ON-LINE SIMULTANEOUS SORPTION PRECONCENTRATION AND DETERMINATION OF CHROMIUM(III) AND CHROMIUM(VI) WITH AAS DETECTION

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Speciation and simultaneous preconcentration of Cr(III) and Cr(VI) is based on the sorption of the reaction product of Cr(III) with Chromazurol S in weakly acidic solution and the sorption of the reaction product of Cr(VI) with sodium diethylcarbamate in strongly acidic solution. Reversed C18 phase was used for sorption of both the products. Both the complexes were eluted from columns directly into an AAS nebulizer using methanol. All the processes were automated. This method can be used for initial concentrations of Cr(III) and Cr(VI) below 1 ppm. The detection limits were 0.2 μg l^{-1} for Cr(III) and 2.4 μg l^{-1} for Cr(VI). This method was tested for analysis of practical samples (drinking and surface waters and soil extracts).

Key words: Speciation; Preconcentration; Atomic absorption; Chromium.

Chromium occurs in nature in the +3 and +6 oxidation states, each of which acts on living tissue in a completely different manner. In trace amounts, Cr(III) is an important essential element for the metabolism of glucose, lipids and proteins[1]. It acts as a cofactor for insulin and assists in facilitation of the interaction of insulin with specific sites in the cellular membrane. Thus, it assists in the elimination of glucose from the blood bed, termed glucose tolerance[2]. In trace amounts, Cr (III) stimulates the activity of some enzymes, such as trypsin phosphoglucomutase and renin, and inhibits the activity, *e.g.*, of thromboplasts and β-glucuronidase.

In contrast, Cr(VI) is highly toxic, mutagenic and carcinogenic[3]. Its toxicity is caused by its strong oxidizing ability. The inhalation of the dust of Cr(VI) compounds produces asthma and damage to the mucous membranes of the respiratory system. When ingested, these compounds initially cauterize the mucous membranes of the gastrointestinal tract, and then cause shock leading to death. This is accompanied by damage to the kidneys (nephrotoxicity) and liver (hepatotoxicity)[4]. Soluble salts such as CrO_4^{2-} and $Cr_2O_7^{2-}$ are also absorbed through the skin, cauterize mucous membranes and are highly carcinogenic. Ascorbic acid acts as an antidote, reducing Cr(VI) to Cr(III).

Speciation and preconcentration determination of chromium can be carried out using one of the common techniques followed by detection using a spectral method – usually atomic absorption spectrometry.

Coprecipitation is a simple technique. Cr(III) can be coprecipitated with Fe(III), but this approach has the disadvantage of Cr(VI) being partly adsorbed on the precipitate[5]. $PbSO_4$ can also be used for coprecipitation of Cr(VI).

The use of liquid–liquid extraction for preconcentration of chromium was described by Rao and Sastri[6], among others. These techniques are based on the extraction of the Cr(VI) – complexing agent ion pair (the complexing agent can be trioctylphosphine oxide, trioctylamine, tetrabutylammonium bromide or Aliquat 336)[7] into an organic solvent. Other methods are based on the formation of a complex with a coupling agent, such as sodium carbamate. Only a few papers have been published describing the extraction of Cr(III) because the most stable complexes of Cr(III) have only a very low ligand exchange rate[8].

Liquid–solid extraction is the most frequently used technique for preconcentration of Cr (ref.[9]). The solid phase can be an ion-exchange resin, chelating resin or functional groups bound on a solid sorbent, which is very useful for on-line separation[10]. There is an increasing interest in the use of modified ion-exchange resins with bonded chelating agents (chelating sorbents with iminodiacetate, salicylate and quinolin-8-ol groups, such as Chelex 100, Chelites)[11,12].

Preconcentration of an element on classical sorbents is a relatively lengthy process compared to the fast flame atomic absorption determination. These processes have been combined with suitable preconcentration and speciation of chromium on a sorbent and AAS determination to a form an on-line continuous system[13–17]. The sample is placed on a microcolumn with a sorbent on which the analyte is adsorbed, the latter is then eluted directly into the nebulizer of the AA spectrometer. Several tens of samples per hour can be analyzed using this method. All the samples and standards are subjected to the same procedure from the instant of addition to the column through to detection. One or more line systems can be used, with one or more column systems and co-current or counter-current elution.

