Extraction-Spectrophotometric Determination of Chromium(VI) with *O,O'*-Dibutyl Dithiophosphate¹

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Chromium(VI) reacts with *O,O'*-dibutyl dithiophosphate ion to form tris(dibutyl dithiophosphato)chromium(III) and tetrabutyl thiophosphoryl disulfide in an acidic solution (pH 1.2 – 1.7). Both of the products are extracted into hexane and the absorbance at 278 nm based on these products is utilized for the determination of chromium(VI). The chromium(III) complex corresponding to two-thirds of the initial chromium(VI) concentration and the disulfide corresponding to three-halves of the initial chromium(VI) concentration are extracted under the optimum conditions. The calibration graph obtained is linear over the range of 2×10^{-6} – 1×10^{-4} mol/dm³ chromium(VI) concentration, and the apparent molar absorptivity (absorbance per initial chromium(VI) concentration in aqueous phase) is 1.69×10^4 mol⁻¹ dm³ cm⁻¹. This method is subject to interference from Cu^{II}, Fe^{II}, Cd^{II}, Pb^{II}, Hg^{II}, Pd^{II}, Sn^{IV}, Sb^{III}, Se^{IV}, Au^{III}, nitrite, sulfite, thiosulfate and ascorbic acid. This method was applied to the determination of chromium in steel samples, and good results were obtained.

Keywords Solvent extraction, spectrophotometry, chromium(VI), chromium(III), hexane, *O,O'*-dibutyl dithiophosphate, tetrabutyl thiophosphoryl disulfide

Potassium *O,O'*-dialkyl dithiophosphates, (RO)₂P(S)-S⁻K⁺, have been used widely as flotation or extraction reagents for a large number of metal ions. Busev and Ivanyutin² provided information on many metal complexes with *O,O'*-dialkyl dithiophosphates. Bode and Arnswald³ carried out a series of experiments on the extraction of metal ions with the diethyl derivative from the mineral acid solutions. And Handley and Dean⁴ also carried out a similar investigation by the use of the dibutyl derivative.

Both groups reported that chromium(III) was not extracted and only a part of chromium(VI) could be extracted with these ligands. There has been no paper on the determination of chromium with *O,O'*-dialkyl dithiophosphate. However, several tris(dialkyl dithiophosphato)chromium(III) complexes were synthesized by the reaction between chromium(III) and these ligands, and their electronic spectra in chloroform were investigated from the standpoint of complex chemistry.⁵

The authors have been studying the analytical application of these ligands, and have reported the extraction-spectrophotometry of some metal ions.⁶⁻¹⁰ We also investigated the possibility of the extraction of chromium into hexane with *O,O'*-dialkyl dithiophosphates (alkyl group=methyl, ethyl, propyl and butyl). We found that chromium(VI) could be determined extraction-spectrophotometrically with sufficient accuracy, precision and sensitivity by using the dibutyl derivative. We also found that all chromium(VI) was reduced preferentially to chromium(III) with the dithiophosphate in the first place and then only two-

thirds of the amount of the reduced chromium(III) were extracted into hexane as tris(dibutyl dithiophosphato) complex.

Experimental

Reagents

Potassium *O,O'*-dibutyl dithiophosphate (Kdtp) was synthesized and purified according to the method described in a preceding paper.¹¹ Its purity (above 99%) was confirmed by iodometry.¹² And its melting point (145 – 147°C) was close to *ca.* 150°C, the value reported in the literature.¹¹ Its aqueous solution was prepared daily.

A stock solution of chromium(VI) (0.1000 mol/dm³) was prepared by dissolving 14.71 g of a primary standard potassium dichromate in water and diluting the solution to 1.000 dm³ with water. A working solution was prepared by diluting it appropriately with water.

Tris(*O,O'*-dibutyl dithiophosphato)chromium(III) was synthesized with Kdtp and chromium(III) nitrate nonahydrate in ethanol, and purified by recrystallization in hexane. The content of chromium in the complex was 6.70% (theoretical: 6.70%). The electronic spectrum of the complex in chloroform agreed with that reported in the literature.⁵

Tetrabutyl thiophosphoryl disulfide, {(C₄H₉O)₂-P(S)SSP(S)(OC₄H₉)₂, (dtp)₂}, was prepared by oxidizing 1.2×10^{-4} mol/dm³ Kdtp with 0.2 mol/dm³ hydrogen peroxide in the aqueous medium at pH 1.5 for 5 h. The

disulfide formed was extracted into hexane and the hexane solution was used as such. It was confirmed by spectrophotometric experiments that both the formation and the extraction of the disulfide were achieved perfectly under these conditions.

