

SEPARATION AND PRECONCENTRATION OF Cr(VI) AS ION ASSOCIATE USING SOLID PHASE EXTRACTION

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Received July 12, 2000

Accepted December 17, 2000

A method of separation and preconcentration of Cr(VI) was developed based on sorption on modified silica gel (C18) of an ion associate of Cr(VI) anion with a quaternary base. The study was performed with the following quaternary onium salts: [1-(ethoxycarbonyl)-pentadecyl]trimethylammonium bromide, 1-hexadecylpyridinium chloride, benzyl(dodecyl)-dimethylammonium bromide, butyl(triphenyl)phosphonium bromide and tetraphenylarsonium chloride. Benzyl(dodecyl)dimethylammonium bromide was found the optimum ion-pairing reagent. Sample containing Cr(III) and Cr(VI) in the presence of 0.005 mol/l of benzyl(dodecyl)dimethylammonium bromide was pumped with a peristaltic pump through the column containing the sorbent. The optimum pH range 4–5 was maintained with 0.05 mol/l phosphate buffer. Elution was accomplished using 95 vol.% ethanol and the recovery of Cr(VI) was $(96 \pm 6)\%$ in the concentration range 0.005–1 mg/l of Cr(VI); even in a tenfold excess of Cr(III) the recovery of Cr(VI) was 99.8% with the relative standard deviation of repeatability about 2.4%. Cr in the eluate was determined by emission flame spectrometry (Cr I 425.435 nm) in an air-acetylene or N₂O-acetylene flame with the limits of detection 10 or 2 ng/ml, respectively. Hence, with a typical preconcentration factor of 200, the limits of detection in natural aqueous samples were 50 and 10 pg/ml, respectively. Calibrations were linear at least up to 10 mg/l.

Key words: Chromium; Chromates; Ion associates; Surfactants; Solid phase extraction; Flame emission spectrometry; Silica gel C18; Sorption; Quaternary ammonium salts.

Of the trace elements, chromium deserves particular regard because it is both essential and toxic depending on its oxidation state. While Cr(III) is essential in a certain concentration range, Cr(VI) exhibits toxicity and unfavourable biological effects at relatively low concentrations. Chromate ion is considered a carcinogen, mutagen and potential teratogen because Cr(VI) exhibits affinity for nucleophilic receptors in DNA and RNA molecules and bounds to DNA polymerase¹. Maximum permissible concentrations of total chromium in drinking water, aqueous extracts of non-contaminated soils

and in wastes are about 50 ng/ml both in Europe and in the U.S.A. Permissible concentrations of Cr(VI) range from 10 to 50 ng/ml (ref.²).

Studies on solvent extraction of ion associates of Cr(VI) as well as application of extraction spectrophotometry to the determination of chromium in various materials preceded the later aspiration for speciation analysis. The ion associate of Cr(VI) anion with an onium cation (B^+) exhibits affinity to less polar organic phases due to its electroneutrality and the lipophilic character of organic substituents bound to the central atom (P, S, N, As, Sb, Sn, *etc.*) of the onium cation. The extraction of ion associates of Cr(VI) with ammonium, phosphonium, arsonium, pyridinium and tetrazolium cations was studied³ and methods of separation and preconcentration of Cr(VI) were based on the extraction of ion pairs⁴⁻⁶. The extraction species were $\{(B^+)_2 CrO_4^{2-}\}$ and $\{B^+ HCrO_4^-\}$. Chromium was determined spectrophotometrically in steels after its oxidation and extraction of ion pairs⁷⁻⁹.

Chromium speciation in itself gained an increasing importance for environmental and biological samples due to the essentiality of Cr(III) and toxicity of Cr(VI). Many methods based on liquid-liquid extraction, solid-phase extraction, liquid chromatography (LC) and gas chromatography (GC) were developed for this purpose.

Indirect determination of Cr(VI) in waters was based on the extraction of the complex of Cr(III) with quinoline-8-ol into isobutyl methyl ketone followed by analysis of both the extract and original sample using atomic absorption spectrometry with electrothermal atomization¹⁰. The speciation of Cr(VI) in fumes of arc welding by flow injection analysis was developed using sequentially coupled UV-VIS spectrophotometer for the measurement of the Cr(VI) chelate with 1,5-diphenylcarbazine and a flame atomic absorption spectrometer (FAAS) for the determination of total Cr (ref.¹¹).

