# Sequential injection determination of chromium(VI) by transient oxidation of brucine with spectrophotometric detection and in-line dilution

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A sequential injection method for the determination of chromium(VI) in residual waters from electroplating baths and steels is proposed. The method is based on monitoring the absorbance at 525 nm due to an aminochrome intermediate compound resulting from oxidation of the alkaloid brucine. The intermediate brucichrome is unstable so that its analytical use is only possible in closed flowing systems where the precise and reproducible control of time and mixing is possible. The method gave a linear calibration curve from 0.2 to 2 mg l$^{-1}$ Cr(VI) and a detection limit of 0.045 mg l$^{-1}$ Cr(VI). A sampling frequency of 120 h$^{-1}$ is possible. Industrial samples from electroplating baths and residual washing waters were analyzed, and in this case a sequential injection in line dilution was performed, permitting real time determination of samples with Cr(VI) concentrations up to 100 mg l$^{-1}$ with a sampling frequency of 80 h$^{-1}$.

## Introduction

Sequential injection analysis (SIA) was proposed in 1990 by Ruzicka and Marshall[1] as a rugged flow analysis technique that would meet the requirements for industrial process control, with minimal needs for maintenance and recalibration.[2] The original system consisted of a syringe pump connected by a holding coil to the common port of a multi-port selection valve. The common port can access, by electrical actuation, each of the other ports, that are connected to reagents, samples, standards and detector. The system is completely computer controlled and, on operation, the appropriate program sequentially aspirates carrier, sample and reagents into the holding coil. On reversing the flow, the mixture zone is propelled through a reaction coil to the detector flow cell and waste.[3] Volumes of carrier, sample and reagents are controlled by precise timing of the pump movements, which saves sample and reagents and minimizes the accumulation of toxic residues. The principles of reproducible time and mixing in SIA are similar to those of flow injection analysis (FIA), so that the chemical reactions do not need going to completeness for analytical use.[4]

Den Boef[5] studied the use of unstable reagents in flow analysis, and pointed out that the instability of reagents may be as minor an objection as is the incompleteness of the analytical reaction, since the decomposition of the reagent is reproducible. Yamane and Mottola[6] proposed a closed loop unsegmented continuous flow system for the determination of Cr(VI) using brucine as a colorimetric reagent. Brucine is an alkaloid that is oxidized by Cr(VI) in acidic medium containing oxalic acid as catalyst, producing an unstable aminochrome intermediate (brucichrome) with a high molar absorptivity in the range 510–540 nm. A recent study of the electrochemical properties of brucine suggests that the brucichrome dimerizes in a slow reaction, producing a final product (also an aminochrome) that presents maximum absorptivity in the range 420–430 nm.[7] It is noteworthy that the first reaction is much faster than the dimerization, and the intermediate brucichrome has a higher molar absorptivity than the final product. Hence monitoring the absorbance due to the intermediate would result in significantly higher sensitivity than monitoring the final product, a feature that is only possible to be explored in flowing systems.

Owing to the significance of Cr(VI) monitoring in industrial electroplating processes and waste waters and in environmental samples, this work revisited the chemistry of brucine oxidation by Cr(VI), and a sequential injection method for determination of Cr(VI) was developed. In such samples, a wide range of Cr(VI) concentration is found, ranging from a few μg l$^{-1}$ in non-contaminated environmental samples to several tenths of mg l$^{-1}$ in electroplating washing waters and electroplating baths. The mechanical simplicity of sequential injection systems permits the automation of preconcentration[8] and in-line dilution[9,10] of samples with minimal reconfiguration of the system. In the present work we studied in-line dilution for the determination of Cr(VI) in steels and electroplating residual waters.

## Experimental

### Apparatus

A Fialab 3500 instrument (Alitea USA, Medina, WA, USA) was used in all experiments in the sequential injection mode according to Fig. 1. Solutions were driven by a 5.00 ml syringe pump and an eight port rotary selection valve (Valco Instruments, Houston, TX, USA). The holding coil was made of 2 m × 0.8 mm id Teflon (PTFE) tubing. The reaction and dilution coil were 0.50 and 1.5 m × 0.8 mm id PTFE tubing, respectively. All other tubing connections were made of 0.5 mm id PTFE tubing and PTFE nuts and ferrules (Upchurch, Oak Harbor, WA, USA). A Micronal (São Paulo, Brazil) B382 spectrophotometer was used as a detector with a Micronal U-flow cell with a 10 mm light pathlength and 180 μl internal volume. Control of the pump and valve was effected by the Fialab 3500 software. Acquisition of data was performed with a PC-LPM-16 board (National Instruments, Austin, TX, USA).

