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Original Article

EXTRACTION OF CHROMIUM (VI) FROM SOILS BY TRI-n-OCTYL AMINE OXIDE

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Abstract
The extraction of chromium(VI) from aqueous phosphoric and acetic acid media using tri-n-octyl amine oxide (TOAO) in benzene solutions was studied. It was found that the quantitative recovery of chromium(VI) was attained after extraction with 0.01 M TOAO solution for 10 min followed by back extraction with 0.2 M HNO

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Experimental
The aqueous phase contained 104 µg/mL of chromium (VI) prepared by dissolving potassium dichromate in water acidifying the solution having required ionic strength. Effect of parameters such as the volume of the aqueous phase, the time and temperature of drying soil samples, the number of extraction steps, and the concentration of chromium in the test samples on the recovery of chromium (VI) have been studied.

Extraction of chromium (VI).
10 mL portions of Cr (VI) and [phosphoric and acetic] acid of different molarity & organic phase (Tri n-Octyl amine oxide in benzene) (TOAO) solutions were placed in test samples on the recovery of chromium (VI) have been studied.

The determination of chromium species is mainly dependent on pH and oxidative conditions. In our earlier communication we have reported studies on the extraction of chromium (VI) by Tri-n-Octyl amine oxide (TOAO) from mineral acid solutions [1].

In chromium bearing soils chromium (III) is oxidized to chromium (VI) by the available oxidants. The determination of the optimum conditions for the traction of chromium (III) and chromium (VI) from soil samples or from aqueous solutions obtained after leaching is of utmost importance. Selective determination of chromium (VI) in the presence of chromium (III) is due to its relative toxic nature. Therefore it is necessary to separate these two forms at the stage of sample preparation itself before determination of chromium in soils is done. Analytical procedure is to be provided for the selective determination of various chromium species in equilibrium [2-5]. The aim of this investigation is to develop a procedure for the determination chromium (VI) in soils by atomic absorption spectrometry [AAS] after its extraction using a system of tri n-Octyl amine oxide in benzene. It is very difficult to optimize the conditions for extraction of chromium (VI) and for the separation chromium (VI) from chromium (III).

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Introduction
The two forms of chromium are most stable and highly important in physiological processes. Chromium (VI) is a necessary component in the glucose and lipid metabolism; chromium (VI) is an irritant of skin and mucous membranes and may cause tumors. The relation between the two species strongly depends on pH and oxidative conditions. In our earlier communication we have reported studies on the extraction of chromium (VI) by Tri-n-Octyl amine oxide (TOAO) from mineral acid solutions [1].

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Extraction of chromium (VI).
10 mL portions of Cr (VI) and [phosphoric and acetic] acid of different molarity & organic phase (Tri n-Octyl amine oxide in benzene) (TOAO) solutions were placed in the thermostatic (100-mL) vessels (25 + 5~ using a vibro-shaker with frequency120-140 rpm and vibration amplitude 35–40 mm). Preliminary studies showed that the phase equilibrium was attained after shaking for 10 min (maximum extraction efficiency is obtained within 10 min). 1-mL portions of the organic and aqueous phases were analyzed as given below. The aqueous sample is acidified with 2 M acid and diluted up to 50-mL with DD water. Back extraction of chromium from the organic phase was performed twice with 0.2 M HNO

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chromium (VI) in the resulting solution was determined by AAS.

**Extraction of chromium (VI) from soil samples**

Soil samples with specified amount of chromium (VI) were mellowed and dried in air for 40 days. The air-dried samples were powdered in an agate mortar and sifted through a sieve (mesh size 0.25 mm). The samples were dried thoroughly at 20 to 120°C for about 190 min. after the addition of chromium (VI). The extraction of Cr(VI) from the prepared samples was performed in 100-mL vessels. In both the acid media followed by TOAO solution in benzene (10 mL) as per the procedure described earlier. After equilibration and phase separation, the aqueous phase was filtered and diluted to 50-mL. Back extraction and the concentration of chromium (VI) in both the phases were determined as described earlier. Interferences were eliminated, with ammonium chloride solutions before performing the analysis [6]. The final concentration of the salt in the test solution was about 1.98%. The analytical signals were measured at 357.9 nm. Reference solutions (0-5 ppm) were used to calibrate the spectrometer.

