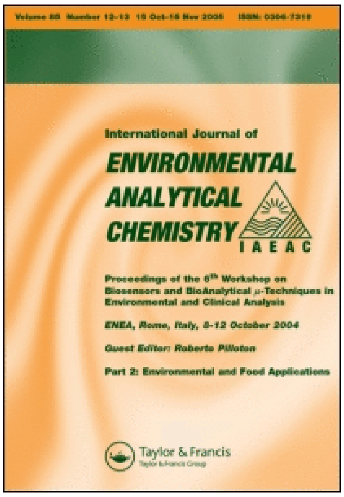

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Spectrophotometric Determination of Chromium(VI) with Cr(VI)-*o*-Cl-PF-TDPC Ternary Complex after Preconcentration on an Organic Solvent-soluble Membrane Filter

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To cite this Article Li, Wen-Jun , Tai, Chao and Gu, Xue-Xun(2001) 'Spectrophotometric Determination of Chromium(VI) with Cr(VI)-*o*-Cl-PF-TDPC Ternary Complex after Preconcentration on an Organic Solvent-soluble Membrane Filter', International Journal of Environmental Analytical Chemistry, 81: 2, 127 — 135

To link to this Article: DOI: 10.1080/03067310108044350

URL: http://dx.doi.org/10.1080/03067310108044350

Intern. J. Environ. Anal. Chem., Vol. 81, pp. 127–135
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SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM(VI) WITH Cr(VI)–*o*-Cl-PF–TDPC TERNARY COMPLEX AFTER PRECONCENTRATION ON AN ORGANIC SOLVENT-SOLUBLE MEMBRANE FILTER

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(Received 23 March 2001; In final form 1 June 2001)

A simple and rapid preconcentration technique, based on collecting trace hexavalent chromium on an organic soluble membrane filter is described. At pH 5.0, chromium(VI), o-chlorophenylfluorone (*o*-Cl-PF) and tetradecylpyridinium chloride (TDPC) form the ternary ion-associate chelate, which can be collected on a 0.2 µm nitrocellulose membrane. The filter is dissolved in a small volume of dimethyl sulfoxide (DMSO) acidified with 0.15 mL 3 mol/L sulfuric acid, and the absorbance of the resulting solution is measured at 545 nm wavelength against the reagent blank. The absorbance is proportional to the content of hexavalent chromium in the range of 0.1–1.8 µg, in 5 mL solvent. The sensitivity of the ternary complex reaction is very high with molar absorptivity of 1.2×10^5. A detection limit better than 0.3 µg/L can be achieved. The ions normally present in water do not interfere when mixed masking agents are added. The proposed method has been applied to the analysis of water samples from several sources, the recoveries of the hexavalent chromium added to the samples are quantitative, and results found are satisfactory.

Keywords: Chromium(VI); Photometric determination; Preconcentration; Soluble filter

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INTRODUCTION

The determination of trace amounts of chromium(VI) in the environment has recently received much attention for its carcinogenicity, although chromium(VI) probably exists at μg/L level (or even lower) in natural waters. In China, the concentration of chromium(VI) in natural water is required to be lower than 10 μg/L [1]. The low concentration makes it difficult to determine directly, so the concentration prior the use of various analytical methods is necessary. Several separation methods, such as solvent extraction [1,2], ion exchange [3,4] and ion floation [5,6] have been used for preconcentration of chromium(VI), but they often are time-consuming for treatment of large volume of water samples. Hence, a new preconcentration method for chromium(VI) is necessary and valuable. In recent years, Taguchi et al. [7,8] proposed an organic solvent-soluble membrane filter technique, which is based on collection of trace components on a membrane filter and dissolving the filter with the analyte in a small volume of organic solvent. The enrichment factor of this technique is very high, and can enrich the trace component from a 200–500 mL water sample or even 1000 mL [9]. Recently, the technique has been successfully used in the determination of trace compounds in the natural water [10–12].

Diphenylcarbazide is the traditional reagent in the spectrophotometric determination of chromium(VI) [13]. But the sensitivity of the method is not enough high (mg/L) and the complex is unstable. Azo compounds [14], derivatives of triphenylmethane [15], are the sensitive reagents for the spectrophotometric determination of hexavalent chromium, however, their specificity is not very good and it is necessary to separate the diverse ions before determination. Xuexin Gu [11] proposed the preconcentration and determination of trace chromium(VI) in water by means of the formation of triiodide ion by oxidation of iodide with chromium(VI) and the collection of the ion-associate of the anion with a cation surfactant on a membrane filter. But the iodide ion is not stable in air and easy to volatilize, so it is necessary to control the experiment conditions.