Apparatus

A Shimadzu Model UV-240 recording spectrophotometer with 10-mm quartz cells was used for all absorption measurements. A Shimadzu Model AA-625-11 atomic absorption spectrometer (air-acetylene flame) was used for the determination of chromium in the organic phase. A Hitachi-Horiba Model F-11 pH meter with a combined glass electrode was used for all pH measurements. An Iwaki Model KM shaker was used for the extractions.

Standard procedure

A 5.0 cm³ portion of a 0.5 mol/dm³ sulfate buffer solution (pH 1.5) was taken into a 50-cm³ separatory funnel. A 1.0 cm³ of a 4.0×10⁻⁴ mol/dm³ chromium(VI) standard solution (or a sample solution containing 1–50 µg chromium(VI)) and 1.0 cm³ of a 0.08 mol/dm³ Kdtp solution were added, and the total volume of the solution was finally made up to 10.0 cm³ with water. After mixing, the solution was allowed to stand for 10 min at room temperature. A 10.0 cm³ volume of hexane was added and the funnel was shaken vigorously for 30 min. After the phase separation, the hexane phase was transferred to another separatory funnel. A 5.0 cm³ volume of a 1 mol/dm³ potassium hydroxide solution was added as a back-washing solution of hexane phase, then the funnel was shaken vigorously for 10 min. The hexane phase was taken out and dried over anhydrous sodium sulfate. The absorbance of the hexane phase was measured at 278 nm against pure solvent.

Results and Discussion

Absorption spectra

Figure 1 shows the absorption spectra of hexane phases before (spectrum a) and after (b) back-washing, the disulfide (c) extracted into hexane and Cr(dtp)₃ (d) dissolved in hexane.

The chromium(III) complex (spectrum d) exhibited three absorption maxima at 694 nm (molar absorptivity, ϵ , was 360 mol⁻¹ dm³ cm⁻¹), 534 nm (ϵ was 259 mol⁻¹ dm³ cm⁻¹) and 278 nm (ϵ was 1.74×10⁴ mol⁻¹ dm³ cm⁻¹). The disulfide absorbed only UV light, and its molar absorptivity at 278 nm was 3.49×10³ mol⁻¹ dm³ cm⁻¹. The difference between spectra a and b in the UV region was due to the absorption by *O,O'*-dibutyl dithiophosphoric acid (Hdtp) which was extracted into hexane from an acidic aqueous phase and was removed into a back-washing solution.

It was reasonable to understand that spectrum b consisted of spectra c and d, because a same spectrum was

Fig. 1 UV-visible absorption spectra of hexane phases before (a) and after (b) back-washing, the disulfide (c) extracted into hexane and Cr(dtp)₃ (d) dissolved in hexane.

Fig. 2 Effect of pH of the aqueous phase on the extraction of 4.0×10⁻⁵ mol/dm³ chromium(VI) with 8.0×10⁻³ mol/dm³ Kdtp.

obtained from the hexane solution containing proper amounts of the chromium(III) complex and the disulfide.

Effect of some factors on the absorbance

The effect of factors on the absorbance was investigated according to the standard procedure, except for the factor in question.

The shaking time of 10 min was sufficient for the extraction process, and the maximum and steady absorbance was obtained up to at least 3 h.

The optimum pH range of the aqueous phase was 1.2–1.7 for the extraction process, as shown in Fig. 2. The decrease of absorbance out of the optimum pH range was due to the protonation of dtp⁻ (below pH 1.2) and to a noticeable drop in redox potential for the Cr^{VI}–Cr^{III} redox system (above pH 1.7).

The optimum concentration of Kdtp was 3.2×10⁻³–2.4×10⁻² mol/dm³ as shown by using open circles in Fig. 3. At Kdtp concentrations higher than 2.4×10⁻² mol/dm³, a steep rise in absorbance was observed owing

Fig. 3 Effect of Kdtp concentration on the absorbance of hexane phase and the concentrations of chromium(III) complex and disulfide extracted in the extraction of 4.0×10^{-5} mol/dm³ chromium(VI) at pH 1.5. ○: absorbance of hexane phase; ■: absorbance corresponding to chromium(III) complex; ●: absorbance corresponding to disulfide.

to the absorption by the reagent blank.

The shaking time of 10 min was sufficient for the back-washing process in which Hdtp was entirely removed from the hexane phase. The chromium(III) complex was resistant to this process and only 10% of the complex was back-extracted by the shaking for 12 h.