A flow-injection technique has been described for subsequent spectrophotometric separation of Cr(III) from Cr(VI) using 1,5-diphenylcarbonohydrazide, however, the detection limits were not suitable for the determination of Cr in natural waters[18]. Milosavljevic describes the on-line flow injection preconcentration of Cr(III) on a column filled with quinolin-8-ol adsorbed on porous glass. Chromium was then determined in an AAS flame in the 2 M HNO_3 eluate[19]. Cr(VI) can be determined colorimetrically using diphenylcarbonohydrazide[20]. Cr(VI) is reduced to Cr(III) in the presence of succinate or glutamate.

Most of the methods described above used a lot of eluent and the obtained preconcentration factor was therefore low. Large volumes of samples were then necessary to

achieve sufficient sensitivity. In these papers, only one of the oxidation forms was determined and the content of the other was found by difference from total Cr.

Other methods include electrodeposition, a preconcentration method based on electrochemical deposition of the metal directly from the solution on a cuvette or platform of pyrolytic graphite[21]. Electrochemical deposition permits a suitable decrease in the detection limit and also completely eliminates possible spectral and chemical interferences from the sample matrix.

The aim of this work was to exploit the possibilities of using the approach of on-line sorbent extraction for the simultaneous preconcentration and speciation of Cr(III) and Cr(VI). The speciation was based on the sorption of the reaction product of Cr(III) with Chromazurol S in weakly acidic solution and the sorption of the reaction product of Cr(VI) with sodium diethyldithiocarbamate in strongly acidic solution. Silica with bonded octadecyl groups (reversed phase C18) was selected as the sorbent material. The advantage of the proposed method consists in simultaneous determination of both oxidation states of Cr in a single operation.

EXPERIMENTAL

Apparatus

A Varian Spectra AA-300 atomic absorption spectrometer (Mulgrave, Australia) was used in the flame arrangement. The measurement was carried out at 357.9 nm and bandwidth of 1 nm with deuterium background correction. Only peak heights were evaluated and blank values were obtained for each sample.

Computer-controlled eight-channel peristaltic pumps (Cole–Parmer Instrument Co., Chicago, U.S.A.) with Ismatec heads were used for the preconcentration step.

A low-pressure, four-way Teflon switch valve (Valco Instruments, Houston, U.S.A.), Teflon solenoid three-way valves (Cole–Parmer Instrument Co., Chicago, U.S.A.) and tygon, polyethylene and Teflon tubings with various diameters (Cole–Parmer Instrument Co., Chicago, U.S.A.) were also used.

Preconcentration Apparatus

A scheme of the apparatus for preconcentration of both oxidation states is given in Fig. 1. The apparatus consists of two peristaltic pumps 1 and 2, tygon pump tubings with internal diameter of 1.5, 0.89, 1.42, and 2.06 mm, Teflon coils and connecting tubings with internal diameter 0.7 mm, three Teflon solenoid three-way valves A, B and C, Teflon low-pressure four-way switch valve D, two columns for preconcentration of Cr(VI) and Cr(III) and an AA spectrometer as detector connected with a computer (all the valves and the peristaltic pump are computer-controlled). In all the measurements, the apparatus was arranged to ensure the shortest possible column–detector connection (small spreading of the elution zone).

Figure 2 gives the time dependence of the preconcentration process.

Four-way valve D provides for both outlet of the solution into the waste after passing through the apparatus and drawing of the rinsing solution into the AAS flame during the preconcentration step to ensure stable nebulization conditions. When the given product was adsorbed on both columns, they were eluted by switching valve A.

During desorption, pump 1 is turned off, three-way solenoid valve B was switched over and pump 2 was turned on. The four-way valve was switched to the position where the eluate flows into the detector. Signal recording was simultaneously turned on. After elution of one oxidation state, valve B was switched to the previous position and valve C switched to the elution position. After elution of the second oxidation state, pump 2 was turned off. The four-way valve was returned to the original position. After rinsing with the rinse solution, the apparatus was ready for another determination.

The peristaltic pump software controls the switching of valves A, B and C, four-way valve D and peristaltic pumps 1 and 2.

All measurements were performed at 20 °C.