Recently, the application of phenylfluorones in analysis of chromium(VI) has drew much attention [16–18]. In the present investigation, we propose a simple and convenient method for preconcentration and determination of trace chromium(VI) in water by means of the formation of an anionic chelate of chromium(VI) with *o*-chlorophenylfluorone and the collection of the ion-associate of the anion with tetradecylpyridinium chloride on a membrane filter. In this paper the main improvements using soluble-membrane preconcentration of chromium(VI) have been suggested and optimum conditions for its determination are reported.

EXPERIMENTAL

Reagents

Standard chromium solution (1 mg/mL): 0.2829 g of pure potassium dichromate were dissolved in 100 mL water. A working solution was prepared by suitable dilution.

o-Cl-PF solution: 0.0887 g of *o*-Cl-PF were dissolved in 250 mL 95% ethanol with 2 mL concentrated hydrochloric acid and stored in a brown bottle under refrigeration.

TDPC solution: 0.330 g of TDPC were dissolved in 1 L water.

Mixed masking agents solution: A mixture of 1 mL each of 1% ammonium fluoride and 10% sodium citrate was prepared.

Unless stated otherwise, all reagents used were of analytical pure grade, and all solutions were diluted with water purified by distillation.

Apparatus

UV–Vis spectrophotometer: UV-265 Model (Shimadzu, Japan). Vis spectrophotometer: 723 Model (Shanghai Third Analytical Instruments Factory, China).

pH Meter: pHS-2 Model (Shanghai Second Analytical Instruments Factory, China).

Membrane filters and holder: Most of the data presented in this paper were obtained with nitrocellulose membrane (50 mm in diameter, 0.2–1.2 μm pore size, Adjective Factory of Chemical Engineering College of Beijing, China). A Toyo KG-25 filter holder (effective filtration area 8 cm^2) and a vacuum pump with water circulation system were used.

Procedure

A 200 mL of sample solution containing less than 1.8 μg chromium(VI) were placed in a 400 mL beaker, and 20 mL pH 5 buffer solution of acetic acid–sodium acetate and 2 mL *o*-Cl-PF were added. After swirling, 10 mL TDPC were also added and mixed thoroughly. The solution was heated in a water-bath at 60–65°C for 15 min to develop the color fully. After cooling under running water, the ion-associate was immediately filtered off on the membrane filter under suction with flow rate 50 mL/min and pressure drop about 0.05 MPa, and the membrane was washed with 10 mL water. The filter was dissolved in 5 mL dimethyl sulfoxide acidified with 0.15 mL 3 mol/L sulfuric acid and the absorbance of the resulting solution measured in a 10 mm cell at 545 nm wavelength against reagent blank. The concentration of chromium(VI) was found from a calibration graph or regression equation constructed under the same conditions.

RESULTS AND DISCUSSION

Absorption spectra

The absorption spectra of the analyte formed by dissolving the ternary ion-associate in dimethyl sulfoxide acidified with 0.15 mL 3 mol/L sulfuric acid is shown in Fig. 1. The maximum absorption wavelength of the analyte in the organic solvent is at 545 nm and the maximum absorption wavelength of the reagent blank is at 485 nm. The sensitivity after enrichment is about 30 times higher than that of before enrichment.

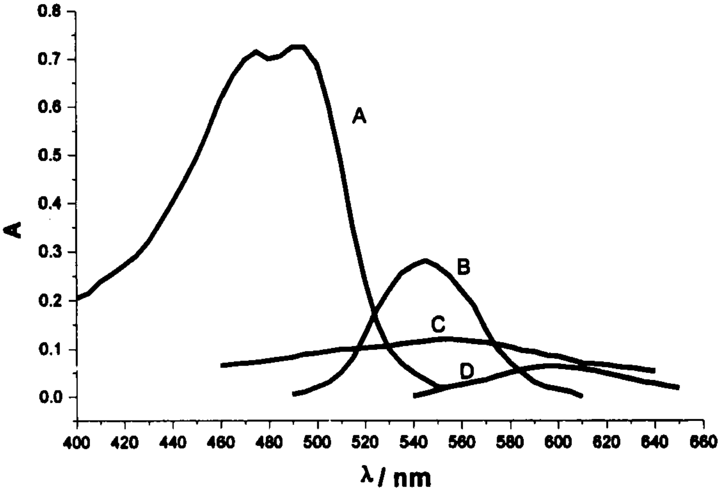
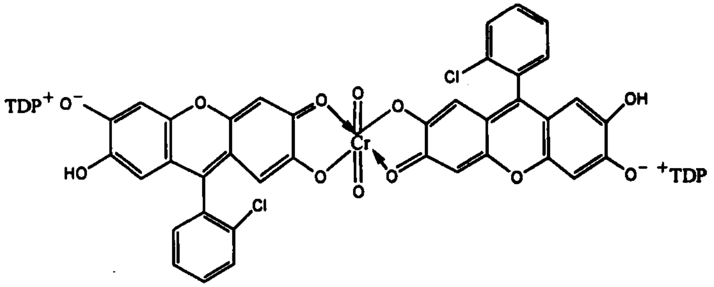


