Notes

Extraction of Chromium(VI) with a Crown Ether

Hideko KOSHIMA[†] and Hiroshi ONISHI^{††}

University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Keywords Extraction, chromium(VI), crown ether, dicyclohexano-18-crown-6

The authors have been studying the extraction, with crown ethers, of analytes as anionic species, namely, chloro complexes, perrhenate, and tetrafluoroborate.^{1,2} During the extraction of tetrafluoroborate², chromium(VI) also was found to be extracted.

This note describes briefly the extraction behavior of chromium(VI) with dicyclohexano(or dicyclohexyl)-18-crown-6 (DC18C6). At first, chromium(VI) was thought to be extracted as its dichromate, but this is not the case. After back-extraction, chromium(VI) is determined spectrophotometrically by a flow injection method. In comparison with the available extractive separation methods³, this extraction and back-extraction give a simple method for the separation of chromium(VI) from concomitant iron(III).

Experimental

Reagents

A standard chromium(VI) solution was prepared by dissolving potassium dichromate in water. As a crown ether DC18C6 (Tokyo Kasei Kogyo) was generally used.

Procedure for extraction study

Three milliliters of aqueous solution that was 1 mM in chromium(VI) was shaken for 3 min with 3 ml of 0.02 M DC18C6 in 1,2-dichloroethane at room temperature (about 20°C). After centrifugation (3000 rpm), chromium remaining in the aqueous phase was determined in dilute sulfuric acid medium by a flow injection method (absorbance at 542 nm) using diphenylcarbazide.⁴ The measurement time in the flow injection method was about 1 min per sample.

Results and Discussion

DC18C6 was chosen for our study of the extraction of

chromium(VI) because it gave the highest distribution ratio (D ; organic to aqueous) among the eight crown ethers examined in preliminary experiments. The extent of extraction of chromium from acid solutions was in the decreasing order $\text{HCl} > \text{HF} > \text{HNO}_3$, and increased with the acid concentration. Chromium was hardly extracted from sulfuric acid solutions and none was extracted from basic solutions; this is a great contrast to the extraction of rhenium(VII) as KReO_4 .⁵ Chloride and fluoride affected the extraction of chromium as anions. Figure 1 shows the effect of the concentration of potassium chloride or potassium fluoride in dilute sulfuric acid medium on the distribution ratio of chromium(VI) with DC18C6. In short, the distribution ratio increased as the concentrations of H^+ , K^+ , Cl^- , and F^- increased and as the initial Cr(VI) concentration decreased.

Chromium(III) was not appreciably extracted with DC18C6 from HCl , H_2SO_4 , HF , and $\text{H}_2\text{SO}_4\text{-KCl}$

Fig. 1 Effect of potassium chloride or potassium fluoride concentration on extraction of chromium(VI) with DC18C6.

[†] Present address: Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520-21, Japan.

To whom correspondence should be addressed.

^{††} Present address: Kasuga 3-chome 15-5, Tsukuba, Ibaraki 305, Japan.

Table 1 Separation of chromium(VI) from iron(III)

Taken/mM		Recovery, %	
Cr	Fe	Cr	Fe
Extraction from 0.1 M H ₂ SO ₄ -0.1 M KCl			
0	10		0.084
0.1	10	98.1	0.12, 0.15
1	10	95.3	0.072, 0.012
0	100		0.12
1	100	96.3	0.058, 0.077
Extraction from 0.5 M H ₂ SO ₄ -1 M KF			
0	10		0.036
0.1	10	97.9	0.089, 0.181
1	10	96.2	0.009, 0.12
0	100		0.004
1	100	96.3	0.024, 0.039

solutions.

The dependence of the distribution ratio on the DC18C6 concentration indicated that the molar ratio of DC18C6 to Cr(VI) in the extracted species was 1:1 from 0.1 M HCl-0.1 M K₂SO₄ and 0.1 M HF-0.1 M K₂SO₄ solutions.

After extraction of 0.02–1 mM Cr(VI) from 0.1 M H₂SO₄-0.1 M KCl and 0.5 M H₂SO₄-1 M KF solutions (3 ml each), each organic phase was shaken for 3 min with an equal volume of 0.1 M NaOH for back-extraction;

recoveries of 98–102% and 98–100% were obtained from the respective aqueous media. The extraction and back-extraction method affords separation of chromium(VI) from iron(III) (Table 1); iron in the back-extract was determined by atomic absorption spectrometry. Because chromium(VI) extracted from the chloride media is gradually reduced, the procedure must be carried out without undue delay.

This work was presented at the 40th Annual Meeting of the Japan Society for Analytical Chemistry, Yokohama, November 1991.

References

1. H. Onishi and H. Koshima, *Anal. Sci.*, **7** (Supplement), 45 (1991).
2. H. Koshima and H. Onishi, *Fresenius' J. Anal. Chem.*, **343**, 287 (1992).
3. H. Onishi, "Photometric Determination of Traces of Metals, Part II A: Individual Metals, Aluminum to Lithium", 4th ed., Chap. 10, Wiley, New York, 1986.
4. J. C. de Andrade, J. C. Rocha and N. Baccan, *Analyst* [London], **110**, 197 (1985).
5. H. Koshima and H. Onishi, *Anal. Chim. Acta*, **232**, 287 (1990).

(Received July 8, 1992)

(Accepted November 25, 1992)