Columns

Preconcentration columns were prepared from Teflon tubing with an internal diameter of 1.5 mm, packed with C18 reverse phase bonded to silica gel (grain size 60 μm). The phase weight was 0.1 g. The packing was fixed at both ends with pieces of foam rubber.

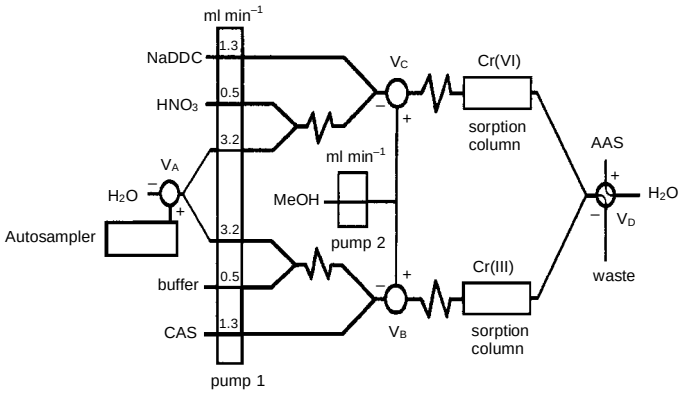

FIG. 1

Scheme of the apparatus for preconcentration of both oxidation states of Cr

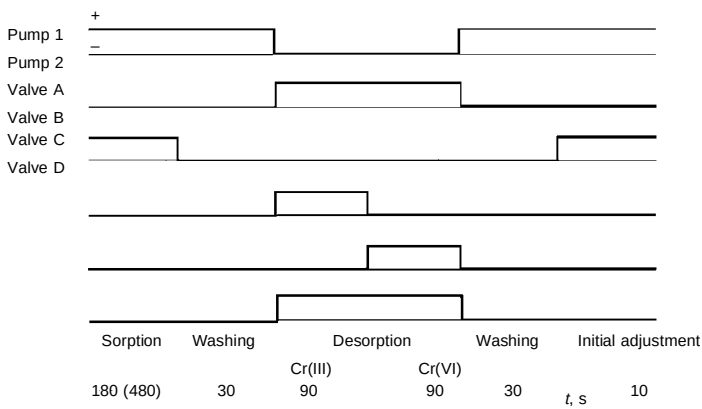

FIG. 2

Time dependence of the switching of the two peristaltic pumps and all the valves

Reagents

Sodium diethyldithiocarbamate (NaDDC): The stock solution with a concentration of $2.5 \cdot 10^{-3}$ mol l^{-1} was prepared by dissolving of NaDDC (Lachema Brno) in pH 9 buffer, prepared by mixing 0.06 mol l^{-1} NH_4OH and 0.03 mol l^{-1} CH_3COOH in the ratio of 30 : 9.

Chromazurol S: The stock solution with a concentration of $8 \cdot 10^{-4}$ mol l^{-1} was prepared by dissolving Chromazurol S (Merck, Darmstadt) in redistilled water.

Acetate buffer was prepared by mixing 0.01 mol l^{-1} CH_3COONa and 0.01 mol l^{-1} CH_3COOH in the ratio of 16 : 1.

The reverse stationary phase was Separon SGX C18 with a grain size of 60 μm (Tessek, Prague).

Potassium dichromate was used to prepare a stock standard solution of hexavalent chromium with a concentration of 1.000 g l^{-1} (Lachema Brno) in redistilled water.

The stock solution of Cr(III) with a concentration of 100 μg ml^{-1} was prepared by diluting a standard chromium solution (Analytika, Prague; concentration 1.000 g l^{-1}) with redistilled water.

Working solutions of different concentrations were prepared by diluting the above solutions.

The acids were of Merck Suprapur® purity; all other chemicals were of reagent grade purity.

RESULTS

Preconcentration of Cr(VI)

Hexavalent chromium was preconcentrated using the complexing reaction with sodium diethyldithiocarbamate[15,22] (NaDDC). The reagent yields a sufficiently stable complex with Cr(VI) immediately after mixing, while it reacts very slowly with Cr(III). The formation of the DDC–Cr(III) complex takes more than 20 h at 20 °C and 25 min at 60 °C (ref.[16]).

The complex formed was adsorbed on a column packed with C18 reverse phase (grain size 60 μm).