Speciation of Cr(III) and Cr(VI) by GC is based on formation of volatile compounds. The chelate of Cr(VI) with *N,N*-bis(trifluoroethyl) dithiocarbamate was extracted and determined, then Cr(III) was oxidized and determined in the same way¹². Cr(III) was determined in natural waters using GC of its trifluoroacetylacetonate complex and total chromium was determined after reduction of Cr(VI) (ref.¹³).

Speciation of Cr(VI) and Cr(III) is frequently based on selective sorption of one of the species on chelating or ion-exchange resins. Amount of the other chromium species is obtained either differentially by subtracting contents of sorbed species and total chromium or by direct determination after its oxidation or reduction followed by sorption^{14,15}. Combination of cation-exchanging and ion-pairing sorbents was used for on-line preconcentration of Cr(III) and Cr(VI), respectively, followed by the flow-injection

determination using the FAAS (ref.¹⁶). The flow-injection on-line preconcentration of Cr(III) and Cr(VI) on activated alumina at pH 7 and 2, respectively, was combined with the FAAS determination¹⁷. For separation of Cr(VI) and Cr(III), ion exchange on Dowex 1-X8 resin was used after a sample treatment with EDTA (ref.¹⁸) or ion chromatography with anion exchanger ANX 1710 followed by the inductively coupled plasma atomic emission spectrometry (ICP-AES) determination¹⁹. A dual-column ion-exchange high-performance liquid chromatography (HPLC) system consisting of the IC-Pak anion exchanger and the Guard-Pak CM/D cation exchanger was used for speciation of chromium with inductively coupled plasma mass spectrometry²⁰ (ICP-MS).

The determination of Cr(III) and Cr(VI) in galvanic electrolytes and wastewaters was performed using ion-pair chromatography on Silasorb-C18 with tetrabutylammonium butyrate as ion-pairing agent for Cr(VI). The ion associate was eluted with an acetonitrile–water mixture and detected by conductometry. The concentration of Cr(III) was found differentially after oxidation²¹. Reverse-phase (RP) HPLC was used for speciation of Cr(III) and Cr(VI) in waste water from plating works after treatment with ammonium pyrrolidine-1-carbodithioate followed by extraction and subsequent separation on a LiChrosorb RP-18 column using an aqueous-acetonitrile mobile phase and spectrophotometric detection²². Similarly, the Cr(III) and Cr(VI) species were determined after EDTA chelation of Cr(III) by RP-HPLC separation on a Supelcosil LC-8 column using a mobile phase of acetonitrile in tetrabutylammonium hydroxide and spectrophotometric detection²³.

An ion-pair chromatography technique combined *via* a hydraulic high-pressure nebulizer with FAAS was used for preconcentration and separation of Cr(VI) on modified silica gel (C18) using tetrabutylammonium acetate as an ion-pair reagent and methanol as an eluent. Detection limits were 30 ng/ml of Cr(III) and 20 ng/ml of Cr(VI) (ref.²⁴). In another paper²⁵, the formation of the ion associate of Cr(VI) with tetrabutylammonium cation followed with retaining on a C-18 column (Eurospher 100-C18) was employed for the Cr(IV) preconcentration. After adsorption, Cr(VI) was eluted with 60 vol.% methanol. For the Cr(III) preconcentration, an aqueous sample solution with added potassium hydrogen phthalate was introduced onto a C18 column. The phthalate layer formed on the column was able to bind Cr(III) ions, which were subsequently eluted with 80 vol.% methanol. Emission flame spectrometry was used for the determination of Cr using the Cr I 425.43 nm line which, with the on-line preconcentration, led to the limits of detection 25 pg/ml Cr(III) and 20 pg/ml Cr(VI) (refs^{25,26}).