**Verification of the mass balance of chromium in soil samples.**

The mass balance of chromium was verified using model soil samples with a mixture of HNO₃ and HClO₄ as described by Korenman et al [8]. Weighed portions of the soil (3.0000 g) were dried, powdered, and placed in a 100-mL vessel. The samples were moistened with water and acidified with concentrated HNO₃ (10 mL) and concentrated HClO₄ (5 mL). The vessel was covered with a watch glass and heated to 90–120°C for an hour. Next, a 15-mL portion of HCl (1:1) was added. The mixture was again heated for an hour. The watch glass was washed with a hot solution of 1% HCl; the wash solution was filtered to a 100-mL flask, mixed with NH₄Cl, and diluted to the mark with water. Chromium (VI) concentration in the resulting solutions was determined by AAS. Blank solutions containing all the reagents but chromium (VI) were prepared simultaneously.

**Conditions for chromium (VI) extraction from soil samples**

The variation of one of the parameters at the stage of sample preparation (temperature or the time of drying) or the conditions of chromium (VI) extraction (organic solvent, TOAO concentration, the number of extraction steps, extraction time) leads to ambiguous results. The results are unstable unless the soil samples are dried thoroughly. It is the condition at which the biological and physicochemical equilibrium in the soil is attained and chromium (VI) does not undergo any transformations (e.g., reduction and formation of difficultly soluble compounds). Soil samples were air-dried, powdered, and sifted. A weighed portion of the test soil was placed in a 100-mL flask, acidified with 30 mL of H₃PO₄ (15M), and extracted three times with 15-mL portions of a 0.01 M TOAO solution in benzene. The extraction was performed for 10 min. Next, the contents of the flask were placed in a tube and centrifuged. The organic phase was placed into a 50-mL flask and diluted to the mark with benzene. The back-extraction of chromium (VI) was performed twice.

**RESULTS AND DISCUSSION**

The results obtained on the variation of distribution ratio as a function of aqueous phase concentration of the acid (H₃PO₄ and CH₃COOH) are presented in Fig. 1. In the case of phosphoric and acetic acid solutions the extraction of chromium (VI) by TOAO in benzene as a function of acidity, the distribution ratio (Kₘ) was found constant from 0.5–1.25 M followed by decrease in efficiency. (Fig. 1) where as from acetic acid media distribution ration decreased with increasing acidity. Organic solvents of different classes were examined (as diluents) such as carbon tetrachloride, chloroform, pentanol, and methyl isobutyl ketone etc. The results are presented in Table 1. Stripping of chromium (VI) from the organic phase has been attempted with different reagents. Based on the data obtained, 0.2M Mn(OH)₃ was used as back-extractant in these studies. The effect of the concentration of TOAO in benzene on the recovery of chromium (VI) was studied The log-log plots of Kₘ Vs. TOAO from both the acid solutions gave straight lines of unit slope[8]. Representative data from phosphoric acid solutions has been provided in Fig. 2.

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**Fig. 1 Effect of acidity on Extraction**

Using two 20-mL portions of 0.2 M HNO₃. The back-extracts were merged, ammonium chloride was added (to the final concentration of about 1.98%), and the mixture was diluted to 50 mL with water. The chromium (VI) concentration in the aqueous and organic phases was determined by AAS.

**Fig. 2 Extractant variation (H₃PO₄ medium)**

The log-log plots of Kₘ Vs. TOAO from both the acid solutions gave straight lines of unit slope[8]. Representative data from phosphoric acid solutions has been provided in Fig. 2.
An increase in the TOAO concentration is accompanied with a regular increase the recovery of chromium. The optimal TOAO concentration was found to be 0.01 M. Under these conditions, the chromium (VI) recovery at acid concentration of 1.0M was 99.02%, whereas chromium (III) was not extracted under these conditions. The results of experiment on variation of volume of the aqueous phase indicated that the recovery of chromium (VI) remained constant. The effect of the time of drying on the recovery of chromium (VI) indicated that it remained constant after drying for 190 min. The effect of drying temperature on the recovery of chromium was studied in the range 20-120°C (Fig. 3). Drying was performed for 45 min. An increase in the temperature resulted in a gradual decrease in recovery. Similar dependence was obtained in studying the effect of the chromium added to the model samples on the recovery of chromium. It is increased following repeated extraction procedure. The recovery attained a maximum at the first step and regularly decreased at the subsequent extraction steps. After three subsequent extraction procedures, chromium (VI) was extracted almost completely. In sufficient extraction depends on 1) the formation of compounds during drying process not extractable to the organic phase and 2) the reduction of chromium(VI) to non-extractable chromium(III) probably due to the presence of reductants in the soil.

Conclusions

The developed procedure for the selective chromium(VI) determination in soil samples in the presence of chromium(III) were verified using model and real samples. It is recommended for routine analyses of soil samples.

REFERENCES