Analytical Conditions for Preconcentration of Cr(VI)

Continuous preconcentration of Cr(VI) was carried out using the apparatus depicted in Fig. 1, where the complexing agent was NaDDC, pH was adjusted using nitric acid and the desorption agent was methanol.

First the basic dependence was measured for optimization of the sorption step. The effect of the NaDDC concentration, HNO_3 concentration, and the overall flow rates of solutions through the column were studied, the breakthrough curve was measured and the preconcentration factor was found.

The desorption step was similarly optimized. A suitable eluent was chosen and the effect of the desorption rate was studied. Finally, possible interference from various Cr(III) concentrations was determined.

In the measurement of all these dependences, 10 ml of Cr(VI) solution with a concentration of 1 μg ml^{-1} was preconcentrated (sorption time *ca* 180 s).

In all cases, the height of the elution peak was chosen as a criterion of the attained sensitivity. The optimum conditions were selected as those values at which the highest

determination sensitivity was achieved, provided that the apparatus was not subjected to excessive pressure.

The effect of the concentration of sodium diethyldithiocarbamate was studied in the range 0–2 . 10^{-2} mol l^{-1}. The dependence obtained is shown in Fig. 3. A value of 2.5 . 10^{-3} mol l^{-1} was found as a sufficient NaDDC concentration for quantitative complexation reaction.

The reaction of Cr(VI) with NaDDC occurs in a highly acidic medium. The stock solution of complexing agent must be prepared in highly alkaline medium (solubility, stability) and a buffer cannot be used (under the given flow-rate conditions) to adjust the pH to the required very low value (approximately pH 1); thus, the acidity was adjusted with an HNO_3 solution. The pH value required for the given reaction is achieved using 0.6–0.75 M HNO_3. The final pH of the reaction mixture (at given flow rates of the sample, acid and reagent) was measured with a pH-meter in a solution sample taken from the space prior to the column. In subsequent experiments, 0.6 M HNO_3 was used, in agreement with the literature[15].

The overall flow rates of all the solutions through the column were varied in the range 3.2–10.0 ml min^{-1}. A slow flow rate provides for a long reaction time for the reaction of the sample with the reagents and a sufficiently long time for sorption of the reaction product on the column. However, the use of very low flow rates prolongs the determination. On the other hand, too fast flow rates do not permit complete sorption of the complex formed. The high flow rates also produce adverse overpressure in the apparatus. The optimum sorption rate was 5.0 ml min^{-1}.

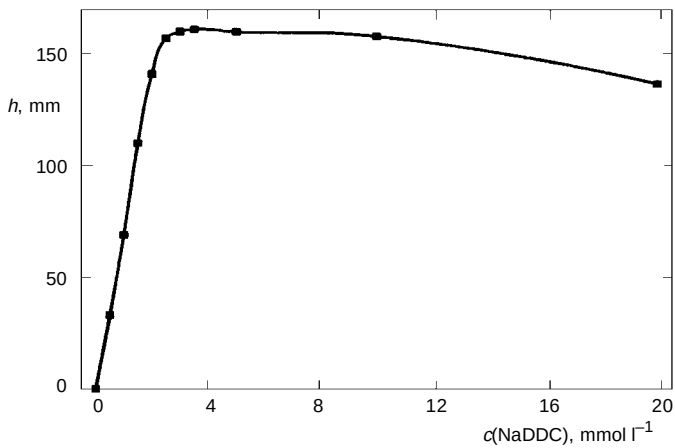

FIG. 3

Dependence of the signal height *h* on the NaDDC concentration. Sorption of 1 μg ml^{-1} Cr(VI) (180 s); $c(HNO_3)$ = 0.6 mol l^{-1}; q_v(preconcentration) = 5.0 ml min^{-1}; q_v(desorption) = 2.5 ml min^{-1}; desorption agent MeOH

Methanol was chosen as the optimum desorption agent for elution of the adsorbed complex. The desorption rate is determined by the flow rate of the elution reagent. The effect of the flow rates of methanol through the column was measured in the interval 0.8–4.0 ml min^{-1}. At lower elution reagent flow rates, the peaks are low and broad. High desorption rates ensure a narrow zone of the eluted sample. On the other hand, too fast desorption rates lead to dilution of the preconcentrated analyte. An eluent flow rate of 2.5 ml min^{-1} was the optimum desorption rate.

