

Simultaneous Spectrophotometric Determination of Chromium and Iron in Chromite Ore

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Summary: We have developed an experimental procedure to perform analysis of chromium and iron simultaneously in chromite ore. Chromium and iron were extracted from fused ore by one molar sulphuric acid. The reduction of Cr(VI) to Cr(III) and Fe(III) to Fe(II) was carried out by sodium sulphate. Iron was estimated as $[\text{Fe}(\text{phen})_3]^{2+}$ (phen = o-phenanthroline) and chromium as Cr(III) ions in solution. In several determinations of synthetic mixture the accuracy of the result for chromium and iron was found to be within 2.0 %.

Introduction

Simultaneous determination of chromium and iron will save the time of those who analyse these metals in chromite ore. The analysis can be done with simple visible range spectrophotometers and the expensive atomic absorption spectrophotometer can be avoided without losing much sensitivity for iron. Very sensitive method for chromium is not required due to its sufficient percentage in chromite ore. This experiment can be included in analytical chemistry practical course as an interesting experiment. Students always like those experiments where they are analysing real samples. There are very few practical applications of simultaneous determinations [1,2], although this method is always taught in basic analytical chemistry course.

Initially we tried to develop simultaneous determination of chromium and iron as $\text{K}_2\text{Cr}_2\text{O}_7$ and $[\text{Fe}(\text{SCN})]^{2+}$. We found iron estimation through $[\text{Fe}(\text{SCN})]^{2+}$ to be unsatisfactory as recommended [3]. Molar absorptivity (ϵ) of $[\text{Fe}(\text{SCN})]^{2+}$ at 480 nm was very pH dependent, even ± 0.1 pH change, changes the " ϵ " value below pH 1. Above pH 1 stepwise formation of $\text{Fe}(\text{OH})_{1-3}$ occurs.

Several reducing agents were tried to reduce Cr(VI) to Cr(III) and Fe(III) to Fe(II) but Na_2SO_3 was found to be most effective. Cr(III) ions form a green colour solution ($\lambda_{\text{max}} = 586$ n.m.) and $[\text{Fe}(\text{phen})_3]^{2+}$ forms a red colour solution ($\lambda_{\text{max}} = 511$ n.m.). The absorption characteristics of the two species make them suitable for simultaneous determination. Other metals present in the chromite ore

do not interfere with the estimation of chromium and iron [4].

Experimental

Prepared 13 mg/ml chromium stock solution by dissolving 9.1934 g of A.R. quality $\text{K}_2\text{Cr}_2\text{O}_7$ in 250 ml 1M H_2SO_4 . 33.6 $\mu\text{g}/\text{ml}$ solution of iron was prepared by dissolving 0.06 g of A.R. quality $\text{Fe}_2(\text{SO}_4)_3$ in 500 ml 1M H_2SO_4 . Dissolve 2.5 g o-phenanthroline in 100 ml ethanol, then add 900 ml of distilled water and store in amber bottle. Prepare tri-sodium citrate solution by dissolving 25 g in one litre distilled water. Prepare also 1M NaOH solution using distilled water.

In a series of 50 ml volumetric flasks add 4, 6, 8, 10, 12, and 14 ml of $\text{K}_2\text{Cr}_2\text{O}_7$ stock solution to achieve concentrations ranging from 1.04 to 3.64 mg/ml in the final volume. Introduce 0.2 g, 0.3 g, 0.4, 0.5 g 0.6 g and 0.7 g of Na_2SO_3 respectively for reduction of Cr(VI). The volume was made up to the mark after adjusting the pH to 3.5 with the help of NaOH first and then with tri-sodium citrate using a pH meter. Take another set of 50 ml stoppered conical flasks and 4, 6, 8, 10, 12, and 14 ml of $\text{Fe}_2(\text{SO}_4)_3$ stock solution to yield concentrations ranging from 2.688 to 9.408 $\mu\text{g}/\text{ml}$ in the final volume. Add 4 ml o-phenanthroline solution to each flask. Introduce 0.6 g, 0.9 g, 1.2 g, 1.5 g, 1.8 g and 2.1 g of Na_2SO_3 for reduction, stopper the flask and wait 30 minutes for reduction and complex formation. Adjust the pH of each flask to 3.5 initially with NaOH and finally with tri-sodium citrate. Transfer the contents of the flask to a series of 50 ml volumetric flasks and make up the volume.

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Measure the absorbance of both sets on precision spectrophotometer at 511 n.m. and 586 n.m. after adjusting the zero of spectrophotometer using the blank only. Plot a graph of concentration versus absorbance to verify the region of linear response. Calculate molar absorptivity of $[\text{Fe}(\text{phen})_3]^{2+}$ and Cr^{3+} ions from slope of the curve.