Kinetic studies of brucine oxidation were performed with a Hewlett-Packard (Avondale, PA, USA) HP8542 spectrophotometer using a 1 cm pathlength quartz cuvette.

## Reagents and solutions

All chemicals were of analytical-reagent grade from Aldrich (Milwaukee, WI, USA) or Merck (Rio de Janeiro, Brazil). Solutions were prepared in de-ionized water (NANOpure II, Sybron Barnstead, Dubuque, IA, USA).

A 98.90 mg l$^{-1}$ Cr(vi) stock standard solution was prepared by dissolving 0.2798 g of potassium dichromate (Merck), previously dried in an oven at 140 °C for 1 h, in water. Working standard solutions were prepared by appropriate dilution of the stock standard solution.

The colorimetric reagent was prepared by dissolving 0.95 g of oxalic acid (Merck), 0.22 g of brucine (Aldrich) and 3.33 ml of concentrated sulfuric acid (Merck) in water and diluting the mixture to 100 ml. This solution containing 0.075 mol l$^{-1}$ oxalic acid, 0.0025 mol l$^{-1}$ brucine and 0.6 mol l$^{-1}$ sulfuric acid. When stored in a refrigerator in a dark flask, this solution is stable for several months. The carrier solution was 0.6 mol l$^{-1}$ sulfuric acid or de-ionized water.

## Samples and sample preparation

**Industrial effluent.** Samples of waste water from Cr(vi) electroplating baths were collected at two points, one before and the other after the waste treatment plant, where three steps are carried out: reduction of Cr(vi) to Cr(iii) with sulfite, precipitation of Cr(OH)$_3$ and filtration. Chromium(vi) was determined directly in the sample after in-line sequential injection dilution. For total chromium determination, 50.00 ml of sample were treated with 5 ml of peroxodisulfate in the presence of silver nitrate and boiled for 15 min, before appropriate dilution and analysis.

**Steels.** Three certified reference samples, a 16% m/m chromium (IPT AISI 440 A No. 22) stainless steel, a 0.820% m/m chromium (IPT 17-A AISI No. 4340) low alloy steel and a 0.084% m/m chromium plain carbon steel (IPT 39, AISI No. 1005), were supplied in chip form by the Instituto de Pesquisas Tecnológicas (São Paulo, Brazil).[11] Sample dissolution was performed by boiling 0.2 g (±0.1 mg) of steel with a 1 + 1 nitric acid in a glass covered beaker until complete dissolution of the solid. A 10.00 ml volume of concentrated perchloric acid was

added and the boiling was continued until the solutions turned red.[12] The mixture was evaporated to dryness and liberation of white fumes. The salts were dissolved in water, filtered through a Whatman No. 42 filter paper and diluted in a suitable calibrated flask.

## Sequential injection analysis procedure

The SI manifold is illustrated in Fig. 1. The HC, DC and the RC tubings are filled with carrier and the tubings connected to ports 2 and 3 of the selection valve, V, are filled with colorimetric reagent and sample/standard, respectively. The syringe valve, S, connects the syringe and the carrier reservoir, C. At a flow rate of 200 µl s$^{-1}$, 1.5 ml of carrier are aspirated into the syringe. The S switches to connect the syringe with V, and at a flow rate of 100 µl s$^{-1}$, 200 µl of the colorimetric reagent (R) and $S_v$ µl of sample or standard ($S1$) are sequentially aspirated into the HC by reversal movements of the syringe pump, P. The pump is stopped while the valve is rotating to avoid pressure surges and consequent bubble formation. A forward movement of P drives the reaction zone at a flow rate of 100 µl s$^{-1}$, through the RC to the detector and waste, emptying the syringe. For an $S_v$ of 100 µl, a linear response between absorbance and Cr(vi) concentration was observed from 0.1 to 1.0 mg l$^{-1}$ Cr(vi). For an $S_v$ of 50 µl, a linear response was observed between 0.8 and 8.0 mg/l Cr(vi). For concentrated samples obtained from the Cr(vi) electroplating baths, or residual washing waters from the electroplating process collected before the waste treatment plant, an in-line sequential injection dilution is needed. For this, 2.0 ml of carrier were aspirated into the syringe. Then, 50 µl of sample were aspirated into the HC, and 150 µl of sample plus carrier solution contained in the HC were injected through the dilution coil, DC, connected to port 8 of V, performing the desired dilution. In the sequence, 200 µl of brucine reagent were aspirated to HC, followed by 50 µl of the sample zone in DC adjacent to the selection valve, and then injected through RC to the detector and waste using 1.5 ml of carrier. Finally, the remaining volume of carrier into S was used to wash out the Cr(vi) present in DC, so that the system was then ready for a new sample.