The Effect of the Presence of Cr(III)

In the optimization of this determination, it was important to examine the selectivity of the given complexing reaction for the chromium (VI). The selectivity was verified in the following experiment: to a Cr(VI) solution was gradually added a Cr(III) solution in a concentration ratio of 1 : 1, 1 : 2, 1 : 10, 1 : 20, 1 : 50, 1 : 100, 1 : 1 000. The signal of Cr(VI) was measured with addition of Cr(III) and also with addition of redistilled water in the appropriate ratio instead of Cr(III). The measured concentration of Cr(VI) is not affected by addition of Cr(III), even at the largest excess of 1 : 1 000. As mentioned in the theoretical part, the rate of the reaction of Cr(III) with NaDDC is very low.

Effect of the Column Packing

Various literature references give different pH stabilities of the given C18 reverse phase. According to one source[23], this corresponds to 2–7 pH units, while a different sources[24] gives 1–9 pH units. In highly acidic medium, the octadecyl chain is split off and the column ceases to act as a reverse phase. As the pertinent complexing reaction occurs at pH ≈ 1 and the column is eluted with a 0.1 M HNO_3 solution, the complex was also sorbed on silica gel. The column with the silica gel packing was prepared in the same manner as the column with the C18 packing, using silica gel with the same grain size, 60 μm (Tessek, Prague). It follows from the measured values that the silica gel is responsible for about 20% of the adsorption of the complex. Similarly, the lifetime of the column was tested using the sorption and desorption conditions. It was found that the column must undergo one sorption and desorption cycle prior to the actual measurement (*i.e.* without the sample). The column then yields reproducible results for at least 50 cycles.

Breakthrough Capacity of the Sorbent

The sorption capacity of the sorbent was determined using the dynamic method of infinite adsorbed solution volume. The estimated sorption capacity of the column for the Cr(VI)–DDC complex was 12.3 mg Cr(VI) per gram of sorbent.

Preconcentration of Cr(III)

It is difficult to find a suitable complexing reaction for Cr(III), as most reactions occur only at elevated temperatures. The reactions are generally very slow, are often not selective and a complex is also formed with Cr(VI) oxidation state.

The reaction with Chromazurol S was selected for determination of Cr(III). In acid medium it yields a stable complex with Cr(III) immediately after mixing the reagents at room temperature. The reaction does not occur[25] with Cr(VI) at 20 °C. The product of the complexation reaction of Cr(III) was preconcentrated on a column packed with C18 reverse phase.

Analytical Conditions for Preconcentration of Cr(III)

Cr was preconcentrated using the apparatus depicted in Fig. 1, where Chromazurol S is the complexing agent, the sample was acidified with acetate buffer and methanol was used as an eluent.

Similarly to the preconcentration of Cr(VI), the optimum sorption and desorption conditions were first found. The effect of the concentration of the reagent, pH of the acetate buffer and sorption and desorption rates were measured using the preconcentration of 10 ml of Cr(III) with a concentration of 1 ppm (sorption time *ca* 180 s).

A study was first made of the effect of excess of the reagent on the reaction with Cr(III). The dependence (Fig. 4) was measured in the range $1 \cdot 10^{-4}$–$5 \cdot 10^{-3}$ mol l^{-1}. Low reagent concentrations cannot complex all the chromium present and the reaction is not quantitative. A reagent concentration of $8 \cdot 10^{-4}$ mol l^{-1} was found as optimum.

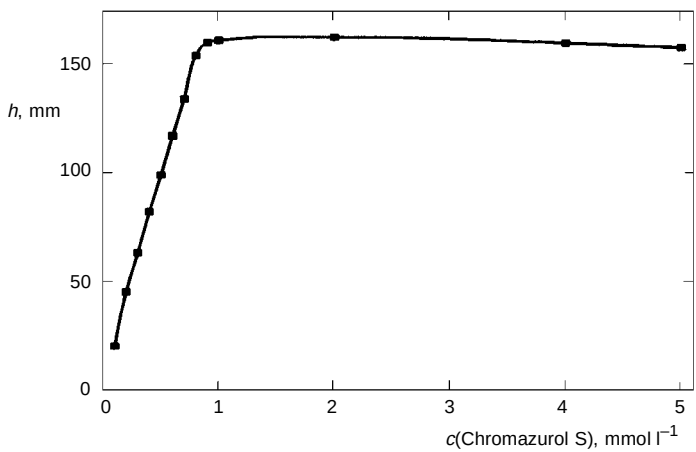

FIG. 4

Dependence of the signal height *h* on the Chromazurol S concentration. Sorption of 1 μg ml^{-1} Cr(III) (180 s); pH buffer 3.60; q_v(preconcentration) = 5.0 ml min^{-1}; q_v(desorption) = 2.5 ml min^{-1}; desorption agent MeOH

