# Flow injection direct spectrophotometric assay for the speciation of trace chromium(III) and chromium(VI) using chromotropic acid as chromogenic reagent

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## Abstract

A new rapid and sensitive FI assay is reported for the simultaneous direct spectrophotometric determination of trace Cr(VI) and Cr(III) in real samples. The method is based upon the reaction of Cr(VI) with chromotropic acid (CA) in highly acidic medium to form a water-soluble complex ($\lambda_{max} = 370$ nm). Cr(III) reacts with CA only after its on-line oxidation to Cr(VI) by alkaline $KIO_4$. The determination of each chromium species in the sample was achieved by absorbance differences. The calibration curves were linear over the range 3–4000 $\mu g\,l^{-1}$ and 30–1200 $\mu g\,l^{-1}$ for Cr(VI) and Cr(III), respectively, while the precision close to the quantitation limit was satisfactory in both cases ($s_r = 3.0\%$ for Cr(VI) and 4.0% for Cr(III) ($n = 10$) at 10 and 50 $\mu g\,l^{-1}$ level, respectively). The method developed proved to be adequately selective and sensitive ($c_L = 1$ and 10 $\mu g\,l^{-1}$ for Cr(VI) and Cr(III), respectively). The application of the method to the analysis of water samples (tap and mineral water) gave accurate results based on recovery studies (93–106%). Analytical results of real sample analysis were in good agreement with certified values.
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## 1. Introduction

The identification and quantitation of ultra trace of specific metal species is currently an important challenge for the analytical community. Speciation measurements are made for a variety of reasons, including characterization and evaluation of systems in environmental science, medicine, biological processes monitoring nutrition and industry.

In this work, the focus was on the speciation of trace chromium. Chromium is a naturally occurring element, mainly found in minerals, rocks, plants, soil, water and in volcano dust and gases. Trivalent Cr(III) and hexavalent Cr(VI) enter the environment as a result of effluent discharge, electroplating, tanning industries and oxidative dyeing. Although chromium is known to exist in all oxidation states from Cr(0) to Cr(VI), the Cr(III) and Cr(VI) species are the most widespread in nature. The "paradox" with chromium is that its toxicity varies according to its oxidation state. While trivalent Cr(III) is considered to play an essential role in the proper function of living organisms, hexavalent Cr(VI) is a potential carcinogenic agent and exerts serious toxic effects on biological systems. Its toxicological action is mainly based on its oxidizing properties and on the formation of free radicals during reduction of Cr(VI) to Cr(III) occuring inside the cells [1].

The speciation of chromium can be achieved by many different methods. The predominant trend in recently proposed methods for the separation—speciation of chromium is the use of liquid chromatography (LC) and flow methods of analysis. Considering the great analytical interest in the speciation of chromium, the development of an inexpensive, on-line procedure for the trace determination of chromium is both desirable and very useful. Flow injection (FI) analysis offers great advantages in chromium speciation analysis, in terms of instrumental versatility, cost-effectiveness, sample throughput and simplicity. In addition, the improvement in accuracy and precision enables the effective incorporation of pre-concentration and separation steps in the flow system, prior to the final measurement in order to increase the sensitivity of the analytical assays.

