

The Field Sampling Method for the Speciation of Chromium in Waters

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Off-line ion-exchange chromatography followed by flame atomic absorption spectrometry (FAAS) determination was applied to the separation and preconcentration of Cr(III) and Cr(VI) in various types of waters. Reliability results with spiked solutions containing equimolar mixture of Cr(III) along with Cr(VI) were achieved with the anion-exchange resin Amberlite IRA-410 as well as cation exchanger Amberlite IR-120. With regard to the possible redox changes of the chromium species which can proceed after sampling before their determination the batch technique was found to be optimal because it enables the separation of the species directly at a sampling site and thus avoids the risk of the conversion of chromium species during sample pretreatment and transfer to the laboratory. The accuracy of the method was verified and the absence of appropriate reference material was overcome by the standard addition method in which both chromium species were added. Photometry with diphenylcarbazide solution as the additional alternative for validation of the proposed separation method was also applied to the determination of Cr(VI).

The interest in the speciation of chromium is closely related to different biochemical behaviour and physiological effects of its species on humans [1]. Cr(III) was found essential affecting glucose, lipid, and protein metabolism, whereas Cr(VI) is known for its ability to destroy biological membranes, and for carcinogenic and mutagenic effects. Therefore, a strict control of the occurrence of the Cr species and their differentiation in the environment is required.

In recent years, a growing number of papers have been published on the speciation of chromium. The methods of separation and preconcentration include solvent extraction in waters [2, 3] and in soils extracts [4], coprecipitation on $\text{La}(\text{OH})_3$ [5], $\text{Ga}(\text{OH})_3$ [6], $\text{Al}(\text{OH})_3$ [7], the utilization of ion exchanger [8, 9], chelating resins [10, 11], and of activated alumina in minicolumn [12]. For chromium speciation one of the most effective techniques used is the combination of HPLC with spectroscopic methods [13–15]. Among the preconcentration techniques, the field sampling methods have recently been proposed [16–18].

The introduction gives an overview of analytical methods which have recently been applied to the preconcentration and separation of individual Cr species. However, majority of them cannot be utilized directly at a sampling site. Therefore our aim was to suggest and work out a simple and easy-to-perform method which would be suitable in field conditions directly at a sampling site and which would ensure that no post-sampling redox changes of the Cr species occurred and hence the true information about Cr(III) and Cr(VI)

distribution in the sample would be obtained. General properties of ion exchangers were taken as the basis for method development.

Various types of waters (drinking, surface, waste waters) have been analyzed by the proposed method. Among the analyzed waters for the verification of the method the waste waters seemed to be the most suitable because the matrix of these waters is rather complex and hence the analysis can be complicated. The analyzed drinking and riverine waters contained very low concentrations of Cr often below the limit of detection of the analytical technique applied. The required volumes of these waters were 5–10 dm^3 and the preconcentration factors 500–1000. The concentrations of individual Cr species determined after preconcentration and separation of these waters were 0.1–2 $\mu\text{g dm}^{-3}$.

EXPERIMENTAL

All chemicals utilized in this work were of analytical reagent grade quality or better. Chromium stock solutions: calculated amounts of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Lachema, Czech Republic) and $\text{K}_2\text{Cr}_2\text{O}_7$ (Lachema, Czech Republic) were dissolved in the appropriate volume of redistilled water to give the stock solutions of 1000 mg dm^{-3} Cr(III) and 1000 mg dm^{-3} Cr(VI), respectively. Standard Cr(III) and Cr(VI) mixtures containing 10 $\mu\text{g cm}^{-3}$ of each chromium species were used as external comparison standards in the analysis of the spiked water sample. These standards were

found to be stable for at least six months. Diphenylcarbazide solution (DPC) for photometric determination of Cr(VI) was prepared by dissolving 0.1 g of 1,5-diphenylcarbazide (Lachema, Czech Republic) in 10 cm³ of acetic acid (Lachema, Czech Republic) and making up to 100 cm³ with redistilled water. Cr(VI) was determined by the standard photometric method [19]. The real sample of tap water was taken from the tap in our laboratory and the sample of the environmental water was collected from the river Danube. Two samples of waste water from the leather-processing industry were taken for experiments.