FIGURE 1 Absorption spectra of Cr(VI)–*o*-Cl-PF–TDPC ternary complex system: A: reagent blank vs. organic solvent after enrichment; B: Cr(VI)–*o*-Cl-PF–TDPC vs. reagent blank after enrichment (1.5 μg chromium(VI) in 5 mL DMSO); C: reagent blank vs. water before enrichment; D: Cr(VI)–*o*-Cl-PF–TDPC vs. reagent blank before enrichment (3 μg chromium(VI) in 25 mL of aqueous solution).

Reaction system

There are four levels of ionization equilibrium for *o*-Cl-PF. In the condition of the experiment, at pH = 4.5–5.5, *o*-Cl-PF takes part in the reaction mainly in the form of H_2R^-, and the main form of chromium(VI) is $HCrO_4^-$, whose oxidation ability is poor. When there is no cationic surfactant, chromium(VI) can only develop a light color with *o*-Cl-PF. But in the presence of an appropriate amount of some cationic surfactant, the color is deepened, probably because the cationic surfactant enhances the ionization of *o*-Cl-PF. It was determinated by continuous variations and mole-ratio methods that the molar ratio of chromium(VI), *o*-Cl-PF and TDPC is 1 : 2 : 2. So we deduced that the possible structure for complex is:



Effect of pH

The effect of pH is shown in Fig. 2. The results indicated that the ternary complex forms in weak acidic solution and maximum absorbance is obtained at pH 4.5–5.5. When pH is lower than 2, the complex is hard to form, and when pH is higher than 6, it needs longer time to develop the full color. In the present investigation the pH 5 is recommended.

Selection of counter ion

In order to totally collect the Cr(VI)–*o*-Cl-PF on the membrane filter, the selection of the counter ion is important. The counter ion can transform the chelate anion into a large ion-associate which can easily be captured on the membrane. Tetradecylpyridinium bromide (TDPB), TDPC, cetyltrimethylammonium bromide (CTMAB), benzyldimethyl

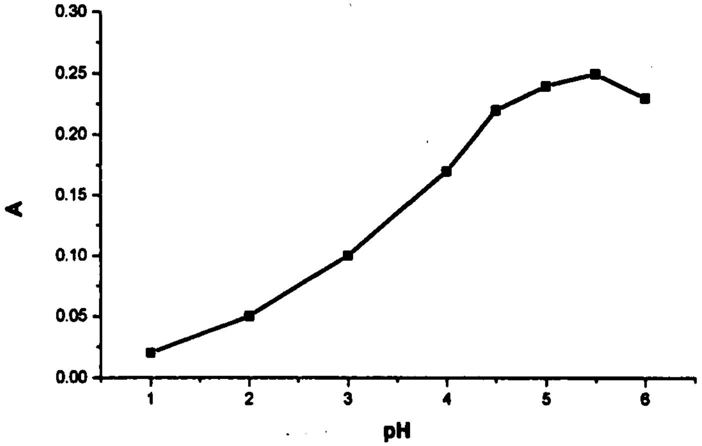


FIGURE 2 Effect of pH, 1.5 μg chromium(VI) in 5 mL DMSO acidified with 0.15 mL 3 mol/L sulfuric acid.

tetradecylammonium chloride (Zeph), and cetylpyridinium chloride (CPC) were investigated as the source of counter ion. The results suggested that TDPB and TDPC may give the similar collecting efficiency, and the reagent blank of TDPC after enrichment is lower. The favorite amount of TDPC is 7–13 mL. In the present investigation 10 mL are recommended.

Enrichment mechanism

Taguchi *et al.* [7,19] hold that the enrichment mechanism is not a simple precipitated capture, and the liquid–solid extraction and the interface reaction are more important. A serial of experiments using the membrane with the pore size range from 0.2 to 1.2 μm were performed to investigate the influence of the pore size. Figure 3 shows that when the pore size varies from 0.2 to 0.4 μm, the collecting efficiency changes little, but when the pore size is bigger than 0.4 μm, the collecting efficiency drops quickly to a stable value. Consequently, we propose that the enrichment mechanism is the common action of the interface adsorption and the pore size capture.