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Thus, Naghmush et al. used cellulose-based sorbent materials for the speciation of chromium with on-line FAAS detection [2]. The low detection limits (around $1 \mu g \, l^{-1}$) were achieved using 50 ml samples, which correspond to an analysis time of, ca. 20 min. Cespon-Romero et al. coupled on-line chelating ion-exchange resins to FAAS with a low detection limit of $0.2 \mu g \, l^{-1}$ for the determination of total chromium [3]. However, they used off-line reduction of Cr(VI) to achieve speciation. The same off-line reduction step was adopted by Hirata et al., using an iminodiacetate resin for Cr(III) pre-concentration and ICP-MS detection [4]. The detection limit was very low ($0.02 \mu g \, l^{-1}$ at 120 s sample loading time) but the instrumentation employed was expensive with high running costs that limit the applicability of the method to routine analysis. Recently, Motomizu et al. reported an on-line collection of trace of Cr(III) and Cr(VI) species via small-sized thin solid phase column resin reactors using ICP-AES detection [5]. Although the detection limit was very low ($0.04$ and $0.02 \mu g \, l^{-1}$ for Cr(VI) and Cr(III), respectively) the manifold used was rather complicated and modifications of resin disks for both cation- and anion-exchange resin disks should be made to obtain quantitative recoveries depending on the matrix cations and anions of the examined solutions. Additionally the method is time consuming as 8.5 min are needed for each injection and the necessity for expensive instrumentation that is not commonly available makes the method unattractive to routine analysis. Finally, Marques et al. used activated alumina microcolumns for chromium speciation and Sequential Injection (SI-FAAS) [6] with lower sensitivity ($c_L > 40 \mu g \, l^{-1}$). An interesting alternative to column based pre-concentration assays are methods based on off- and on-line cloud point extraction, proposed by Paleologos et al. [7,8] using either fluorimetric or AAS detection. The detection limit achieved for the on-line assay is low ($c_L = 0.2 \mu g \, l^{-1}$) but the dynamic working range is rather limited ($0.5–10 \mu g \, l^{-1}$). Finally a hyphenated system coupling FI, capillary electrophoresis (CE) and ICP-MS was proposed recently by Giné et al. [9]. The detection limits were 6 and $8 \mu g \, l^{-1}$ for Cr(VI) and Cr(III), respectively, with a rather limited linear working range ($50–200 \mu g \, l^{-1}$).

The most commonly used chromogenic reagent for chromium speciation in FI is diphenyl carbazide (DPC), which is selective for Cr(VI). Several approaches have been adopted for Cr(III)–Cr(VI) speciation based on the above-mentioned reaction. The early work of Bubnis et al. [10] and Ruz et al. [11] was based on the on-line oxidation of Cr(III) to Cr(VI) by Ce(IV) ions. Later, Girard et al. employed two detectors in series for the simultaneous determination of the two species of chromium. Cr(VI) was determined spectrophotometrically using the classic DPC reaction, while total chromium was determined subsequently by FAAS [12]. Also, Anderson reported the use of $H_2O_2$ as an alternative oxidation reagent for chromium speciation, also based on the DPC reaction [13]. More recently, two sequential injection (SI) approaches were developed for the spectrophotometric DPC speciation of Cr(III) and Cr(VI). In one of them Luo et al. [14], using a SI-wetting film extraction procedure, determined Cr(VI) up to $100 \mu g \, l^{-1}$ with a detection limit of $2 \mu g \, l^{-1}$. The oxidation of Cr(III) to Cr(VI) was made off-line by Ce(IV). In the second one, Mulaudzi et al. [15], using

the same chemistry, but without extraction, determined Cr(III) and Cr(VI) with detection limits of 42 and $23 \mu g \, l^{-1}$ for Cr(III) and Cr(VI), respectively. Finally, Paleologos et al. [16] reported the fluorimetric speciative determination of these analytes using 2-(α-pyridyl)thioquinaldinamide (PTQA) as a non-fluorescing reagent, which after reaction with Cr(VI) yields a fluorescent product ($\lambda_{ex} = 360$ nm; $\lambda_{em} = 500$ nm). Cr(III) was oxidized on-line to Cr(VI) with sodium metaperiodate. The detection limits achieved were 50 and $20 \mu g \, l^{-1}$ for Cr(III) and Cr(VI), respectively.

The spectrophotometric and fluorometric procedures mentioned above, although simple and convenient, suffer from poor sensitivity, as their detection limits vary in the range $7–500 \mu g \, l^{-1}$. The present work reports for the first time the use of chromotropic acid (CA) as a sensitive and selective chromogenic reagent for the speciation of chromium using FI spectrophotometry with better analytical figures of merits and without the limitations of the above spectrophotometric and fluorometric methods. The developed assay is based on the reaction of Cr(VI) with CA in acidic medium [17]. Cr(III) reacts only after its on-line oxidation to Cr(VI) by alkaline $KIO_4$. The selectivity of the assay is enhanced by the highly acidic medium of the reaction and by using NaF as a masking agent. Low detection limits ($1 \mu g \, l^{-1}$ for Cr(VI) and $10 \mu g \, l^{-1}$ for Cr(III)) and broad linear dynamic ranges ($3–4000 \mu g \, l^{-1}$ and $30–1200 \mu g \, l^{-1}$ for Cr(VI) and Cr(III), respectively) were achieved without any pre-concentration step, while simple and cost-effective instrumentation is used throughout the work. The applicability of the developed procedure was assessed by successfully analyzing water (tap and mineral) samples as well as a CRM 544 certified reference material, No. 66 (lyophilized solution).