The acetic acid/sodium acetate buffer solution was prepared by dissolving 240 g of sodium acetate (Merck, Germany) in redistilled water and adjusted to pH 7 with acetic acid (Labora, Slovakia).

The HNO₃ used as an eluting agent in concentrations 1, 2, 3, 4, and 5 mol dm⁻³, respectively was prepared by diluting appropriate volume of concentrated nitric acid (Lachema, Czech Republic), purified by sub-boiling distillation with redistilled water.

Anion exchanger Amberlite IRA-410 (100–200 mesh, Rohm Haan, U.S.A.) to retain Cr(VI), cation exchanger Amberlite IR-120 (100–200 mesh, Rohm Haan, U.S.A.) to retain Cr(III) were used.

A PHM-64 research pH-meter (Radiometer, Denmark) was utilized to adjust pH of solutions. Concentration of Cr(VI) was measured with photometer MA-9510 (Iskra, Slovenia).

The contents of separated Cr species were determined by FAAS using the Perkin–Elmer 1100 atomic absorption spectrometer under following conditions: Cr-hollow cathode lamp, wavelength 357.9 nm, fuel-rich air-acetylene flame, slit 0.7 nm [20].

Batch Technique – Field Conditions

A waste water sample for the determination of Cr(III) and Cr(VI) was collected separately into two 1000–10 000 cm³ plastic containers according to the anticipated content of Cr (limit of determination for FAAS is 50 µg dm⁻³). The pH of the sample was adjusted to 7 by the addition of 15 cm³ of acetic acid/sodium acetate buffer per 1000 cm³ of the sample. Then, 0.5 g of wet and pretreated cation exchanger Amberlite IR-120 in order to bind Cr(III)

was added to one of the containers and 0.5 g of wet and pretreated anion exchanger Amberlite IRA-410 in order to trap Cr(VI) was added to the other container with the water sample. Both containers were shaken well and after transferring them to the laboratory, the ion exchangers were removed by filtration. Cr(VI) species bonded on Amberlite IRA-410 and Cr(III) trapped on Amberlite IR-120 were eluted from the exchangers deposited on filters with 10 cm³ of HNO₃ aqueous solution (*c* = 5 mol dm⁻³) to 25 or 50 cm³ volumetric flasks, made up to volume with redistilled water and determined by flame AAS. The separation method is based on the cationic behaviour of Cr(III) and the anionic behaviour of Cr(VI) species. Water samples (250 dm³) for determination of total chromium were collected separately.

RESULTS AND DISCUSSION

The reliability of column as well as batch separation of Cr species on anion (Amberlite IRA-410) and cation (Amberlite IR-120) exchangers are shown in Table 1. Each result shown is the average of twelve measurements. The relative standard deviation (RSD) is also given as a measurement of precision of the analyses. In all cases, better than 5.3 % RSDs were obtained for each procedure and Cr species, respectively. As shown in Table 1, good recoveries of added species of chromium (98.5–101.5 %) were obtained in spiked solutions, too.

Both exchangers were proved to be suitable for chromium speciation purposes. Batch separation technique is highly recommended for retaining the Cr species directly at a sampling site; it is advantageous because by trapping a chromium ion of particular oxidation state it prevents the occurrence of post-sampling redox alternations of the Cr species.