Selection of solvent

Several water miscible organic solvents were tested as solvents for the wet membrane. Dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), and 2-methoxyethanol can all dissolve the membrane and the

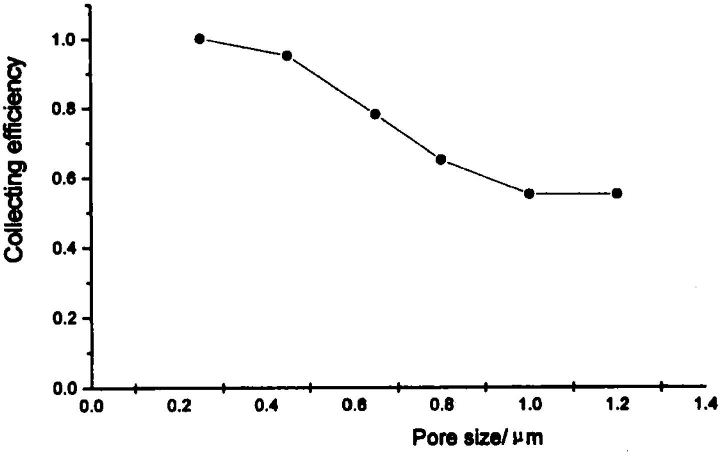


FIGURE 3 Effect of the pore size, 1.5 μg chromium(VI) in 5 mL DMSO acidified with 0.15 mL 3 mol/L sulfuric acid under optimized preconcentration conditions.

complex when acidified with 0.15 mL 3 mol/L sulfuric acid. But DMSO is the most favorite because the complex is more stable in DMSO. Other water miscible solvents, such as ethanol, methanol will not dissolve the membrane under normal conditions.

Effect of other factors

Other factors, such as the amounts of reagents, temperature and time, recommended for the formation of the complex and its collection on membrane filter, are shown in Table I.

The volume of sample can be increased to 500 mL and a good concentration is still obtained on condition that the amount of reagents should be increased accordingly.

Linear calibration, precision and sensitivity

Based on the optimum conditions, Beer's law holds well in the concentration ranges 0.1–1.8 μg and the regression equation is $Y = 0.0038 + 0.1669X$ with a correlation coefficient of 0.9992. Relative standard deviations for different levels of chromium(VI) were 2.4–3.2%. The lower limit of determination (taken as three times the standard deviation of the blank) was 0.3 μg/L.

Effect of diverse components

The influence of various diverse components on the formation of the colored species and collection of the ternary complex by membrane filter were examined in the presence of 1 mL mixed masking agents solution, in 50 mL aqueous solution, with the result shown in Table II. In this study the tolerance limit was set as the amount which caused an error of ± 5% in the recovery of 1.00 μg of chromium(VI). In these experiments cations were added as chloride, nitrate or sulfate, and anions were added as sodium, potassium or ammonium.

Application to analysis of water samples

The proposed method was applied to the determination of chromium(VI) in various water samples. The river water was acidified with 2 mL 3 mol/L sulfuric acid, stand over night and filtered off on a 0.45 μm membrane. Table III shows the analytical results of original samples and samples to which known amounts of chromium(VI) had been added. Recovery of the added chromium(VI) was nearly quantitative as shown in Table III. Each result is the mean of 5 measurements.

TABLE I Effect of other factors on formation and collection of the complex

Variable	*Tested*	*Optimum*	*Prefereed*
Amount of *o*-Cl-PF (mL)	0.5–3	1–2.5	2
Amount of TDPC (mL)	3–15	7–13	10
Amount of solvent (mL)	5	5	5
Temperature (°C)	40–100	55–70	60–65
Flowing speed (mL/min)	10–100	10–60	50
Pore size (μm)	0.2–1.2	0.2–0.4	0.2

TABLE II Effect of diverse components of the determination of 1.00 μg of chromium(VI)

Ion	*Amount added* (mg)	*Cr(VI) found* (μg)	*Ion*	*Amount added* (mg)	*Cr(VI) found* (μg)
Na^+	10	1.00	Cd^{2+}	1	1.00
NO_3^-	10	1.02	Ni^{2+}	1	1.05
F^-	10	1.00	Fe^{3+}	0.2	1.03
Cl^-	10	1.05	Cu^{2+}	0.1	1.04
$NH4^+$	10	0.98	Al^{3+}	0.4	0.96
Ca^{2+}	5	1.00	Pb^{2+}	0.05	0.95
Mg^{2+}	5	1.01	W (VI)	0.0003	1.04
PO_4^{3-}	5	0.95	Mo (VI)	0.0002	1.05

TABLE III Analytical results of several water samples

Sample	*Added* μg	*Found* μg	*Recovery* %
River water 1 (200 mL)	0	0.33	
	0.4	0.73	100
River water 2 (200 mL)	0	0.67	
	0.4	1.08	103
Pure water (200 mL)	0	0	
	0.4	0.39	98
Mine water (200 mL)	0	0	
	0.4	0.42	105

Acknowledgement

The authors wish to express their heartfelt thanks to the Beijing Municipal Natural Science Foundation (BNSF) for financial support by Grant No. 2972003.

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