

Use of high surface area TiO₂ for preconcentration and following determination of Cr species by on-line flow injection inductively coupled plasma atomic emission spectrometry

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Abstract. A flow-injection analysis (FIA) system incorporating two microcolumns of TiO₂ was used for the developing of an on-line method for preconcentration and sequential determination of Cr³⁺ and Cr⁶⁺ species by inductively coupled plasma atomic emission spectrometry (ICP-AES). The optimal conditions for both analytes have been obtained. With a sample volume of 10-50 ml and an elution volume of 500 µl, a signal was 20-100 times higher than the signal given by a continuous aspiration system. The method gave good reproducibility with precisions less than 7 % RSD for 5 replicates at the 10 ng/ml level for both Cr-species. Recoveries between 95 and 98 % were obtained for Cr³⁺ and Cr⁶⁺. The preconcentration system and the methodology proposed were validated on several natural water samples, on reference water samples as well as on synthetic seawater. It was found that the on-line detection using ICP-AES allows sequential Cr speciation analysis at the low concentration levels (ng/l) usually encountered in these media.

Keywords. *Inductively coupled plasma atomic emission spectrometry – on-line preconcentration – flow-injection analysis – high surface TiO₂ (anatase) – Cr species – natural waters.*

Introduction

Numerous papers concerning the determination of Cr³⁺ and Cr⁶⁺ contents in various samples were published in the last two decades. The main reason for this interest is the dependence of the toxicity on the chemical form in which an element appears. For chromium this dependence is strongly pronounced.

The two primary oxidation states of chromium (Cr³⁺ and Cr⁶⁺) in natural waters differ significantly in biological, geochemical and toxicological properties [1-3]. While Cr³⁺ is considered essential for man in glucose lipid and protein metabolisms [4], Cr⁶⁺ is toxic because of its ability to oxidize other species and its undesirable effects on lung, liver and kidney [5].

Because of different toxicity and bio-availability of chromium species, the determination of its total content does not give a full information about possible health hazards. Hence a monitoring of individual chromium species is necessary.

Traditional methods for the speciation of inorganic chromium are, however, relatively time-consuming, involving species separation based on solvent extraction [6,7], coprecipitation [8,9], electrochemical separation [10], ion exchange [11-14] and solid-phase extraction [15-17].

The first and major obstacle encountered in the development of a reliable method for chromium speciation is preserving its original speciation state in the sample. Sampling, separation and preconcentration procedures may disturb equilibria between various species present in the sample. In natural waters, one of the greatest difficulties results from the redox equilibrium between Cr³⁺ and Cr⁶⁺.

Methods developed for chromium speciation analysis based on a separation of the individual species and followed by a direct quantitation are preferred because they are relatively fast and require a minimal sample pretreatment. The latter is particularly important because a complex and prolonged sample handling may affect the distribution of chromium species.

For the selective measurement of chromium species, only a few techniques are available. The electrochemical behavior of Cr³⁺ and Cr⁶⁺ is significantly different, allowing species-selective determination by polarographic and other voltametric techniques [4,18,19]. Techniques based on the separation of different chromium species before the detection present the advantage to combine the selectivity and sensitivity.

The predominant trend in recently proposed methods for the speciation of chromium is the use of liquid chromatography and flow methods of analysis [20,21]. Coupled

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methods combining liquid chromatography with spectroscopic techniques (atomic absorption, ICP-atomic emission or mass spectrometry, UV-VIS spectrophotometry) have been developed. Between the chromatographic methods available, ion chromatography [22,23], reversed-phase liquid chromatography [24,25], or ion pairing chromatography [26] are generally utilized. In some cases, extremely low detection limits in the range of 0.1-1 $\mu\text{g/L}$ have been reported. Inconveniences of chromatographic methods are associated to complex procedures employed and to long analytical time required. Moreover, in some cases, the separation of the two-valent form is poor.