0.5 g of powdered chromite ore was fused with 2.5 g of Na_2CO_3 and 3.5 g CaO in a china crucible at 1000°C in a furnace for about 4 hours. The fused ore was leached with 1M H_2SO_4 and the extract was transferred to 250 ml volumetric flask and volume was made up to the mark. 5 ml of ore extract was taken in a 50 ml stoppered flask already containing 0.7 g Na_2SO_3 dissolved in 10 ml distilled water. Add 4 ml o-phenanthroline solution to the stoppered flask and 2.1 g of Na_2SO_4 and stopper the flask for 30 minutes. Transfer the contents after adjusting the pH to 3.5 with NaOH and tri-sodium citrate, into 50 ml volumetric flask and make up the volume to the mark. Measure the absorbance at 511 n.m. and 586 n.m. after adjusting the zero of spectrophotometer with blank. Calculate chromium and iron concentrations using simultaneous equations. All the spectra were recorded on Shimadzu UV-vis spectrophotometer UV-160A and the related graphs were plotted by using computer programs on IBM compatible Personal Computer.

Observations and Calculations.

The visible range spectra of $[\text{Fe}(\text{phen})_3]^{2+}$, Cr^{3+} ions and the composite spectrum of $[\text{Fe}(\text{phen})_3]^{2+}$ and Cr^{3+} ions are shown in Figure 1. Mutual spectral overlaps are evident from the composite spectrum. In simultaneous determination the first requirement is to calculate the molar absorptivities of $[\text{Fe}(\text{phen})_3]^{2+}$ and Cr^{3+} ions in solution by recording absorbance of known concentrations of these species at 511 n.m. and 586 n.m. The calculated values of molar absorptivities of these species obtained in this study are shown in Table 1.

The next step is to record the absorbance of unknown ore sample at 511 n.m. and 586 n.m.

The absorbance of the mixture is given by the simultaneous equations.

$$A_{\text{Total}} = \epsilon_{\text{Fe}} \cdot b \cdot C_{\text{Fe}} + \epsilon_{\text{Cr}} \cdot b \cdot C_{\text{Cr}} \text{ at } 511 \text{ n.m.}$$

$$A_{\text{Total}} = \epsilon_{\text{Fe}} \cdot b \cdot C_{\text{Fe}} + \epsilon_{\text{Cr}} \cdot b \cdot C_{\text{Cr}} \text{ at } 586 \text{ n.m.}$$

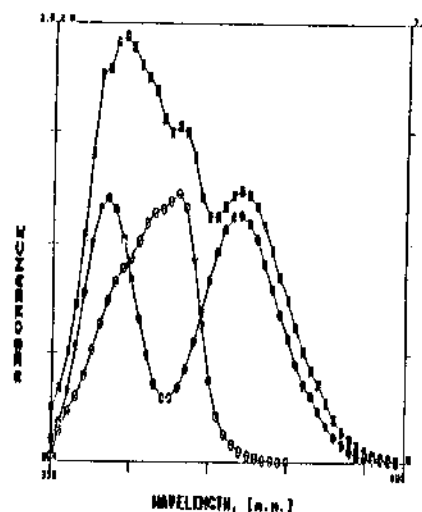


Fig.1: The visible range spectra of $[\text{Fe}(\text{phen})_3]^{2+}$ (-O-O-) Cr^{3+} ions (-●-●-) and the mixture of both (-■-■-)

Table 1: Approximate values of " ϵ " for $[\text{Fe}(\text{phen})_3]^{2+}$ and Cr^{3+} ions

Element	Wavelength n.m.	" ϵ ", l.mol ⁻¹ .cm ⁻¹ .
Cr	511	6.303
	586	20.79
Fe	511	9135
	586	460.7

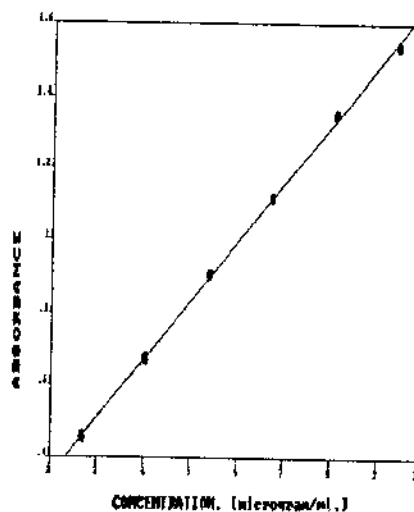


Fig.2: Plot of $[\text{Fe}(\text{phen})_3]^{2+}$ concentration versus absorbance at 511 n.m.

All the parameters except C_{Fe} and C_{Cr} are known in these equations. The concentration of iron and chromium can be calculated by solving these simultaneous equation [5,6].

Results and Discussion

The graph of $[\text{Fe}(\text{phen})_3]^{2+}$ concentration versus absorbance shows a linear concentration response in the range of 2.688 to 9.408 $\mu\text{g}/\text{ml}$ at 511 n.m. 586 n.m. (Figure 2 and 3). A linear concentration response for Cr^{3+} ions in the range of 1.04 to 3.64 mg/ml at 511 n.m. and 586 n.m. is also observed (Figure 4 and 5). The absorbance of Cr^{3+} ions and $[\text{Fe}(\text{phen})_3]^{2+}$ are additive at 511 n.m. and 586 n.m., but are not additive at 415 n.m. In order to check the accuracy and precision of this method, we prepared five sets of synthetic mixtures. The average results of simultaneous determinations are shown in Table 2. The relative precision for chromium determinations was within 2% and for iron it was 3%. The accuracy of the results for both iron and chromium was within 2%.