## 2. Experimental

### 2.1. Apparatus

The FI setup consisted of a Tecator 5010 analyzer (Tecator, Hoganas, Sweden) with a Tecator chemifold Type III SR manifold shown schematically in Fig. 1. The detector was a Jasco model 875 UV-spectrophotometer. The absorbance of the coloured Cr(VI)-CA complex was monitored at 370 nm. 0.5 mm i.d. PTFE tubing was used throughout the flow system, while the aqueous solutions were delivered by Tygon pump tubes.

### 2.2. Chemicals and reagents

All chemicals were of analytical-reagent grade and were provided by Merck (Darmstadt, Germany), unless stated otherwise, and all the solutions were made up by doubly de-ionized water.

The standard solution of chromotropic acid ($c(CA) = 0.01 \, mol \, l^{-1}$) was prepared daily, by dissolving the appropriate amount of chromotropic acid disodium salt (dihydrate) in 25 ml of water.

The standard stock solutions of Cr(III) and Cr(VI) ($\gamma = 1000 \, mg \, l^{-1}$ for each ion, respectively) were prepared by dissolving the appropriate amounts of $Cr(NO_3)_3 \cdot 9H_2O$ in $0.1 \, mol \, l^{-1}$ HCl and $K_2CrO_4$ in water.
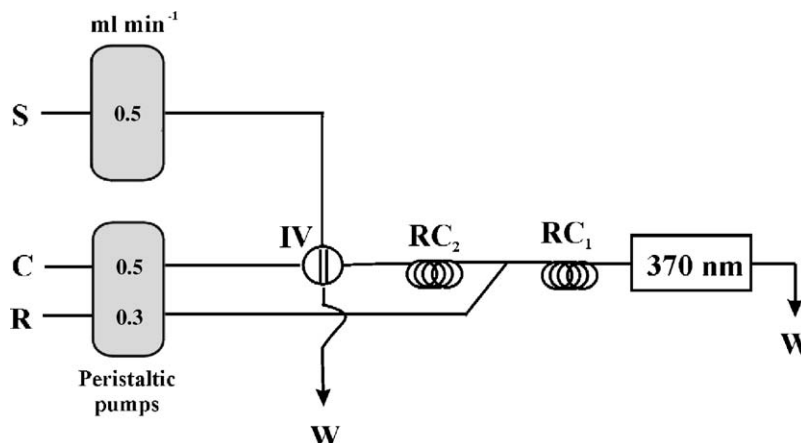
Fig. 1. Prefered FI setup for the determination of chromium(VI) and chromium(III), where C: $0.15\,mol\,l^{-1}$ NaF for Cr(VI) analysis and $0.15\,mol\,l^{-1}$ NaF, $1 \times 10^{-4}\,mol\,l^{-1}$ KIO$_4$, $5 \times 10^{-2}\,mol\,l^{-1}$ NaOH for total chromium analysis. S: sample; R: $1 \times 10^{-2}\,mol\,l^{-1}$ CA, $1\,mol\,l^{-1}$ HCl; IV: injection valve (sample loop = 100 μl); RC$_1$ and RC$_2$ = 60 cm and 200 cm/0.5 mm i.d reaction coils, respectively.

Stock solutions of NaF ($\gamma = 5000\,mg\,l^{-1}$) and KIO$_4$ ($c = 0.01\,mol\,l^{-1}$) were prepared in doubly de-ionized water.

Working solutions of Cr(III), Cr (VI) and CA were prepared daily by serial dilution.

### 2.3. Procedure for aqueous solutions

The simultaneous determination of the analytes involved a two-stage process. Cr(VI) was determined in the first run using a solution of NaF as the carrier stream (Fig. 1). One hundred microliters of the samples/standards are injected directly into the carrier and were merged with the acidic CA stream. The Cr(VI)–CA complex was formed on passage through a suitable reaction coil (RC$_1$) and was detected at 370 nm.

Total chromium (Cr(VI) + Cr(III)) was determined in a second run where a solution of NaF, KIO$_4$ and NaOH was used as a carrier (Fig. 1). Cr(III) was effectively oxidized to Cr(VI) on passage through a reaction coil (RC$_2$) which subsequently reacted with the color-forming reagent. Cr(III) was determined by absorbance differences.