In our previous work, we employed modified silica gel Separon™ SGX C18 for the preconcentration of platinum from 0.1 M HCl in the presence of benzyl(dodecyl)dimethylammonium bromide, with subsequent elution with 96 vol.% ethanol. The emission spectrography of Pt in a plant ash matrix was carried out in a 15 A dc electric arc²⁷. Thallium was preconcentrated on silica gel C18 from 0.1 M HCl in the presence of various onium cations as ion pairs with tetrachlorothallate(III) and subsequently eluted with 96 vol.% ethanol. Atomic emission spectrometry in N₂O-acetylene flame (FAES) was suitable for the determination of thallium in plants²⁸ and in water or aqueous extracts of wastes and soils²⁹. A selective preconcentration of Pt and Pd in the form of ion pairs of Pt(IV) and Pd(II) chlorocomplexes with cationic surfactant Septonex® on Separon™ SGX C18 column was used in combination with ICP-AES and ICP-MS for the analysis of airborne particulate material and engine soot. In addition to Pt and Pd, sorption of Au, Ru, Rh, Os and Ir was studied³⁰.

Separation of Cr(VI) from Cr(III) and preconcentration of Cr(VI) in the form of ion associate with a cationic surfactant on modified silica gel C18 is described in this paper. After elution of ion associate with 95 vol.% ethanol, Cr is determined by FAES in N₂O-acetylene flame or in an air-acetylene flame. In our previous work, we obtained the limit of detection of Cr 2 ng/ml using FAES in N₂O-acetylene with a high-resolution spectrometer of laboratory construction³¹. Later on, the FAES in N₂O-acetylene was used for the determination of Cr after preconcentration and separation of Cr(III) and Cr(VI) (refs^{25,26}).

The advantage of the described procedure consists in simplicity of experimental setup, which, in contrast to refs²⁴⁻²⁶, requires neither an HPLC pump nor a hydraulic high-pressure nebulizer. Moreover, the *in situ* preconcentration of river water samples can be accomplished by replacing the peristaltic pump feeding with the action of hydrostatic pressure, similarly to that employed in the case of thallium²⁹.

EXPERIMENTAL

Instruments

A peristaltic pump ID-100 (Skala Brno, Medical Technology) provided with Tygon® tubings was used for preconcentration. The solution flow rate in experiments was set between 1 and 7 ml/min by changing the pump speed and the tubing diameter. Alternatively, instead of the peristaltic pump, the reservoir with a sample can be placed in a suitable height above the sorption column and the hydrostatic pressure can ensure the corresponding flow rate.

The flame emission spectrometer used was assembled in our laboratory. Double monochromator GDM-1000 (Carl Zeiss, Jena, Germany) is provided with two planar gratings 90×110 mm (651 lines/mm) in Littrow mounting. Two concave mirrors with focal lengths of 1 100 mm and effective diameters of 200 mm are aluminized. Entrance and exit slits are 100 mm high and their width is adjustable between 0 and 3 mm with the step of 0.01 mm. For the described measurements, the 0.1 mm slit width is used. Characteristics for the 2nd spectral order: practical resolution 132 000, working range 360–600 nm, reciprocal linear dispersion 0.3 nm/mm. Monochromators are separated by a rotating modulator (25 Hz), the scattered light offset is $1.3 \cdot 10^{-12}$ at 572 nm. Synchronized (25 Hz) detection of radiation is performed using a photomultiplier M12FC51 with multialkaline cathode of the S-20 type. The detector output voltage is registered with a chart recorder K-101 or a digital converter TEC-1 (both Carl Zeiss, Jena). The spray chamber and slot burner (5 cm) of an atomic absorption spectrometer Perkin–Elmer 306 are used. The flame is imaged on the entrance slit with the magnification 1 : 1 using of a single converging lens with a focal length of 80 mm.