## Results and discussion

The initial reaction between Cr(vi) and brucine was studied in detail by Yamane and Mottola,[6] who showed that the rate is dependent on the acidity and the presence of oxalic acid as catalyst. The optimum conditions for the concentration of reagents determined by Yamane and Mottola[6] were used in the present work: 2.5 mmol l$^{-1}$ brucine and 0.075 mol l$^{-1}$ oxalic acid in 0.6 mol l$^{-1}$ sulfuric acid. The transient oxidation of brucine in this medium is illustrated in Fig. 2, which shows the spectrophotometric monitoring of the reaction of 1 ml of the colorimetric reagent and 1.0 ml of 0.0769 mmol l$^{-1}$ Cr(vi) during the first 20 s and after the reaction had reached equilibrium. As previously observed for brucine oxidation with Ce(vi) ions,[7] a red intermediate (brucichrome) with maximum absorptivity at 513 and 537 nm is formed almost instantaneously, followed by a dimerization reaction that leads to a product with maximum absorptivity at 450 nm. Also shown in Fig. 2 is an absorption maximum at 360 nm, which disappears at the same rate as the 513–540 nm plateau, indicating that the red brucichrome also absorbs in the ultraviolet wavelength range. Monitoring the UV peak would provide a higher sensitivity than monitoring the visible peak, but this would result in a methodology more susceptible to spectral interference. The linear relationship between $1/A$ (where $A$ is the absorbance at 525 or 360 nm) and reaction time suggests that the intermediate consumption follows second order kinetics, which
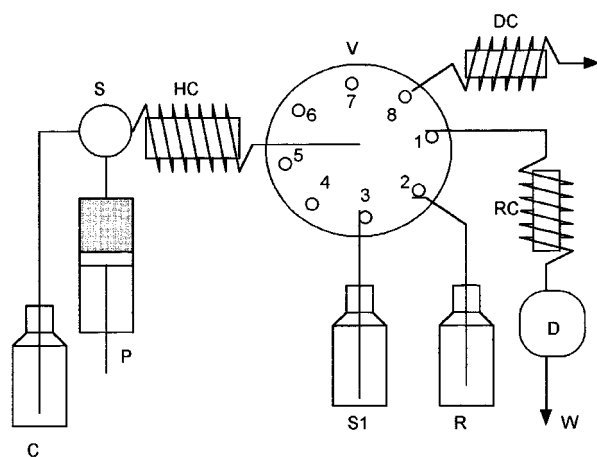


**Fig. 1** Sequential injection manifold for Cr(vi) determination. C = 0.60 mol l$^{-1}$ sulfuric acid carrier or de-ionized water; S = syringe valve; P = syringe pump; HC = holding coil; V = eight port selection valve; R = colorimetric reagent reservoir, S1 = sample or standard reservoir; RC = reaction coil; DC = dilution coil; D = detector (525 nm); W = waste.

is in agreement with the dimerization mechanism proposed previously.[7]

## Method optimization

**Carrier solution.** Distilled, de-ionized water was used as the carrier stream for samples with Cr(vi) concentrations higher than 1.0 mg l$^{-1}$, and it was used in the experiments with steels and residual waters collected before the waste treatment plant. For diluted samples such as sediment extracts and residual waters after treatment, the use of water as the carrier is not appropriate owing to the differences between the viscosities of the reagent and sample zones, which lead to a background signal, known as the Schlieren effect.[13,14] When all samples, reagent and carrier were prepared in 0.6 mol l$^{-1}$ sulfuric acid, the Schlieren effect disappeared. Therefore, 0.6 mol l$^{-1}$ sulfuric acid was used as the carrier in the analysis of dilute samples. When sulfuric acid is not added to the standards and samples to match the carrier concentration, the blank signal appears, but it is very reproducible, so that it can be subtracted from the signal of samples/standards, leading to a linear working range between 0.1 and 1.0 mg l$^{-1}$ Cr(vi).