A higher reagent concentration is not suitable as the reagent itself is partly adsorbed on the column packing and the high concentration could lead to overloading of the column, especially in the preconcentration of large sample volumes.

The effect of pH on the complexing reaction was studied by changing the pH of the acetate buffer. A series of buffer solutions with pH values in the range 3.0–6.0 was prepared. A relatively narrow maximum can be seen on the curve obtained for the dependence of the height of the elution peak on pH, at pH 3.0–4.0. Buffer with pH 3.6 was used in subsequent work. A decrease in pH below 2.0 or an increase above 5.0 corresponds to a decrease in the sensitivity of the measurement below 50% of the value at the optimum pH.

The effect of the flow rate of the reagents through the column on the preconcentration of Cr(III) was studied in the range 3.2–11.0 ml min^{-1}. A flow rate above about 6.4 ml min^{-1} causes overpressure in the column 5.0 ml min^{-1}, the same flow rate as for the determination of Cr(VI) was chosen as optimum. At this flow rate of the reagents, the elution peak is highest and this is an ideal state for combination of the two preconcentration systems.

The effect of the flow rate of the eluent on the measurement sensitivity was studied in the interval 0.4–3.0 ml min^{-1}. It follows that complete desorption is possible only at flow rates higher than 1.8 ml min^{-1}. A value of 2.5 ml min^{-1} was chosen for subsequent measurements, which is identical with the desorption rate used for the determination of Cr(VI). This is again a favourable result for the expected simultaneous preconcentration of the two oxidation states.

Effect of the Presence of Cr(VI)

In the optimization of the determination, similarly to Cr(VI), it was very important to verify the selectivity of the given complexing reaction to Cr(III). The selectivity was verified in the following experiment: Cr(VI) solution was successively added to a Cr(III) solution in a concentration ratio of 1 : 1, 1 : 2, 1 : 10, 1 : 20, 1 : 50, 1 : 100, 1 : 1 000. The signal of Cr(III) was measured on addition of Cr(VI) and was compared with the signal of Cr(III). The measured concentration of Cr(III) was not affected by addition of Cr(VI), even at the largest excess of 1 : 1 000.

Breakthrough Capacity of the Sorbent

The breakthrough capacity of the sorbent was found using the same method as for Cr(VI). The estimated sorption capacity of the column for the Cr(III)–reagent complex was 13.0 mg Cr per gram of sorbent.

Calibration Curves, Reproducibility of the Determination, Limits of Detection and Determination

Following the determination of optimum conditions for the preconcentration of Cr(VI) and Cr(III), calibration curves were measured for both oxidation states. Concentration

series between 0.01 and 2.0 μg ml^{-1} were prepared for Cr(VI) and Cr(III) (sorption 480 s, sorption volume *ca* 25 ml). Both calibration curves are linear up to 1 μg ml^{-1}.

Similarly, calibration curves were measured for both oxidation states preconcentrated together. A series of solutions with various concentrations of Cr(VI) and Cr(III) in the range 0–500 μg l^{-1} was prepared, the concentration ratio of the two oxidation states being 0 : 100, 25 : 75, 50 : 50, 75 : 25, and 100 : 0 (total Cr concentration was always 500 μg l^{-1}). The sorption time was again 480 s (c*a* 25 ml for preconcentration of each oxidation state) and the elution peaks were recorded (Fig. 5). The calibration curves obtained in the determination of the two oxidation states have the same slopes as in the previous cases.

Similarly, the repeatability of the preconcentration determination of both oxidation states Cr(VI) and Cr(III) was found by repeated measurement (10×) of standards with concentrations of 0.1, 0.5 and 1.0 μg ml^{-1} (sorption 480 s). An average repeatability of 5.1% was obtained for Cr(VI) and 7.2% for Cr(III).