Chemicals and Solutions

Standard stock solutions containing 1 000 mg/l of Cr(III) and 1 000 mg/l of Cr(VI) were prepared by dissolving $\text{Cr}(\text{NO}_3)_3$ and $\text{K}_2\text{Cr}_2\text{O}_7$ in water. Aqueous stock solutions containing 0.01 mol/l of the following quaternary onium salts were prepared: [1-(ethoxycarbonyl)-pentadecyl]trimethylammonium bromide (Septonex®, Spofa Co., Prague), benzyl(dodecyl)-dimethylammonium bromide (Ajatin®, Spofa Co., Prague), 1-hexadecylpyridinium chloride (CPC, Sigma Chemicals Co.), tetraphenylarsonium chloride (TPA, Lachema Inc., Brno), butyltriphenylphosphonium bromide (BTTP, Lachema Inc., Brno). Ethanol 95 vol.% with 5 vol.% methanol was ultrasonically deaerated. For the study of interferences of common anions, their potassium salts were used: K_2SO_4 , KNO_3 , KCl (Lachema Co., Brno). All the chemicals were of analytical grade quality. Cartridges Bakerbond SPE® octadecyl (J. T. Baker, U.S.A.) containing 50 mg of C18-modified silica gel, size 40 μm , were used. A dead volume of the cartridge, peristaltic tubings and capillaries was 0.6 ml.

Procedure

The column with the sorbent was first conditioned with 95 vol.% ethanol and then with distilled water, both for 5 min at the flow rate of 1–2 ml/min. Then Cr(VI) was retained from aqueous samples in the form of ion associate of the onium cation with hydrogenchromate anion. The sample was pumped through the column at a flow rate between 1 and 7 ml/min (typically 1 ml/min). Then the washing out of non-sorbed species was performed with 5 ml of distilled water. The ion associate sorbed on the C18-modified silica gel was eluted with 5 ml of 95 vol.% ethanol and the resulting eluate in a suitable volumetric flask was filled up to the mark with ethanol. Chromium in the eluate was determined by FAES using the atomic line Cr I at 425.435 nm in an air-acetylene or N_2O -acetylene flame. This procedure is based on our preconcentration methods employed for platinum²⁷, thallium^{28,29} and platinum group metals³⁰.

RESULTS AND DISCUSSION

Selection of Optimum Conditions for Flame Emission Measurement

The composition of gas mixture and the observation height for FAES were optimized with nebulizing solution containing 1 mg/l Cr. The emission intensity exhibited a broad maximum at the acetylene flow rate of 6.0 l/min, slightly decreasing with the increasing observation height. The observation height 13 mm over the burner orifice, and the acetylene flow rate 6.0 l/min were selected for further work. The calibration curve was linear at least up to 10 mg/l and limits of detection ($3\sigma_{\text{blank}}$) were 10 or 2 ng/ml Cr in the air-acetylene or N_2O -acetylene flame, respectively.

Optimization of Conditions for Separation

For separation of Cr(VI), ionic associates with the cations of the following quaternary salts were studied: Septonex, Ajatin, CPC, BTPP and TPA. The sorption recovery was calculated as the ratio of the amount of chromium determined in the eluate to the total amount of chromium in the solution brought onto the column.

On the basis of elution curves (Fig. 1) and recovery percentages (Table I) attained in sorption of the solution containing 1 mg/l of Cr(VI) and $4 \cdot 10^{-4}$ mol/l of an onium cation, Ajatin was chosen for further study of separation of Cr(VI) and Cr(III) as the most promising reagent. The sorption recovery was between 90 and 100% in the concentration range 10^{-4} – 10^{-2} mol/l of Ajatin. No influence of the sample flow rate on the efficiency of sorption was observed at least up to 7 ml/min. The sum of chromium amount passed through the column and the chromium amount found in the ethanolic eluate was $(100 \pm 2)\%$. Further optimization experiments were performed at the concentration of Ajatin 0.005 mol/l.

TABLE I

The sorption recovery for ion associates of Cr(VI) with various onium cations

Quaternary base	Ajatin	Septonex	BTPP	CPC	TPA
Recovery, %	102	97	103	101	61

It follows from Fig. 1 that the ion associate with BTPP (curve 1) was eluted faster in comparison with other ion associates. This could be explained by the considerably shorter aliphatic chain of BTPP in comparison with Septonex, Ajatin and CPC. On the other hand, TPA is a bulky cation and, therefore, the corresponding ion associate can be retained more efficiently than in the case of BTPP (see curve 3).