In speciation studies of trace metals, the main purpose of the use of flow analysis is the improvement of the selective preconcentration of a given species on flow-through micro-columns with solid sorbent prior to elution and transport to the detector. Different solid sorbents have been used for a flow-injection preconcentration, such as chelating ion exchangers [27], iminodiacetate chelate resin [28], activated alumina [29,30], ZnO [31] and TiO_2 [32].

Two papers published by Sperling and Welz [29,30] provide an excellent discussion and a reference list for chromatographic techniques, off-line separation methods and on-line flow injection analyses for chromium speciation. Authors demonstrated that at a certain pHs, an alumina column can be used in an on-line system to preconcentrate both Cr^{3+} and Cr^{6+} species in a sequential run. Linear calibration curves were established for both species over concentrations ranged between 10 and 200 $\mu\text{g/L}$, with detection limits of 1.0 and 0.8 $\mu\text{g/L}$ for Cr^{3+} and Cr^{6+} , respectively.

As a general rule, cations and anions may be adsorbed on amphoteric oxides (Al_2O_3 , TiO_2 , ZrO_2) in basic and acid conditions, respectively. Since Cr^{3+} is present in solutions under a cationic form and Cr^{6+} under an anionic form, one could expect that using a convenient adsorbent and ensuring an appropriate pH, a selective adsorption of the needed chromium form may be achieved. Consequently, this could be used for the separation and the subsequent determination of the two species.

The aim of this work is to develop a method for chromium speciation analysis based on a solid-phase extraction by TiO_2 (anatase) presenting a high surface area. The adsorption of Cr^{3+} and Cr^{6+} has been then investigated over a wide range of pH values on TiO_2 that have demonstrated its good capabilities as a solid-phase adsorbent.

Experimental

Reagent

TiO_2 sample used for the experiments was synthesized from TiCl_4 (for synthesis, Merck, Germany) as described earlier [33]. TiCl_4 were carefully hydrolysed at 5-10 $^\circ\text{C}$ in demineralized water and the obtained solution was alkalinized to pH = 9 by a drop-wise addition of a 12.5 % ammonia solution. The precipitate produced was filtered, well washed with

demineralized water and calcinated at 400 $^\circ\text{C}$ for 2 h. The powder obtained was ground in an agate mortar, washed again to remove residual chloride ions and dried in air at 120 $^\circ\text{C}$. This procedure ensures a formation of the anatase structure. The specific surface area of obtained TiO_2 sample was 68 m^2/g .

Demineralized water was prepared by further purification of de-ionized water using a Milli-Q system (Millipore, Tokyo, Japan). Sample solutions were prepared daily by serial dilutions of stock standard solutions (1000 $\mu\text{g/mL}$ Cr^{6+} and Cr^{3+} , Merck, Germany); they were stored in precleaned polypropylene bottles. HNO_3 and NH_4OH used were of high purity grade (Merck, Germany). Suprapur grade salts (Merck, Germany) were used to prepare working solutions and synthetic test samples. The synthetic seawater was prepared by dissolving 1.87 g of $\text{CaCl}_2 \cdot 4\text{H}_2\text{O}$, 0.4 g of KCl, 13.8 g of $\text{Mg}(\text{NO}_3) \cdot 6\text{H}_2\text{O}$ and 27.4 g of NaCl in 1000 mL. The River water SRM-1643c was from National Institute of Standards and Technology (NIST, USA).

Apparatus

Chromium measurements were performed using a two monochromators ICP-AES system (Spectroflame Compact S/E, Spectro, Germany). The operating conditions are summarized in table I. All measurements were made using the transient scan mode with integration time of 50 ms for each Cr-species and 1000 points per peak. Because transient signals are concerned, the peak area mode was used for all quantification work. The pH adjustment was performed by means of Basis pH meter (Radelkis, Danemark). The specific surface area was determined by the BET method by means of the low temperature nitrogen adsorption. Gilson (France) peristaltic pumps were used as a supply for preconcentration columns.