In addition, the limit of detection (3 *s*) (*s* is standard deviation of 10 replicate measurement near the blank level) was found for Cr(VI) 2.4 μg l^{-1} and for Cr(III) 0.2 μg l^{-1}.

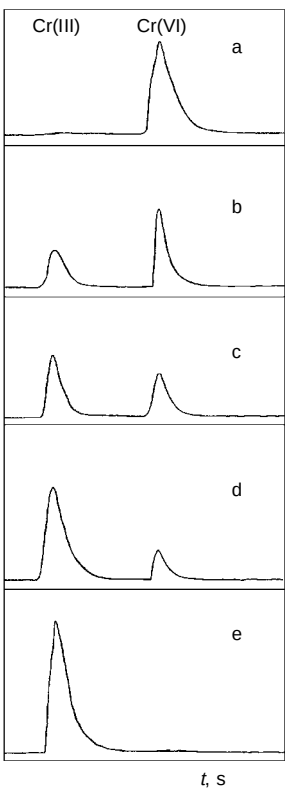

FIG. 5
Elution peaks of Cr(III) and Cr(VI) obtained in measurement of both the calibration curves simultaneously. Total Cr concentration 500 μg l^{-1}; Cr(III)/Cr(VI) ratio: a 0 : 100, b 25 : 75, c 50 : 50, d 75 : 25, e 100 : 0. Sorption of mixture of Cr(III) and Cr(VI) (480 s); *c*(NaDDC) = 2.5 . 10^{-3} mol l^{-1}; *c*(HNO_3) = 0.6 mol l^{-1}; *c*(Chromazurol S) = 8 . 10^{-4} mol l^{-1}; pH buffer 3.60; q_v(preconcentration) = 5.0 ml min^{-1}; q_v(desorption) = 2.5 ml min^{-1}; desorption agent MeOH

Similarly, the limit of determination (10 *s*) was found for Cr(VI) 8.0 μg l^{-1} and for Cr(III) 0.8 μg l^{-1} (sorption time 480 s).

The preconcentration factor is an important quantity characterizing the preconcentration process (giving the ratio between the original sample concentration and the final concentration). Its value was found as follows: The original sample volume was concentrated to a final volume given by the product of the flow rate of the eluent and the time required for quantitative elution of the adsorbed complex. The time required for quantitative elution corresponds to the width of the elution peak at its base. This ratio is also the required preconcentration factor. In our measurements (sorption 480 s), the factor of 12.5 was obtained for Cr(VI) and 12.0 for Cr(III). The factor can be increased by concentrating a larger volume of the original sample (prolonging solution sorption).

Analysis of Practical Samples

As no reference material with certified content of Cr(VI) and Cr(III) was available, we used the proposed method of speciation and preconcentration determination of chromium for the determination of our own field samples (drinking and surface water and soil extract samples).

Drinking water samples were taken from the water mains and surface water samples were taken from the Botic stream (Prague). The soil samples were taken in the outshirts of Prague. The water samples were preserved by addition of HCl (ref.[26]). The soil samples were dried, and the dried samples were passed through several sieves with progressively smaller mesh size (the smallest was 0.075 mm). Prior to the analysis, 1 g of soil sample was extracted with 100 ml of 0.1 M HCl.

As no reference method for verification of the Cr(III) and Cr(VI) contents in field samples was available, only total chromium content in each sample of water and soil was checked by direct AAS determination using electrothermal atomization (ETA).

TABLE I
Determination of Cr(III) and Cr(VI) in practical samples

Sample	$\rho_{Cr(III)}$, μg l^{-1}	*s*	$\rho_{Cr(VI)}$, μg l^{-1}	*s*	Sorption, min	ρ_{total} [b], μg l^{-1}
Tap water	2.1	0.37	<n.d.[a]		30	2.0
Surface water	2.6	0.42	<n.d.[a]		30	2.7
Soil extract I	35.3	2.94	7.4	0.81	3	40.7
Soil extract II	38.2	3.26	9.5	0.81	3	47.8
Soil extract III	32.7	2.45	8.1	1.19	3	40.8

[a] Not detected; [b] by ETA–AAS.

The results of the analyses of the soil and water samples including the original amount of sample used for the preconcentration and the control analysis of the total chromium are given in Table I. These results are averages of three determinations for each sample.

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