The optimum interval for the sorption of ion associate with Ajatin was found between pH 4 and 5. The sorption of 1 mg/l of Cr(III) at pH 1.5–12 proved that practically no Cr(III) was sorbed up to pH 6. At pH > 9, the concentration of Cr in passed solution decreased to zero because of precipitation of $\text{Cr}(\text{OH})_3$ that was mechanically retained by the sorbent. However, in the optimum pH range from 4 to 5, Cr(III) was present in the sample in a soluble form. In the ethanolic eluate, the concentration of Cr(III) was below the limit of detection. For adjusting pH between 4 and 5, the acetate and phosphate buffers were tested. While the recovery of sorption of Cr(VI) was practically constant and close to 100% in the presence of the phosphate buffer in concentrations 10^{-5} – 10^{-1} mol/l, the recovery steeply decreased in the presence of acetate buffer when its concentration exceeded $8 \cdot 10^{-2}$ mol/l. Consequently, the 0.05 mol/l phosphate buffer was selected for further work.

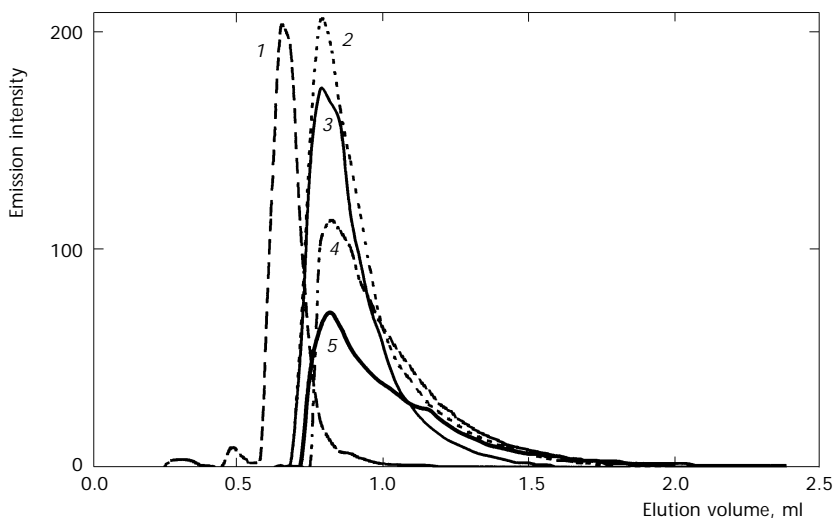


FIG. 1

Elution curves of Cr(VI) associates with various onium cations: 1 BTTP, 2 Ajatin, 3 TPA, 4 Septonex, 5 CPC

Efficiency of sorption was studied in the Cr(VI) range of 0.01–1.0 mg/l in the presence of 0.005 mol/l of Ajatin and 0.05 mol/l of the phosphate buffer (pH 4.1) in the sorbed volume of 1 000 ml. The average recovery of sorption was 96.2% with the standard deviation of 3.5%. The influence of a tenfold excess of Cr(III) over Cr(VI) on the sorption recovery of Cr(VI) was found to be insignificant at least in the range 0.05–1.0 mg/l of Cr(VI) in the sorbed volume of 1 000 ml. For example, the sorption recovery of Cr(VI) from the solution containing 0.5 mg/l Cr(III) and 0.05 mg/l Cr(VI) in the presence of 0.005 mol/l of Ajatin and 0.05 mol/l of phosphate buffer, was on average 99.8% with the standard deviation of 2.8%. The sorption recovery was only $(0.7 \pm 0.4)\%$ for solutions containing 1–10 mg/l of Cr(III) and no Cr(VI).

There was no influence of the sorbed volume on the sorption recovery up to 1 000 ml. The studied solution contained 0.0125 mg/l Cr(VI) and 0.125 mg/l Cr(III). Consequently, the preconcentration can be performed from the volume 1 000 ml to the final amount of 5 ml of ethanolic eluate. The resulting preconcentration factor of 200 yielded the limits of detection in natural aqueous samples 0.05 and 0.01 ng/ml for the determination in air-acetylene and N_2O -acetylene flames, respectively. This allows to determine concentrations of Cr(VI), *e.g.*, in drinking water, where the maximum permissible concentration of total chromium is 50 ng/ml.