The proposed procedure was applied to the separation of Cr(III) and Cr(VI) in waste water samples from the leather-processing industry and other types of waters, too. The accuracy of Cr(VI) determination was checked by VIS-photometric reference method with DPC. The results of direct photometric and FAAS measurements of chromium in original and chromatographically treated (batch method) samples are summarized in Table 2. A good agreement

Table 1. Determination of Cr(III) and Cr(VI) in Spiked Samples (techniques: column and batch separation: Cr(III) on Amberlite IR-120 and Cr(VI) on Amberlite IRA-410, spiked amounts: 2.00 µg cm⁻³ Cr(III) and Cr(VI), respectively)

Parameter	Column		Batch	
	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)
Found/(µg cm ⁻³), <i>n</i> = 12	1.98	2.03	2.02	1.97
Recovery/%	99.0	101.5	101.0	98.5
RSD/%	2.73	5.23	3.94	2.33

RSD – relative standard deviation.

Table 2. Results of Speciation of Chromium in Waters (all results are in $\mu\text{g cm}^{-3}$)

Parameter	Original sample			After separation		
	Cr (total) FAAS	Cr(VI) Photometry	Cr(III) Calculated	Cr(III) FAAS	Cr(VI) FAAS	Cr (total) Calculated
Waste water No. 1						
x	0.099	0.080	0.019	0.017	0.085	0.10
n = 10						
RSD/%	5.2	1.8	34.7	6.9	6.9	6.9
Tap water						
x	< 0.050	< 0.0050	< 0.050	0.00165	0.0008	0.00245
n = 6						
RSD/%				9.30	3.50	2.45
River water						
x	< 0.050	< 0.0050	< 0.050	0.00113	0.00051	0.00164
n = 6						
RSD/%				12.30	9.35	1.64

x = average value, RSD – relative standard deviation, n = number of determinations.

Table 3. Comparison of Speciation of Chromium in Waste Water No. 2 – Original Sample and Spiked Sample (spiked amounts: $0.35 \mu\text{g cm}^{-3}$ Cr(III) and $2.00 \mu\text{g cm}^{-3}$ Cr(VI))

Parameter	Original	Spiked (after separation)			Unspiked (after separation)		
	Cr (total) FAAS	Cr(VI) FAAS	Cr(III) FAAS	Cr (total) Calculated	Cr(VI) FAAS	Cr(III) FAAS	Cr (total) Calculated
Average value	2.73	2.08	0.74	2.82	1.99	0.71	2.70
n = 6							
RSD/%	1.1	4.1	5.1	4.3	1.1	1.8	1.3

RSD – relative standard deviation, all results are in $\mu\text{g cm}^{-3}$, spiked content was subtracted.

between the amounts of Cr(VI) determined by photometry in original samples and Cr(VI) determined by FAAS after separation and between the content of total Cr measured and calculated as a sum of Cr(III) and Cr(VI) determined after separation was achieved. The waste water contained a high quantity of total Cr as determined by FAAS in the original sample. Therefore, the standard addition method was utilized in this case. For chromatographic separation of chromium, either the original sample (waste water No. 2) or sample spiked with $2 \mu\text{g cm}^{-3}$ Cr(VI) together with $0.35 \mu\text{g cm}^{-3}$ Cr(III) were diluted 50 times. All the data measured by FAAS in eluates after batch ion exchange are given in Table 3. Again a good agreement was found with the results obtained for individual Cr species in spiked and unspiked samples after separation and between the total Cr content as measured in the original sample and calculated as a sum of individual Cr(III) and Cr(VI) species determined after separation.

CONCLUSION

The proposed method for the speciation of chromium in waters after preconcentration and separation of

Cr(III) and Cr(VI) on cation exchanger Amberlite IR-120 resp. on anion exchanger Amberlite IRA-410 was proved to be sufficiently reliable reaching an average recovery ($n = 12$) from 98.5 % up to 101.5 % with a maximum relative standard deviation of 5.23 % either for Cr(III) or Cr(VI). The batch modification of the procedure as applied directly at a sampling site makes it simple, rapid, and convenient for routine analyses. The advantage of this method is preconcentration of $\mu\text{g dm}^{-3}$ levels of Cr(III) or Cr(VI) followed by a less expensive flame atomic absorption determination.

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