Various kinds of back-washing solution were tested. Phosphate buffer solutions (pH 6–8), tris(hydroxymethyl)aminomethane buffer solutions (pH 7–9), ammonium buffer solutions (pH 8–11) and potassium hydroxide solutions (pH 12–14) were all suitable for a

back-washing solution.

Calibration graph

A calibration graph for the determination of chromium(VI) was prepared according to the standard procedure. The calibration graph obtained was a straight line coinciding with the origin and having a slope of 1.69×10^4 mol⁻¹ dm³, over the range of 2×10^{-6} – 1×10^{-4} mol/dm³ initial chromium(VI) concentration in aqueous phase.

Effect of diverse ions

The effect of diverse ions on the determination of 4×10^{-5} mol/dm³ chromium(VI) was studied. The tolerance limits (within 3% error) of those ions are summarized in Table 1.

One group of the ions which interfere strongly consists of the metal ions such as Cu^{II}, Cd^{II}, Pb^{II}, Hg^{II}, Pd^{II}, Sb^{III} and Au^{III}, which are extracted as the stable dithiophosphato complexes and are not back-extracted.

Another group of the interfering ions contains Fe^{II}, Sn^{IV}, nitrite, sulfite, thiosulfate and ascorbic acid; these are redox agents and reduce Cr^{VI} to Cr^{III} or oxidize the dithiophosphate to the disulfide.

Application to the analysis of steel

In order to test the utility of this method, it was applied to the determination of chromium in standard steel samples (JSS).

A pretreatment of the samples was carried out in the following way. A known amount of the sample (containing 0.1–5 mg of chromium) was decomposed with 10 cm³ of (1+1) hydrochloric acid and 3 cm³ of (1+2) nitric acid. The solution was heated and

Table 1 Tolerance limits (within 3% error) of diverse ions in the determination of 4.0×10^{-5} mol/dm³ chromium(VI)

Tolerance limit (mol/dm ³)	1×10^{-1}	Na ⁺ , NH ₄ ⁺ , Mg ^{II} , Ca ^{II} , Al ^{III} , NO ₃ ⁻ , ClO ₄ ⁻ , Cl ⁻ , Br ⁻
	1×10^{-2}	Zn ^{II} , F ⁻ , I ⁻ , SCN ⁻ , PO ₄ ³⁻ , CO ₃ ²⁻ , acetate, tartrate, borate, thiourea
	1×10^{-3}	Mn ^{II} , Co ^{II} , Ni ^{II} , citrate, EDTA
	1×10^{-4}	Ba ^{II} , V ^V , Cr ^{III} , Fe ^{III} , W ^{VI} , Ag ^I , In ^{III} , As ^V , Bi ^{IIIa} , hydrazine, hydroxylamine
	1×10^{-5}	Bi ^{III} , Mo ^{VI} , Ti ^{IV} , Sn ^{II} , As ^{III} , Te ^{IV} , Mn ^{VII} , Cu ^{IIa} , oxalate
	$< 1 \times 10^{-5}$	Cu ^{II} , Fe ^{II} , Cd ^{II} , Pb ^{II} , Hg ^{II} , Pd ^{II} , Sn ^{IV} , Sb ^{III} , Se ^{IV} , Au ^{III} , NO ₂ ⁻ , SO ₃ ²⁻ , S ₂ O ₃ ²⁻ , ascorbic acid

a. Thiourea was added as masking reagent.

Table 2 Analytical results on the determination of chromium in the standard steel samples

Sample	Metal contents certified, %						Chromium found ^a , %	RSD, %
	Cr	Cu	Mo	V	Mn	Ni		
JSS 150-4	0.38	0.086	0.19	0.002	0.31	4.11	0.39	2.2
JSS 151-4	0.15	0.46	0.054	0.052	1.51	2.92	0.16 ^b	5.6
JSS 152-4	0.52	0.45	1.02	0.11	0.42	1.95	0.53 ^b	1.0
JSS 153-4	1.01	0.17	1.33	0.22	0.83	0.96	1.04	1.2
JSS 154-4	2.04	0.21	0.71	0.33	1.14	0.50	2.07	1.6
JSS 155-4	3.08	0.30	0.39	0.43	0.27	0.039	3.16	1.3

a. Average of 6 determinations. b. Thiourea was added as masking reagent.

evaporated to dryness. The residue was dissolved in a 25 cm³ of (10+6) hydrochloric acid. Iron and molybdenum in the solution were extracted into 4-methyl-2-pentanone. In order to oxidize chromium(III) to chromium(VI), a potassium permanganate solution was added dropwise to the aqueous solution until the color of the solution became slightly red. Finally, the solution was diluted exactly to 100 cm³ with water.