Interferences with sorption were studied for common anions occurring in surface water, *i.e.* for SO_4^{2-} , NO_3^- and Cl^- . Their interfering effect might be due to competitive formation and sorption of ion associates. The concentration of Cr(VI) was always 1 mg/l. The sorbed volume was always 1 000 ml. As the used onium salts contain halides, these anions are inherent constituents of both analysed and calibration samples and they are in significant excess over Cr(VI). At 200 mg/l Cl^- , the sorption recovery was still 91%, decreasing from 70 to 35% between 500 and 2 000 mg/l Cl^- . The interference of nitrates was negligible up to the concentration of 75 mg/l NO_3^- . Between 125 and 2 500 mg/l NO_3^- , the sorption recovery decreased from 80 to 10%. Of possible interfering species, the sulfate anion was the most significant. In the presence of 150 mg/l SO_4^{2-} , the recovery was only 70% while it decreased to 30% at 3 900 mg/l SO_4^{2-} .

Determination of Cr(VI) in River Water

The preconcentration method was used for the determination of Cr(VI) in water sample of the Svitava river in the city of Brno, Czech Republic. The sample taken in summer (August) was characterized by the following pa-

rameters: pH 8.2, total dissolved solids 400 mg/l, conductivity 51.3 mS m⁻¹, 0.25 mg/l Fe, 0.25 mg/l NH₄⁺, 0.20 mg/l NO₂⁻, 20.4 mg/l NO₃⁻, total phosphorus 0.53 mg/l, 31 mg/l Cl⁻, 74 mg/l SO₄²⁻, 80 mg/l Ca, 12 mg/l Mg, <0.1 µg/l Hg, <1 µg/l Cr (total), 4 µg/l Cd, 8 µg/l Pb, 63 µg/l Zn. Using 0.05 mol/l phosphate buffer, pH of the sample was adjusted to 4.5. Then the stock solution of Ajatin was added to adjust the concentration of benzyl(dodecyl)dimethylammonium bromide to 0.005 mol/l and then the sample (1 000 ml) was pumped through the Bakerbond C18 cartridge. The sorbed sample was then eluted with 5 ml of ethanol and analyzed using FAES in air-acetylene flame. Concentration of Cr(VI) in the original sample was below the limit of detection. The influence of the real matrix was then checked. After a standard addition of 5.0 ng/ml of Cr(VI) to this sample the preconcentration was repeated six times. The average value 4.4 ± 0.5 ng/ml Cr(VI) was found.

CONCLUSIONS

Separation of Cr(VI) from Cr(III) for the determination of toxic species of chromium by flame atomic emission spectrometry was performed using the solid phase extraction on modified silica gel (C18). [1-(Ethoxycarbonyl)-pentadecyl]trimethylammonium bromide (Septonex®) and benzyl-(dodecyl)dimethylammonium bromide (Ajatin®) yielded the sorption recovery close to 100%. The ion associate of chromate with benzyl-(dodecyl)dimethylammonium cation is quantitatively sorbed from aqueous solutions containing 0.005 M Ajatin and 0.05 M phosphate buffer at pH 4.5. Elution with 95 vol.% ethanol yielded the recovery of sorption about 99.8% in pure solutions. Repeatability of sorption was characterized by RSD 2.4%; the limits of detection obtained with an air-acetylene flame and a N₂O-acetylene flame were 10 and 2 ng/ml, respectively. The resulting preconcentration factor 200 yielded the limits of detection in natural aqueous samples 0.05 ng/ml with air-acetylene flame and 0.01 ng/ml N₂O-acetylene flame, respectively.

Sorption interferences occur mainly in the presence of nitrate and sulfate anions. This restricted the applicability of the developed analytical method only to weakly mineralized waters. Analysis of river water was performed with the standard addition of Cr(VI) giving the recovery 88%. In comparison with RP-HPLC, the method does not require chromatographic equipment. *In situ* preconcentration can be performed without a peristaltic pump, just using the hydrostatic pressure.

Authors gratefully acknowledge the Ministry of Education, Youth and Sports of the Czech Republic for bestowing the grant to the project VS 97020.

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