Total analysis time was 45 s corresponding to a sampling rate of 90 injections h$^{-1}$. Five replicates were made in all instances.

### 2.4. Procedure for real samples

Tap and mineral water samples were filtered through a 0.45 μm membrane filter and were analyzed directly and immediately after sampling without acidification and other pretreatment.

The CRM 544 certified reference material, No. 66 (lyophilized solution) was dissolved in 10 ml of doubly de-ionized water and was analyzed also directly and immediately without acidification and other pretreatment.

All the samples were analyzed using the procedure mentioned above for aqueous solutions. Five replicates were made in all instances.

It should be noted that according to the United States Environmental Protection Agency, USEPA, chromium water samples must not be preserved by acidification to avoid the change of chromium species. Instead they have to be transported and stored until time of analysis at 4 °C. The analysis should be carried out as soon as possible but no longer than 24 h after collection to ensure that the distribution of dissolved chromium redox species remains unchanged [18].

## 3. Results and discussion

### 3.1. Preliminary studies

Preliminary experiments were performed in order to study the reaction of Cr(VI) and Cr(III) with CA under flow injection conditions. The experiments proved that Cr(VI) reacted with the reagent readily under flow conditions in strongly acidic media, forming a colored complex ($\lambda_{max} = 370\,nm$). On the contrary, Cr(III) did not react with CA, even at high concentrations.

The effect of different acids in the reagent stream was studied using equal amount concentrations of HCl, H$_2$SO$_4$, HNO$_3$, and H$_3$PO$_4$. All acids yielded identical results in terms of $\lambda_{max}$ (370 nm) and sensitivity, except for HNO$_3$ which also yielded an absorbance peak at the visible region of the spectrum ($\lambda_{max} = 476\,nm$) and half the sensitivity of the other acids. HCl was chosen for subsequent experiments for simplicity reasons.

Stopped-flow experiments showed that the reaction of Cr(VI) with CA is almost instantaneous as the steady-state absorbance value was reached in approximately 5 s.

### 3.2. Study of chemical and instrumental variables

The various chemical and instrumental variables of the FI system were studied using the univariate approach at a fixed Cr(VI) mass concentration of $1.0\,mg\,l^{-1}$. The starting values of the studied variables were: $c(CA) = 0.005\,mol\,l^{-1}$, $c(HCl) = 0.1\,mol\,l^{-1}$, $V(sample) = 100\,μl$, $l(RC_1) = 60\,cm$ and $q_V(C) = q_V(R) = 0.5\,ml\,min^{-1}$. The absorbance was monitored in the flow-through cell at 370 nm.

The influence of the HCl amount concentration in the reagent solution was studied in the range 0.05–2.0 mol l$^{-1}$. Maximum and constant complex formation was achieved at HCl amount concentrations equal or higher than 0.2 mol l$^{-1}$. 1.0 mol l$^{-1}$ HCl was selected for further experiments.

The effect of the amount concentration of CA was studied in the range $5 \times 10^{-4}$ mol l$^{-1}$ to $5 \times 10^{-2}$ mol l$^{-1}$. The signals intensity increased non-linearly in the range $5 \times 10^{-4}$ mol l$^{-1}$ to $5 \times 10^{-3}$ mol l$^{-1}$, and leveled off in the range $1.0 \times 10^{-2}$ mol l$^{-1}$ to $5.0 \times 10^{-2}$ mol l$^{-1}$ CA. A CA amount concentration of $1 \times 10^{-2}$ mol l$^{-1}$ was selected as optimal because at higher values the base-line was noisy and the precision was decreased significantly ($s_r = 5$–6% compared to the usual 1–2%).

The effect of the sample injection volume was studied in the range 30–200 μl by suitable variation of the loop volume of the injection valve. The peak heights increased non-linearly with increasing sample injection volume in the range 30–100 μl, as the injection volume is inversely proportional to the dispersion of the sample zone, and leveled-off at higher injection volumes. One hundred microliters was selected for further studies as a compromise between sensitivity, linear determination range and sampling frequency.

The effect of the length of reaction coil (RC$_1$) on the determination was examined in the range 0–300 cm. The signals were highest in the range 60–100 cm, indicating that the reaction is fast, and decreased at higher values at which dispersion predominated. Sixty centimeters was chosen as optimal.

