Simultaneous spectrophotometric determination of chromium (VI) and iron (III) in alloys

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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 reagents (diphenylcarbazide and 1,10-phenanthroline, diphenylcarbazide and sulphosalicylic acid) is studied. We have applied curve fitting method to separate individual signals of chromium (VI) and iron (III) from overlapped absorption spectrum. Peak shape analysis of pure signals of complexes of chromium (VI) with diphenylcarbazide and iron (III) with the 1,10-phenanthroline and sulphosalicylic acid is previously carried out. For adequate application of curve fitting method we chose the optimal empirical models of signals taking into account preliminary information on their shape. 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 11%.

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]. Chromium can be analyzed by ICP-AES [7], sequential injection analysis [8], spectrophotometry [9], X-ray fluorescence spectrometry [10]. Simultaneous determination of chromium and iron can be realized by ICP-AES [11]. 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 ($\lambda_{\text{max}} = 540 \text{ nm}$) and iron (III) with 1,10-phenanthroline ($\lambda_{\text{max}} = 510 \text{ nm}$) and sulphosalicylic acid ($\lambda_{\text{max}} = 500 \text{ nm}$) are widely applied [12]. 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 [13–17]. 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 overlapped absorption spectrum the different mathematical approaches, such as H-point method, PLS regression, principal component analysis and artificial neural networks were applied [13–17].
In this work we applied the curve fitting approach to resolve overlapped absorption spectrum of chromium (VI) and iron (III). Spectrophotometric signals have a peak shape. The curve fitting method is based on the simulation of complex signal as sum of single peak models, using iterative least squares minimization. Application of the curve fitting method has some specific features. To signal modeling the adequate empirical models should be chose. Special attention has been called to a priori evaluation of partial peaks parameters.

Methodology of curve fitting method was thoroughly described in our previous works [18, 19]. Program Resolution with effective algorithm of resolution overlapped signals based on flexible empirical models was developed. In the Resolution program to approximate the peaks the system of modification and construction of base elementary peaks proposed by the papers [20–22] was applied.

Thus our goal is to study the possibility of simultaneous spectrophotometric determination of Cr (VI) and Fe (III) with mixed organic reagents (diphenylcarbazide and 1,10-phenanthroline, diphenylcarbazide and sulphosalicylic acid) via curve fitting.

2. Results and discussion

We obtained the individual spectra of Cr (VI) with diphenylcarbazide and Fe (III) with 1,10-phenanthroline and sulphosalicylic acid and their sum spectra with mixed organic reagents (diphenylcarbazide and 1,10-phenanthroline, diphenylcarbazide and sulphosalicylic acid). Figure 1 shows the received signals. 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 mm.

As shown in figure 1, spectra of Cr (VI) and Fe (III) complexes are closely overlapped in both cases. 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 mathematical methods of signal resolution is valid. Signal pretreatment and resolution of overlapped signals were carried out with the help of the home-made Assayer and Resolution software (ref. figures 2, 3).

For correct application of curve fitting method the preliminary study of individual peak shapes and choice of optimal models are necessary.

![Figure 1](image-url)

**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); b – (1) Cr(VI) with diphenylcarbazide; (2) Fe(III) with sulphosalicylic acid and (3) Cr (VI) and Fe (III) with the mixed reagent (diphenylcarbazide and sulphosalicylic acid).

It is necessary to subtract residual current before the signals treatment. It highly significantly to give more attention to accurate base line subtraction since the method is very sensitive to even small distortions of the peak shape. Base line subtraction is provided by liner interpolation with help of Assayer program. This program was developed on the basis of statements of work [18]. Shape parameters and peak position [20, 23, 24] are also estimated by the Assayer program.
In Table 1, shape parameters and peak positions of individual absorption spectra of Cr (VI) and Fe (III) are given. Signals parameters are used as initial values at the resolution of overlapped absorption spectra of Cr (VI) and Fe (III) with mixed reagents. Peak shape analysis is also useful for the choice of optimal empirical models of individual signals.

We chose the empirical functions for modeling of individual absorption spectra of Cr (VI) and Fe (III) which are shown in Table 2. As the peak of chromium is symmetrical ($s = 0.02$) we offer to apply the Gaussian peak. In the case of iron the peaks have an asymmetrical shape ($s = –0.50; 0.11$). So we investigated several functions obtained by the modification base elementary peaks (Gaussian peak, peak of the logistic and Cauchy peak) proposed in the papers [21, 22]. Programs Grapher and Statistica are used for signals approximation.

