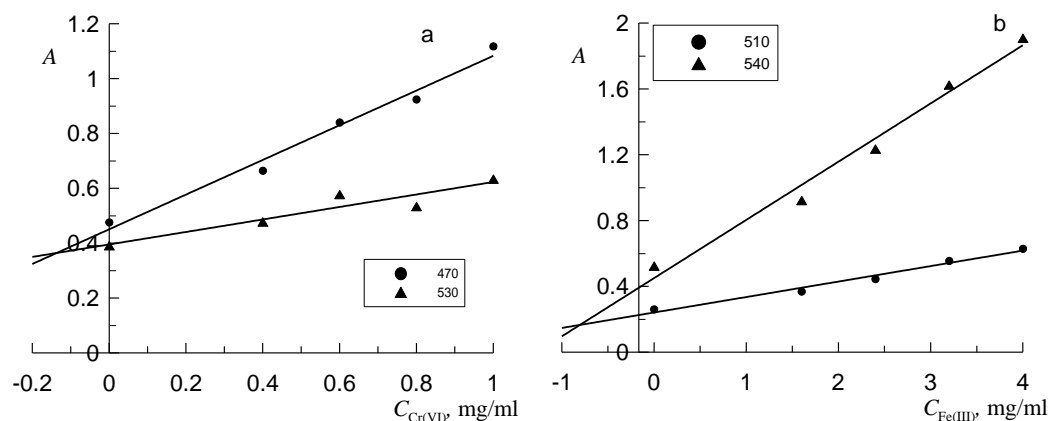

Figure 1. Absorption spectra of: a – (1) Cr(VI) with diphenylcarbazide; (2) Fe(III) with 1,10-phenanthroline and (3) Cr (VI) and Fe (III) with the mixed reagent (diphenylcarbazide and 1,10-phenanthroline).

We obtained the calibration plots of Cr (VI) with diphenylcarbazide in the two concentration ranges (0,8–4,0 and 0,02–0,1 mg/ml) and Fe (III) with 1,10-phenanthroline in the two concentration ranges (0,8–6,4 and 0,1–1,0 mg/ml). The appropriate correlation coefficients obtained (in the range 0.998–0.999) indicate the linearity in the all range of concentrations. The intercepts on the ordinates are negligible in the all graphs. Thus, the H-point method seems to be suitable for use in this system.

Figure 2. Absorption spectra of: (a) 0,8 mg/ml Cr(VI) with mixed reagent (diphenylcarbazide and 1,10-phenanthroline) with the standard addition of 0,0; 0,8; 2,4; 4,0; 5,6; 6,4 mg/ml Fe (III); (b) 0,8 mg/ml Fe(III) with the standard addition of 0,0; 0,8; 1,6; 2,4; 3,2; 4,0 mg/ml Cr(VI).

Firstly to apply the H-point method it is necessary to choose two wavelengths for plotting two calibration plots provided the systematic errors of concentrations determination are minimal [16]. In case of standard addition of Cr (VI) in the concentration range 0,8–4,0 mg/ml we determined the optimal two wavelength 470/530, in the concentration range 0,02–0,10 mg/ml application of the H-point method is not suitable. In case of standard addition of Fe (VI) in the concentration range 0,8–6,4 mg/ml we determined the optimal two wavelength 520/560, in the concentration range 0,1–1,0 mg/ml – 510/540. Then we plotted calibration graphs in case of standard addition of Cr (VI) in the concentration range 0,8–4,0 mg/ml with fixed Fe(III) concentration and standard addition of Fe (VI) in the concentration range 0,8–6,4 mg/ml and 0,1–1,0 mg/ml with fixed Cr (VI) concentration at chosen two wavelengths (Figure 3).

Figure 3. Plots of H-point standard addition method for: (a) fixed Fe(III) concentration and different concentrations of Cr(VI); (a) fixed Cr(VI) concentration and different concentrations of Fe(III).

For the evaluation of correctness of the proposed technique of simultaneous determination of Cr (VI) and Fe (III) we used several synthetic mixtures that had ratios of elements prepared according to some alloys [1]. Concentration of second component (Cr (VI) or Fe (III)) is calculated by the abscissa of intercepts of two calibration plots (Figure 3). Concentration of the first component (Cr (VI) or Fe (III)) is calculated by the ordinate of intercepts of calibration plots and individual calibration plot of first component. Tables 1 and 2 contains the results of concentrations of Cr (VI) and Fe (III) founded by "added-found" method with help of the proposed technique. As it can be seen the error of concentrations determination does not exceed 33 percent.

Table 1. Results of concentration determination of Cr (VI) and Fe (III) by "added-found" method.

Standard addition of C (Cr) (mg/ml)	Added		Found		Δ (%)	
	C_{Cr} (mg/ml)	C_{Fe} (mg/ml)	C_{Cr} (mg/ml)	C_{Fe} (mg/ml)	C_{Cr} (mg/ml)	C_{Fe} (mg/ml)
0,8–4,0	0,8	0,8	0,8	0,8	0	0

Table 2. Results of concentration determination of Cr (VI) and Fe (III) by "added-found" method.

Standard addition of C_{Fe} (mg/ml)	Added		Found		Δ (%)	
	C_{Fe} (mg/ml)	C_{Cr} (mg/ml)	C_{Fe} (mg/ml)	C_{Cr} (mg/ml)	C_{Fe} (mg/ml)	C_{Cr} (mg/ml)
0,8–6,4	0,8	0,8	0,8	0,7	0	13
0,1–1,0	0,1	0,06	0,1	0,08	0	33

3. Conclusion

The problem of simultaneous spectrophotometric determination of Cr (VI) and Fe (III) can be solved by application of mixed reagents and H-point method. For effective application of H-point method the optimal two wavelengths should be chosen, signals must be additive and the Beer's law must be verified. The offered technique can be used for the chromium and iron speciation in alloys. Application of mathematical treatment of signals expands the possibilities of spectrophotometric methods, allows avoiding the chemical pretreatment stages and using high-cost instrumentation and techniques.

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