The flow rate of the CA stream was studied in the range 0.3–0.7 ml min$^{-1}$. The flow rate of the carrier was kept constant at 0.5 ml min$^{-1}$. As expected, the peak heights decreased non-linearly with increasing CA flow rate. The flow rate of 0.3 ml min$^{-1}$ was chosen as optimal (total flow rate of 0.8 ml min$^{-1}$), in terms of sensitivity.

### 3.3. Study of the on-line oxidation of Cr(III)

As already mentioned in Section 3.1, Cr(III) did not react with CA under flow conditions. It only reacted after its oxidation to Cr(VI). Several oxidants were tested for the effective on-line oxidation of Cr(III) by placing the oxidant in the carrier stream. The main demands were rapidity, simplicity, compatibility to the other reagents used and high oxidation yield. Among K$_2$S$_2$O$_8$, KMnO$_4$, H$_2$O$_2$/NaOH and KIO$_4$/NaOH the latter produced the best results in terms of oxidation efficiency and stability of the base line and was kept for further studies. The parameters studied were the amount concentrations of the oxidant and of NaOH and the length of the oxidation reaction coil (RC$_2$). The study was carried out under the chosen chemical and FI variables described in the previous section.

The effect of the amount concentration of KIO$_4$ was studied in the range $5 \times 10^{-5}$ mol l$^{-1}$ to $5 \times 10^{-4}$ mol l$^{-1}$ [$\gamma$(Cr(III)) $= 1$ mg l$^{-1}$, $c$(NaOH) $= 0.01$ mol l$^{-1}$ and $l$(RC$_2$) $=$ 60 cm/0.5 mm i.d.]. Maximum oxidation yield was achieved at $1 \times 10^{-4}$ mol l$^{-1}$ KIO$_4$, which was chosen as optimal.

Table 1
Maximum tolerance mole ratio of various ions on the determination of 0.2 mg l$^{-1}$ Cr(VI) under the optimum conditions for aqueous solutions

| Ion added[a] | Ratio |
|---|---|
| F$^-$ | 3500 |
| CO$_3$$^{2-}$, HCO$_3$$^-$ | 2500 |
| Na(I), Cl$^-$, NO$_3$$^-$ | 1000 |
| Mn(II), Ba(II), citrate, tartrate | 500 |
| Cd(II), SCN$^-$, SO$_4$$^{2-}$ | 400 |
| Ca(II), Pb(II) | 250 |
| Ni(II), Mg(II), Bi(III), PO$_4$$^{3-}$ | 200 |
| Zn(II), Co(II) | 125 |
| Hg(II) | 100 |
| Sn(IV), Al(III), V(IV), V(V) | 50 |
| U(IV) | 40 |
| B(III) | 30 (250)[b] |
| Cu(II), Ti(IV) | 20 |
| Fe(III) | 2 (25)[b] |

[a] These ions in the stated level caused a relative error of $<\pm 5\%$.
[b] After the addition of 0.15 mol l$^{-1}$ NaF.

The effect of the amount concentration of NaOH in the oxidation mixture was studied in the range $1 \times 10^{-3}$ mol l$^{-1}$ to $1 \times 10^{-1}$ mol l$^{-1}$. The results showed that the maximum percent conversion was achieved at $5 \times 10^{-2}$ mol l$^{-1}$ NaOH, which was chosen as optimal.

Finally the effect of the oxidation reaction coil length was studied in the range 0–300 cm. This parameter determines the time that oxidation is allowed to proceed. The best results regarding the oxidation efficiency (ca. 70% oxidation) were achieved at $l$(RC$_2$) $= 200$ cm.

It should be noted that apart from the system KIO$_4$/NaOH, similar results were achieved using Ce(IV)/H$_2$SO$_4$ as oxidant. However, this system was abandoned for two reasons. Firstly it required elevated temperatures for effective action, making the flow manifold more complicated and secondly it could not act in the presence of NaF used as masking agent to increase the selectivity of the proposed assay.

### 3.4. Study of interferences

The tolerance of the proposed method towards many species was examined in detail using the preferred FI setup shown in Fig. 1. The criterion for interference was fixed at a relative error, $e_r$, of less than $\pm 5\%$ in the average absorbance signal taken for a Cr(VI) mass concentration corresponding to 0.2 mg l$^{-1}$. The results are summarized in Table 1.