Table 1. Parameters of individual absorption spectra Cr (VI) and Fe (III).

| Parameters of signals | Cr (VI) with diphenylcarbazide | Fe (III) with 1,10-phenanthroline | Fe (III) with sulphosalicylic acid |
|-----------------------|--------------------------------|----------------------------------|---------------------------------|
| Asymmetry $s$         | 0.02                           | –0.50                            | 0.11                            |
| Asymmetry $s'$        | 0.52                           | 0.25                             | 0.55                            |
| Peak half-width at peak half-height $W$ | 90.38                      | 116.61                           | 147.38                          |
| Peakedness $v$        | 0.44                           | 0.44                             | 0.43                            |
| Tailness $t$          | 0.33                           | 0.29                             | 0.31                            |
| Maximum position $\lambda_{max}$, nm | 543.15                      | 510.38                           | 508.99                          |

As shown in Table 2, the best approximation result is obtained by Gaussian peak ($R = 0.993$) for chromium spectrum and $PM_{S1G}G$ and $PM_{S2G}$ peaks ($R = 0.996; 0.997$) for iron spectra. Figure 4 gives the illustration of the approximation results with help of the optimal empirical functions.

The preliminary information about peak shape and peak position (ref. Table 1) is used as initial values in the optimization process or for the decreasing the quantity of the optimized parameters. Adequate empirical functions are used for modeling signals in the curve fitting process. Figure 5 shows the results of resolution of overlapped spectra of Cr (VI) and Fe (III) with mixed reagents in Resolution program.
Table 2. Results of approximation of individual Cr (VI) and Fe (III) absorption spectra by various empirical models (PG – Gaussian peak, PM$_{G}$ PM$_{s1G}$, PM$_{L}$, PM$_{C}$ – asymmetrical modification of Gaussian peak, peak of the logistic and Cauchy peak.

| Absorption spectra          | Empirical models                                                                 | Correlation coefficient $R$ |
|-----------------------------|----------------------------------------------------------------------------------|------------------------------|
| Cr (VI) with diphenylcarbazide | $q_{PG} = 2^{−4p^2}$                                                              | 0.993                        |
| Fe (III) with 1,10-phenanthroline | $q_{PM_{G}} = 2 \left( \frac{p − s|p|}{1 − s^2} \right)$                           | 0.994                        |
|                             | $q_{PM_{L}} = \cosh^{-2} \left( \log \sqrt{2 + 1} \frac{p − s|p|}{1 − s^2} \right)$ | 0.987                        |
|                             | $q_{PM_{C}} = 1 + \left( \frac{p − s|p|}{1 − s^2} \right)^2$                     | 0.970                        |
|                             | $q_{PM_{s1G}} = 2 \left( \frac{p − s|p|}{1 − s^2} \right)^{-1}$                  | 0.996                        |
| Fe(III) with sulphosalicylic acid | $q_{PM_{G}} = 2 \left( \frac{x−m}{x−m} \right)^{-1}$                           | 0.997                        |

1 $q = \frac{y}{y_n}$, $p = \frac{x−x_m}{W}$, where $y_n$ is a peak maximum, $x_m$ – is a position of peak maximum, $W$ is a peak width;

2 $s$ – an asymmetry parameter;

3 $c_1$ – parameter function, which changes the shape of top and tail of peak.

Figure 4. Absorption spectra of: (a) Cr(VI) with diphenylcarbazide and approximation by the Gaussian peak; (b) Fe(III) with 1,10-phenanthroline and approximation by the PM$_{s1G}$ function; (c) Fe(III) with sulphosalicylic acid and approximation by the PM$_{G}$ function (dotes is experimental absorption spectra, lines is approximation by the empirical function).

As it can be seen the satisfactory coincidence of experimental and theoretically calculated signals is observed.

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]. Concentrations of Cr (VI) and Fe (III) are calculated by the individual calibration plots of Cr (VI) and Fe (III) and peaks heights obtained by the resolution of overlapped spectra. Table 3 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 11 percent.

Figure 5. Overlapped absorption spectra of Cr(VI) and Fe(III) with mixed reagents and individual absorption spectra of Cr(VI) and Fe(III) obtained by curve fitting. Mixed reagents are (a) diphenylcarbazide and sulphosalicylic acid; (b) diphenylcarbazide and 1,10-phenanthroline. Dotes are the experimental absorption spectra, lines are the spectra obtained by curve fitting method.

Table 3. Results of concentration determination of Cr (VI) and Fe (III) by "added-found" method.

| Added                  | Found        | Δ, % |
|------------------------|--------------|------|
| $C_{Cr}$, mg/ml        | $C_{Fe}$, mg/ml |      |
| mixed reagent (diphenylcarbazide and 1,10-phenanthroline) | 0,006 | 0,006 | 0,006 | 0,006 | 0,0058 | 0 | 3,3 |
| 0,0009                  | 0,0053       | 0,009 | 0,0009 | 0,0047 | 0 | 11 |
| 0,0010                  | 0,0046       | 0,009 | 0,0009 | 0,0045 | 10 | 2,2 |
| 0,0013                  | 0,0043       | 0,012 | 0,0043 | 0,0046 | 7,7 | 6,9 |
| mixed reagent (diphenylcarbazide and sulphosalicylic acid) | 0,0005 | 0,0090 | 0,0005 | 0,0100 | 0 | 11 |

3. Conclusion
The problem of simultaneous spectrophotometric determination of Cr (VI) and Fe (III) can be solved by application of mixed reagents and curve fitting method. For effective application of curve fitting method the optimal empirical models of signals and preliminary information on their shape and position should be used. 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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