Column preparation

The aim was to prepare a microcolumn with a high capacity, able to handle large flow rates and allowing an elution of the sample in a small volume. Utilized TiO_2 micro-columns were made by mixing 0.1 g high surface area TiO_2

Table I. FI-ICP-AES operating conditions.

Plasma Ar-flow	16.0 L/min
Intermediate Ar-flow	1.3 L/min
Aerosol carrier Ar-flow	1.1 L/min
Plasma generator frequency	27.12 MHz
Rf power	1.3 kW
Sample flow rate	3.5 mL/min
Elution flow rate	0.5 mL/min
Signal processing	transient
Point per peak	1000
Integration time	50 ms
Wavelength	267.7 nm
Eluent volume	500 μL

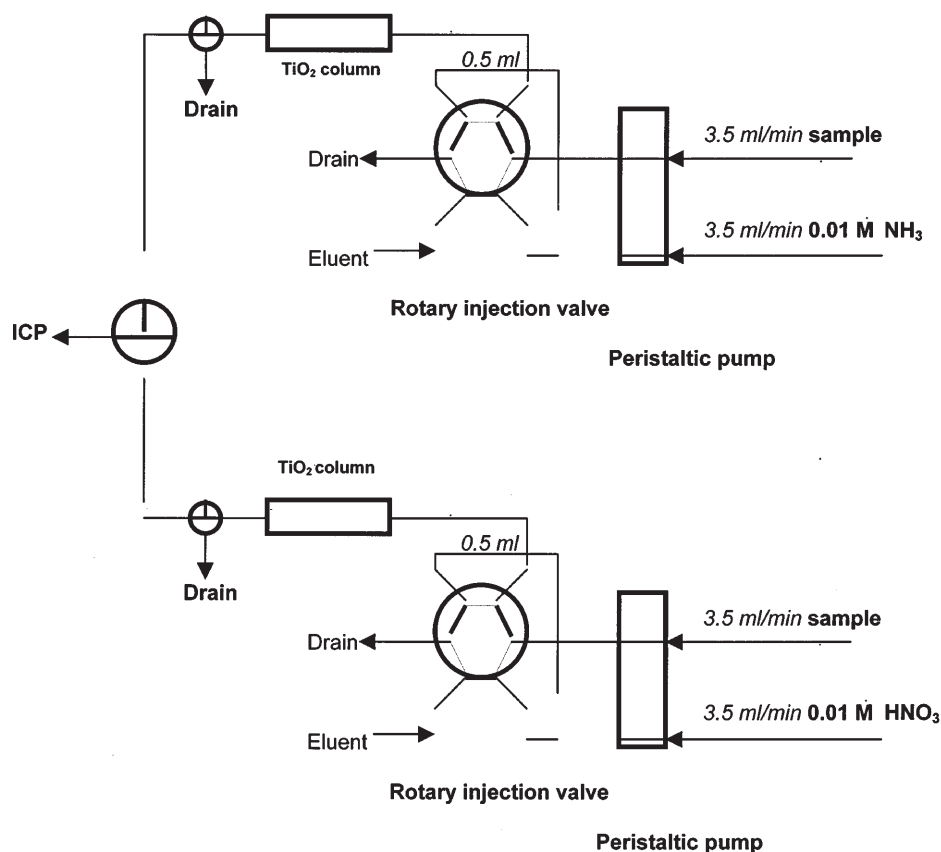


Figure 1. Schematic diagram of the system for FI-ICP-AES determination of Cr^{3+} and Cr^{6+} species.

and 0.1 g glass beads (Hewlett Packard, 40-60 mesh). The packing of the mixture is ensured by a PTFE tube (i.d.: 0.5 mm, length: 30 mm). In order to eliminate possible trace element contaminations before the use, the column was washed three times with 20 ml of 4 M HNO_3 followed by a rinsing with demineralized water.