Using an amount concentration of 0.15 mol l$^{-1}$ NaF in the oxidant stream and an amount concentration of 1.0 mol l$^{-1}$ HCl in the reagent stream, the interferences of Fe(III) and B(III) were effectively eliminated as these species are usually found in water samples.

### 3.5. Features of the proposed method

Using the prefered FI setup shown in Fig. 1 and under the above-mentioned chosen conditions, linear calibration curves were recorded for both Cr(VI) and Cr(III) in the ranges

3–4000 $\mu g\,l^{-1}$ and 30–1200 $\mu g\,l^{-1}$, respectively, described by the respective equations:

$$AU = (105.56 \pm 1.42)\gamma[Cr(VI)] - (0.14 \pm 0.32)$$

$$AU = (60.39 \pm 0.67)\gamma[Cr(III)] - (1.45 \pm 0.15)$$

where AU is arbitrary units, and $\gamma[Cr(VI)]$ and $\gamma[Cr(III)]$ are the mass concentrations of the analytes in the aqueous solutions (in $mg\,l^{-1}$). The correlation coefficient was $r = 0.999$ in both cases. The validity of each calibration curve was evaluated by the response factor (r.f.) test [r.f. = (AU − intercept)/$\gamma$(analyte)] at each point of each calibration curve [19]. The results verified the validity of each regression line, as the deviations of the response factors were in the range −1.6 to +1.5% for Cr(VI) and −1.2 to 1.3% for Cr(III) of the slope of the corresponding calibration curve. The $3\sigma$ detection limits were 1 $\mu g\,l^{-1}$ for Cr(VI) and 10 $\mu g\,l^{-1}$ for Cr(III) ($n = 10$), while their quantitation limits were 3 $\mu g\,l^{-1}$ for Cr(VI) and 30 $\mu g\,l^{-1}$ for Cr(III). Close to the quantitation limits for both analytes the relative standard deviations were 3.0 and 4.0% for Cr(VI) and Cr(III) at 10 and 50 $\mu g\,l^{-1}$ level ($n = 10$), respectively.

## 3.6. Chromium speciation in aqueous solutions

The applicability of the developed assay to the speciation of Cr(VI)–Cr(III) was firstly checked in aqueous solutions, by analyzing various mixtures of the analytes. The experimental results are shown in Table 2. The calculated recoveries were satisfactory in all cases, ranging between 97.4 and 101.5%.

The speciation efficiency of the proposed method was further validated by analyzing a CRM 544, No. 66 certified reference material (lyophilized solution) as shown in Table 4.

## 3.7. Analysis of real samples

The proposed FI assay was applied to the determination of chromium in mineral and tap water (Table 3) as well as in a CRM 544, No. 66 certified reference material (Table 4). No chromium was detected in the examined water samples. Although the sensitivity of the proposed method is not adequate for the analysis of the examined water samples the recovery experiments verified the accuracy of the proposed method and showed that there are no matrix effects on the determination of chromium species in mineral and tap water samples. However, there are many water

Table 2
Simultaneous determination of Cr(III) and Cr(VI) in synthetic samples

| Added | | Found | | Recoveries (%) | |
|---|---|---|---|---|---|
| Cr(VI) (ng ml$^{-1}$) | Cr(III) (ng ml$^{-1}$) | Cr(VI) (ng ml$^{-1}$) | Cr(III)[a] (ng ml$^{-1}$) | Cr(VI) | Cr(III) |
| 50 | 200 | 49.2 ± 1.0 | 201 ± 4 | 98.4 | 100.5 |
| 50 | 400 | 49.2 ± 1.0 | 401 ± 9 | 98.4 | 100.3 |
| 50 | 600 | 49.2 ± 1.1 | 597 ± 11 | 98.4 | 99.5 |
| 100 | 200 | 97.4 ± 2.1 | 202 ± 5 | 97.4 | 101.2 |
| 100 | 400 | 97.4 ± 2.0 | 404 ± 8 | 97.4 | 101.0 |
| 100 | 600 | 97.4 ± 2.2 | 609 ± 12 | 97.4 | 101.5 |
| 200 | 200 | 198.8 ± 4.1 | 197.5 ± 5 | 99.4 | 98.7 |
| 200 | 400 | 198.8 ± 4.2 | 402 ± 7 | 99.4 | 100.5 |
| 200 | 600 | 198.8 ± 4.5 | 602 ± 10 | 99.4 | 100.3 |
| 500 | 200 | 500 ± 10 | 195 ± 5 | 100.0 | 97.5 |
| 500 | 400 | 506 ± 9 | 396 ± 10 | 101.3 | 99.0 |
| 500 | 600 | 504 ± 11 | 597 ± 12 | 100.8 | 99.5 |

[a] Calculated by subtracting Cr(VI) from total chromium.