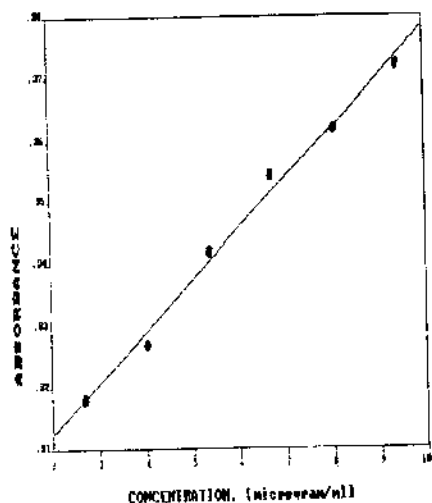


Fig.3: Plot of $[\text{Fe}(\text{phen})_3]^{2+}$ concentration versus absorbance at 586 n.m.

Table 2: Simultaneous spectrophotometric analysis of Cr^{3+} and Fe^{2+} in synthetic mixture.

Number of Determination	Concentration of Cr^{3+} mg/ml		Concentration of Fe^{2+} $\mu\text{g}/\text{ml}$	
	Sought	Found	Sought	Found
5	0.52	0.54	1.344	1.321
5	0.78	0.79	2.016	1.951
5	1.04	1.08	2.688	2.555
5	1.56	1.58	4.032	4.060
5	2.08	2.10	5.376	5.380
5	2.60	2.69	6.720	6.750
5	3.12	3.19	8.064	7.830
5	3.64	3.59	9.408	9.112

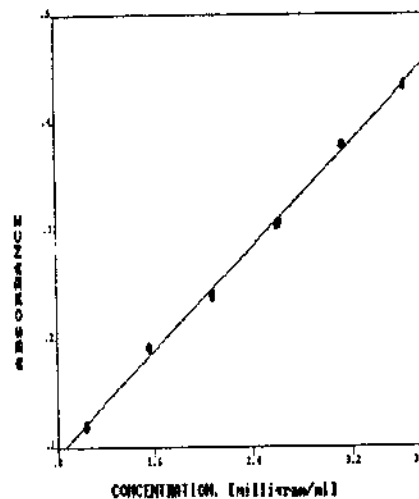


Fig.4: Plot of Cr^{3+} ion concentration versus absorbance at 511 n.m.

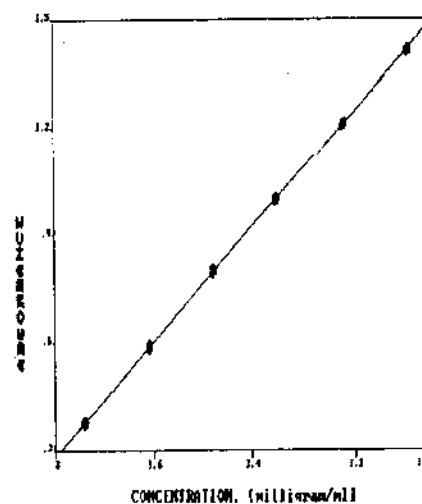
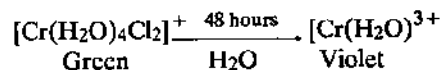


Fig.5: Plot of Cr^{3+} ion concentration versus absorbance at 586 n.m.

Cr^{3+} ions are well known for ligand exchange in solution, for example:



The composition of the complex changes with time.

Sulphuric acid is used to extract iron and chromium from the ore because the composition of Cr^{3+} complex in water does not change for few hours. Nitric acid and hydrochloric acid can not be used as solvent in this estimation due to significant ligand exchange with time. The pH 3.5 is necessary for iron estimation because maximum complex formation occurs at this pH [7]. Small temperature changes do not effect the absorbance values. Na_2SO_3 was used in excess as reducing agent for reduction of Fe^{3+} . The reducing agent reacts preferentially with O_2 as compared to Fe^{3+} . O_2 is a better oxidizing agent than Fe^{3+} (check E° values). Presence of excess O_2 can be avoided by using stoppered conical flasks or by flushing nitrogen through the flask.

Ethyl alcohol, the solvent for o-phenanthroline reacts with $\text{K}_2\text{Cr}_2\text{O}_7$ to form acetic acid. The formation of acetic acid is avoided by adding o-phenanthroline after reduction of Cr^{6+} to Cr^{3+} . But o-phenanthroline is added before reduction of Fe^{3+} to Fe^{2+} to keep the Fe^{2+} formed as stable $[\text{Fe}(\text{phen})_3]^{2+}$ complex.

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