General procedure for FI-ICP-AES measurement

A schematic diagram of FIA system is shown in figure 1. Both columns were connected to peristaltic pumps that ensured a flow-rate of 3.5 mL/min. Sorptions were performed from 10-50 mL solutions containing 10 $\mu\text{g/L}$ Cr^{3+} and Cr^{6+} . Solutions were adjusted on-line to a pH = 9 with 0.01 M ammonia solution in the case of preconcentration of Cr^{3+} on the column 1 and to pH = 2 with 0.01 M nitric acid in the case of preconcentration of Cr^{6+} on the column 2. The preconcentration of investigated species is then performed simultaneously. Sorbed Cr^{3+} and Cr^{6+} ions were eluted with 500 μL 4 M HNO_3 and with 500 μL 2 M ammonia solution, respectively; at a flow rate of 0.5 mL/min. Eluted samples were sequentially analyzed by ICP-AES. The total analytical time for the whole procedure was 15-35 minutes, according to the sample volume used.

To overcome possible clogging of the torch injector with salts when seawater was analyzed, the sample passing

through the column during the preconcentration step was discarded into the drain.

Test solutions

Pure water test sample (50 mL) or artificial seawater test sample (50 mL) were prepared by spiking Milli-Q water or artificial seawater with Cr^{3+} and Cr^{6+} species (10 $\mu\text{g/L}$). The influence of the sample flow rate was studied using a constant flow rate of eluents. Changes in the sample flow rate between 1-5 mL/min resulted in small variations in the signal, which increased at higher flow rates. A flow rate of 3.5 mL/min was chosen for all further investigations. Preliminary tests showed that the initial sample volume is not an important factor when the mass of analyte arriving in the column remains constant.

Results and discussions

Influence of pH

Differences between adsorption energies of Cr^{3+} and Cr^{6+} on oxide surfaces provide the main alternative of their selective preconcentration on TiO_2 . Results concerning the effect of pH on the solid-phase extraction in flow conditions are presented in figure 2. It may be seen that a pH higher than 7.5

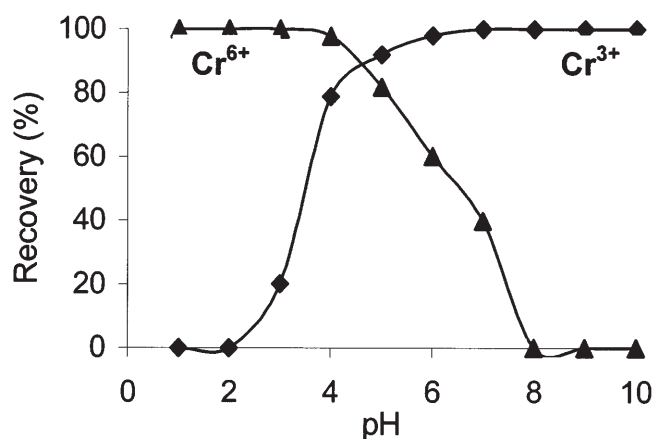


Figure 2. Effect of pH on the sorption (R %) of Cr³⁺ and Cr⁶⁺ ions on TiO₂.

is appropriate for the preconcentration of Cr³⁺ on TiO₂. The quantitative recovery of Cr⁶⁺ is attained at pH values < 3. Depending on the pH, TiO₂ can then selectively adsorb Cr³⁺ or Cr⁶⁺. Results show the possibility of a separate concentration of Cr³⁺ and Cr⁶⁺, working simultaneously at these two pHs. This makes TiO₂ a very promising solid-phase extractant in the chromium speciation analysis. Cr³⁺ precipitates as Cr(OH)₃ when the pH is higher than 6. By addition of an ammonia solution, the precipitate redissolves to the complex [Cr(OH)₂(NH₃)₄]⁺ [34]. When the resulting solution is mixed with TiO₂, the properties of solid media changes becoming a cation exchanger and the complex adsorbs to TiO₂. At pH = 2, stable oxidation states of chromium are HCrO₄⁻ and Cr(H₂O)³⁺, allowing the separation on TiO₂ without further handling [35]. Based on above described results, pH values of 2 and 9 were chosen to preconcentrate Cr⁶⁺ and Cr³⁺, respectively.