A 1 cm³ volume of this solution was taken and the determination of chromium was carried out according to the standard procedure. The analytical results obtained were in good agreement with the certified values (Table 2).

Reaction mechanism

The reaction consists of three steps: that is, redox reaction, complex formation and extraction, as shown by the following equations:

and

in which HCrO_4^- is adopted as the initial species of chromium(VI) considering the given value of pH.

According to the above assumption, the absorbance measured can be represented by the following equation:

$$A_{278} = \varepsilon_1[\text{Cr}(\text{dtp})_3]_{\text{org}} + \varepsilon_2[(\text{dtp})_2]_{\text{org}}, \quad (4)$$

where ε_1 and ε_2 are the molar absorptivity for each species and are known values.

The changes of $\varepsilon_1[\text{Cr}(\text{dtp})_3]_{\text{org}}$ and $\varepsilon_2[(\text{dtp})_2]_{\text{org}}$ with the concentration of Kdtp are individually shown in Fig. 3. The value of $\varepsilon_1[\text{Cr}(\text{dtp})_3]_{\text{org}}$ was obtained from the concentration of chromium in hexane phase, which was determined by AAS following the evaporation of the organic solvent and the decomposition of the residue with a mixture of sulfuric and nitric acids. And the value of $\varepsilon_2[(\text{dtp})_2]_{\text{org}}$ could be estimated by subtracting the value of $\varepsilon_1[\text{Cr}(\text{dtp})_3]_{\text{org}}$ from the absorbance measured.

The value of $\varepsilon_1[\text{Cr}(\text{dtp})_3]_{\text{org}}$ was zero until the mole ratio of Kdtp to chromium went up to 3. A complicated increase was observed with an increase in the concentration of Kdtp at a mole ratio of more than 3. And finally, the value reached a maximum at the Kdtp concentration of more than 3×10^{-3} mol/dm³. At this maximum, however, it was determined by AAS that the percent extraction of chromium was only 67%.

On the other hand, the change in $\varepsilon_2[(\text{dtp})_2]_{\text{org}}$ was simple and understandable from a stoichiometric standpoint, based on Eq. (1). That is, the value of $\varepsilon_2[(\text{dtp})_2]_{\text{org}}$ corresponded to one-half of the Kdtp

concentration until the mole ratio of Kdtp to chromium went up to 3. And above the mole ratio of 3, it was constant, corresponding to three-halves of the total chromium concentration.

These facts lead to these conclusions:

- (i) The redox reaction occurs preferentially until all chromium(VI) is reduced to chromium(III);
- (ii) Then only two-thirds of the amount of chromium(III) form the complex with dtp⁻;
- (iii) Both the complex and the disulfide formed are completely extracted because of their high solubilities in hexane.

The theoretical values of $\varepsilon_2[(\text{dtp})_2]_{\text{org}}$ can be calculated according to this conclusion. These values are shown by a solid line in Fig. 3, and are in good agreement with the observed values. An apparent molar absorptivity (absorbance per initial chromium(VI) concentration in aqueous phase) can be calculated as 1.69×10^4 mol⁻¹ dm³ cm⁻¹. This value coincides with the slope of the calibration graph described above. These are strong pieces of evidence in support of the above conclusion.

It is an interesting fact that the concentration of extracted chromium is exactly two-thirds of that of initial chromium(VI). This simple ratio may be an important key to clarify the reaction mechanism in detail. However, a reasonable explanation could not be found in time for this paper.

Comparison with other methods

The proposed method has some features which compare favorably with those of convenient methods such as diphenylcarbazide(DPC)¹³, 2-methyl-8-hydroxyquinoline (2M8HQ)¹⁴ and 8-aminoquinoline (8AQ)¹⁵ methods.

1. In this method, the absorbance to be measured is based on both the chromium complex and the oxidized product of the ligand. This is a remarkable difference from other methods.

2. This method can be carried out at room temperature, in contrast to the other two methods, in which the reaction temperature must be controlled to 60–70°C (2M8HQ) or 97–98°C (8AQ).

3. The apparent molar absorptivity of this method is larger than that of 2M8HQ method ($\varepsilon = 7.9 \times 10^3$ mol⁻¹ dm³ cm⁻¹ at 410 nm), but is smaller than those of DPC method ($\varepsilon = 2.6 \times 10^4$ at 540 nm) and 8AQ method ($\varepsilon = 2.2 \times 10^4$ at 550 nm).

4. This method is also subject to interference from many oxidizing and reducing agents, similarly to the other methods, but not to 2M8HQ method, which contains no redox reaction.

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