Table 3
Simultaneous determination of Cr(III) and Cr(VI) in water samples

| Sample | Cr(VI) added (ng ml$^{-1}$) | Cr(VI) found[a] (ng ml$^{-1}$) | Recovery[b] (%) | Cr(III) added (ng ml$^{-1}$) | Cr(III) found (ng ml$^{-1}$) | Recovery (%) |
|---|---|---|---|---|---|---|
| Tap water | – | n.d.[c] | – | – | n.d. | – |
| | 10 | 10.6 ± 0.6 | 106.0 | 50 | 48.3 ± 2.1 | 96.6 |
| | 50 | 48.5 ± 1.5 | 97.0 | 100 | 93 ± 3.7 | 93.0 |
| | 100 | 101 ± 2.8 | 101.0 | 200 | 190.5 ± 7.1 | 95.3 |
| Mineral water | – | n.d. | – | – | n.d. | – |
| | 10 | 10.4 ± 0.6 | 104.0 | 50 | 49.2 ± 1.9 | 98.4 |
| | 50 | 49.3 ± 1.3 | 98.6 | 100 | 97.5 ± 3.5 | 97.5 |
| | 100 | 93 ± 2.9 | 93.0 | 200 | 192 ± 6.6 | 96.0 |

[a] Mean of five results.
[b] Mean recovery.
[c] Not detected.

Table 4
Comparison of results obtained for certified reference material by the proposed method with the certified values ($\mu$g l$^{-1}$) for Cr(III) and Cr(VI)

| Sample | CRM 544 (lyophilized solution) |
| --- | --- |
| Certified value ($\mu$g l$^{-1}$) | |
| Cr(III) | 53.6 |
| Cr(VI) | 45.6 |
| Found[a] ($\mu$g l$^{-1}$) | |
| Cr(III) | $51.5 \pm 1.2$ |
| Cr(VI) | $44.4 \pm 1.1$ |
| $e_r$[b] (%) | |
| Cr(III) | $-3.9$ |
| Cr(VI) | $-2.6$ |

[a] Mean of five results.
[b] Relative error.

samples where their Cr(III) and Cr(VI) content is more or equal to 3 and 30 $\mu$g l$^{-1}$, respectively which means that they can easily and accurately be analyzed by the proposed method. For instance these levels for total chromium can be met in surface waters (up to 84 $\mu$g l$^{-1}$ in USA, 0.2–44 $\mu$g l$^{-1}$ in Canada and up to 10 $\mu$g l$^{-1}$ in Rhine). In groundwater in the USA and The Netherlands levels up to 50 and 5 $\mu$g l$^{-1}$ for total chromium have been found, respectively. Approximately 18% of the population of the USA are exposed to total chromium in drinking water levels between 2 and 60 $\mu$g l$^{-1}$ and <0.1% to levels between 60 and 120 $\mu$g l$^{-1}$. These data shows that the drinking water intake of chromium can contribute substantially when total chromium levels are above 25 $\mu$g l$^{-1}$. It should be noted that the maximum contaminant level (MCL) that is allowed in drinking water is 100 $\mu$g l$^{-1}$ in USA and 50 $\mu$g l$^{-1}$ in EU [20]. It also should be noted that the concentration of free Fe(III) in the examined tap and mineral water samples were approximately 30 and 22 $\mu$g l$^{-1}$, respectively. This means that the free Fe(III) can be effectively masked by 0.15 mol l$^{-1}$ NaF according to those mentioned in Section 3.4.

## 4. Conclusions

This work describes a simple, sensitive and rapid FI assay for the speciation of Cr(VI) and Cr(III), using for the first time chromotropic acid as the color-forming reagent. The developed method enabled the accurate and precise simultaneous determination of Cr(III) and Cr(VI) at low $\mu$g l$^{-1}$ level, using a single spectrophotometric detector, without the need of any additional, time-consuming pre-concentration step prior to the final measurement. The method is adequately selective for the direct and accurate determination of the analytes in a variety of real samples (tap and mineral water and lyophilised solution certified reference material).

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