As a rule, adsorption of cations on amphoteric oxides such as TiO₂, proceeds when the pH value of the solution is higher than the isoelectric point (IEP) of the oxide. For anion adsorptions, pH values lower than IEP are required [36]. In general, it is believed that the adsorption of ions on oxide surfaces occurs with participation of the surface hydroxyl groups. At pH values higher than IEP, the oxide surface is covered by OH⁻ groups and is negatively charged. As a result, it becomes active towards cation adsorption. Contrarily, the positive surface charge at a low pH is caused by sorbed protons and it determines the ability of the particle to adsorb anions.

It should be noted that similar observation has been previously reported for a high surface ZrO₂ [32,33]. The knowledge about the nature of adsorption active sites may be very helpful for the synthesis of oxides with a high concentration of adsorption sites, *i.e.* high adsorption capacity.

Evaluation of the capacity

The evaluation of the capacity of TiO₂ was performed in flow conditions. Obtained values are close to 5 mg/g for Cr³⁺ and to 6 mg/g for Cr⁶⁺. From recovery results it is evident that the capacity of TiO₂ is sufficient to adsorb large amounts of both Cr-species. In this study, the adsorption capacity was determined after sorption of the chromium species at pH = 9 and pH = 2 respectively. The not fixed part of species is then eliminated by washing the sample. Hence, the final value concerns the irreversible adsorption only.

It was of interest to check whether the adsorption capacity is changed or not after several sorption/elution procedures. The high stability of TiO₂ resulted in a long lifetime of columns, permitting hundreds cycles to be performed without loss of analytical performance. This indicates that TiO₂ is a suitable substance for repeated extraction procedures.

The high capacity of minicolumns utilized allows preconcentrating large sample volumes without degradation of performances. 100 mL was the upper volume limit selected for evaluation because the treatment of larger volumes requires particularly long loading times, in contradiction with the real utility of FI methodology.

Preconcentration of trace elements in natural waters using solid-phase sorbent is based on their fixation under conditions in which matrix elements are bound ionogenically only or not bound at all. Solid-phase sorbent total capacity should be large compared with amounts of trace elements but also small enough to ensure that only a little part of matrix components will be bound on the sorbent. The column capacity must be optimized in order to balance the tolerance capacity for interferences in sample-loading/elution and determination stages.

Elution

The use of a more concentrated eluent solution should result in a more efficient elution. Obtained results show that 4 M nitric acid and 2 M ammonia solution are appropriate concentrations for quantitative elution of Cr³⁺ and Cr⁶⁺ ions. The increase in HNO₃ or NH₄OH concentrations did not improve recoveries of mentioned species. The small elution volume of species investigated required a more concentrated eluent than for an off-line batch preconcentration with the same material. To minimize the time needed for a quantitative elution and the eluate dispersion, the volume of eluent must be reduced. The injection of smaller eluent volumes contributes to obtain higher preconcentration factor and is more convenient for a work in flow conditions. Figure 3 represents the relation between elution efficiency after preconcentration of 50 mL solution with a Cr-concentration of 10 µg/L for different eluent volumes used. As can be noticed from histograms, 500 µL of 4 M HNO₃ and 500 µL of 2 M NH₄OH are appropriate eluent volumes for the FI-ICP-AES determination of Cr³⁺ and Cr⁶⁺ ions. The Cr-signal increased with increasing eluent volumes up to 500 µL. The influence of

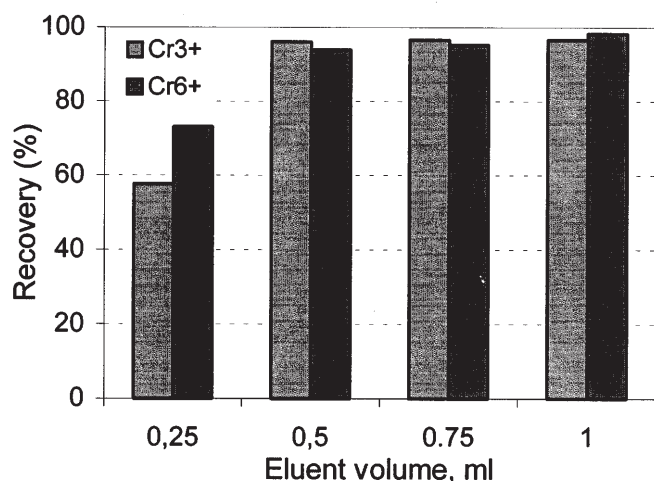


Figure 3. Effect of the elution volume on the recovery (%) of 500 ng Cr³⁺ and Cr⁶⁺, bounded to TiO₂.

the elution flow rate on the sensitivity and the precision for a triplicate determination of 10 ng Cr/mL was investigated in the range of 0.2-4 mL/min. The maximum sensitivity and the highest precision were obtained in range 0.2-0.5 mL/min. Thus, an elution flow rate of 0.5 ml/min was adopted.

Preconcentration efficiency

The efficiency of preconcentration system was determined by passing 50 mL of solution with concentration 10 µg Cr/L through the column. An elution loop was used as a means of a flow-injection sample introduction into the ICP-AES nebulizer. Integrated signals for 0.5 µg/mL solutions for each of analytes in 1 % HNO₃ were compared with integrated signals obtained after a preconcentration. Analyses have been performed in two replicates and integrated intensities were corrected for the background. If the preconcentration is quantitative and the sensitivity remains constant, the compared integrated intensities and emission signals produced

Table II. Recoveries for spiked Cr species in natural waters. Sample volume 50 mL, *n* = 3.

Sample	Spiked ng	R% _{Cr³⁺} ± S _r %	R% _{Cr⁶⁺} ± S _r %
Pure water	50	97.8±1.6	97.1±1.4
River water	50	96.9±2.3	96.1±2.8
Synthetic sea water	50	94.3±7.7	88.4±2.2
	100	98.2±1.2	92.0±2.5
Tap water	60	98.4±1.3	95.6±1.8
	40	97.5±1.7	96.6±2.1
	100	96.5±2.3	98.2±1.8
River water (SRM)	60	96.1±3.3	97.0±2.6
	40	95.6±2.3	95.1±3.1

by Cr-species should be the same, independently of the preconcentration factor. Table II summarizes recoveries of Cr-species from spiked tap-, river- and seawater, using the described methodology. In all cases (seawater excepted) the preconcentration system allows to attain a similar sensitivity than the direct aspiration measurement of Cr-species. The relative precision (RSD) ranged between 1.3 and 3.3 %. For artificial seawater, the proposed procedure allows a quantitative recovery of Cr³⁺ only. The relative precision for preconcentration of 50 mL seawater sample (concentration 10 µg/L of both Cr-species) ranged between 2.2 % and 7.7 %.

Effect of foreign cations and anions

One can expect that in the analysis of natural waters, sorbent exchange sites not occupied by chromium species remain available for magnesium or calcium and that Ca and Mg amounts fixed are dependent on the exchange capacity of the separation column. The higher exchange capacity of the separation column is, the higher remaining amount of alkaline earth metals is. The low affinity of alkali and alkaline earth elements toward TiO₂ results in their remarkable rejection from the column, promising an easy operation with saline waters. Despite this, the column becomes loaded with Ca and Mg on sites not occupied by heavy metals.

We have investigated effects of Ca²⁺, Mg²⁺, Na⁺ and K⁺ (the major constituent of natural water) on the preconcentration of studied Cr-species. The influence of Fe³⁺ and Mn²⁺ was also studied. Matrix element concentrations were varied, whereas the concentration of the analytes was kept at 10 µg/L. Results are presented in table III. It can be seen that the group IA metal ions have the weakest effect, whereas even low concentration of Fe³⁺ and Mn²⁺ suppress the adsorption of Cr³⁺.

A possible invalidation of the accuracy might be expected in the presence of colloidal or organically bound fraction of Cr³⁺ in waters. The effect of some naturally occurring complexing agents present in real water samples was also investigated. Humic acids do not affect the preconcentration and determination of Cr⁶⁺ and have the weakest effect on the preconcentration and determination of Cr³⁺.

Accuracy of the method and analysis of real water samples

To validate the accuracy of the method, a certified reference material (River water SRM-1643c) with total chromium content of 18.53-18.73 µg/L was analysed. The Cr³⁺ content obtained was 18.48±0.20 µg/L, whereas Cr⁶⁺ was not detected. These results demonstrate that chromium in the reference material is present as Cr³⁺ and the concentration value obtained agrees well with the certified value.

Detection limits, expressed as the blank value for the preconcentration of 100 mL pure water sample ± three standard deviations of the blank, are 11 ng/L Cr³⁺ and 17 ng/L Cr⁶⁺.

Table III. Effect of foreign cations on recoveries (%) of the preconcentration and FI-ICP-AES determination of Cr species, using TiO₂ microcolumns.

Foreign cation	Concentration µg/mL	Cr ³⁺	Cr ⁶⁺	Foreign anion	Concentration µg/mL	Cr ³⁺	Cr ⁶⁺
Na ⁺	1000	98.2	98.4	SO ₄ ²⁻	100	97.8	93.4
	3000	96.0	97.6		1000	95.3	89.4
K ⁺	50	100	100	HPO ₄ ²⁻	100	99.0	97.8
	100	100	99.8		500	99.2	93.7
	200	99.0	98.4		1000	96.8	91.3
	500	95.0	96.4		Cl ⁻	100	100
Ca ²⁺	500	99.8	100	1000		99.1	99.6
	1000	98.0	98.6	2000	97.2	95.7	
	3000	92.4	97.6	3000	93.4	91.7	
Mg ²⁺	50	97.2	96.5	HCO ₃ ⁻	100	100	100
	1000	98.6	95.3		500	100	99.5
	3000	96.1	96.3		1000	99.5	98.2
Fe ³⁺	5	93.1	95.6	AsO ₂ ⁻	2000	98.6	97.4
Mn ²⁺	5	94.0	98.1		3000	96.6	95.8
Humic acids	1000	97.2	98.9		50	99.1	97.6
	5000	94.1	97.9	200	96.8	93.4	

Table IV. Concentrations (in µg/l) of Cr³⁺ and Cr⁶⁺ in wastewater samples collected from leather-working industry (*n* = 3, volume of samples = 50 ml).

Samples	Cr ³⁺	Cr ⁶⁺	Cr total
1	0.36	0.26	0.62
2	0.22	0.33	0.45
3	0.37	0.16	0.52
4	0.21	0.19	0.40
5	0.32	0.38	0.70
6	0.51	0.17	0.68

Concerning practical applications, Cr³⁺ and Cr⁶⁺ contents were determined by the proposed procedure in some wastewater samples. Obtained results are shown in table IV.

Conclusions

Depending on pH, a high surface area TiO₂ (anatase) can be useful for a selective adsorption of Cr³⁺ or Cr⁶⁺ from solutions. TiO₂ can act as both anion and cation exchangers depending on pH. Under acidic conditions, it exhibits a high affinity for oxyanions whereas it strongly sorbs cations under basic conditions.

FI-ICP-AES analysis using the described sorbent is proposed as an efficient preconcentration technique allowing a high preconcentration factor. This method provides a good reproducibility, small reagent consumption, simplicity and low detection limits.

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