**Channel length, geometry and flow rate.** Table 1 shows the influence of reaction channel length on the relative peak height, obtained for 0.8 mg l$^{-1}$ Cr(vi) using 0.6 mol l$^{-1}$ sulfuric acid as carrier. No significant differences were observed, which may be explained by the compromise between reaction time and zone penetration. Since the brucine oxidation is an almost instantaneous reaction, it would be expected that increasing the channel length would result in a decrease in the signal, but the relative peak height obtained with the 50 cm reaction coil is only 6% larger than that obtained with a 1.5 m coil. The loss of signal due to increased dispersion and the dimerization of the red brucichrome in the 1.5 m reaction coil is compensated for by better overlapping between the reagent and sample zones that produces more of the red brucichrome.

In all succeeding studies, the 50 cm reaction channel was used in a coiled fashion, since the use of a straight geometry led to poor repeatability, with a relative standard deviation (RSD) of 10%, compared with 0.5% observed for the coiled channel. In addition, for the shorter channel length, the sampling frequency is higher.

The influence of the flow rate was investigated from 20 to 200 µl s$^{-1}$ with 2.0 mg l$^{-1}$ Cr(vi) solution and the 50 cm reaction channel, using water as carrier. The results are shown in Fig. 3, and indicate that on increasing the flow rate from 20 to 100 µl s$^{-1}$ the relative peak height was doubled. A 100 µl s$^{-1}$ flow rate provides the most effective penetration of sample and reagent zones, eliminating the trend to form the doubled peaks as observed at flow rates of 20–60 µl s$^{-1}$. In addition, a flow rate of 100 µl s$^{-1}$ leads to less time for the red brucichrome dimerization and a higher sampling throughput. Larger flow rates did not bring significant improvements, so 100 µl s$^{-1}$ was used in all succeeding experiments.

**Sample volume, analytical curves, and in-line dilution by zone sampling.** The sample volume plays a major role in sensitivity, in both FIA and SIA. Using a sample volume of 50 µl and water as carrier, a linear dynamic range was observed for concentrations from 0.8 to 8 mg l$^{-1}$ Cr(vi). For a sample volume of 100 µl, the linear dynamic range was observed from 0.2 to 1 mg l$^{-1}$, as shown in Fig. 4, and a detection limit of 45 µg l$^{-1}$ was estimated at three times the standard deviation of the absorbance residuals plus the intercept of the calibration graph.[15] For these dilute solutions, as mentioned before, the carrier was a 0.6 mol l$^{-1}$ sulfuric acid solution to minimize the Schlieren effect.

Real time analyses are important in industrial process control, and on-line Cr(vi) monitoring in electroplating baths or residual
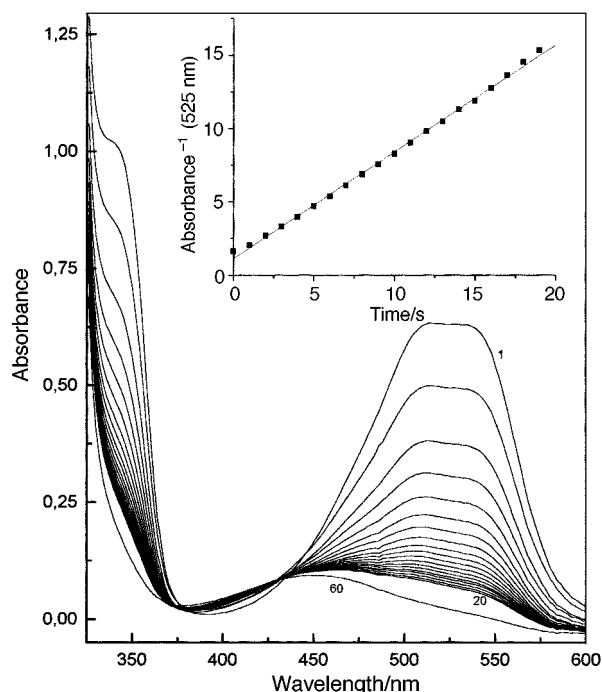


**Fig. 2** Spectrophotometric monitoring of a reaction medium prepared in a cuvette by adding 1 ml of 4 mg l$^{-1}$ Cr(vi) solution to 1 ml of the colorimetric reagent (2.5 mmol l$^{-1}$ brucine and 75 mmol l$^{-1}$ oxalic acid in 0.6 mol l$^{-1}$ sulfuric acid). Spectra 1–20 were taken during the first 20 s of reaction at intervals of 1 s using a 1 cm pathlength quartz cuvette. Spectrum 60 was obtained after the reaction had reached equilibrium.

**Table 1** Influence of reaction channel length on sensitivity and precision. Flow rate = 100 µl s$^{-1}$

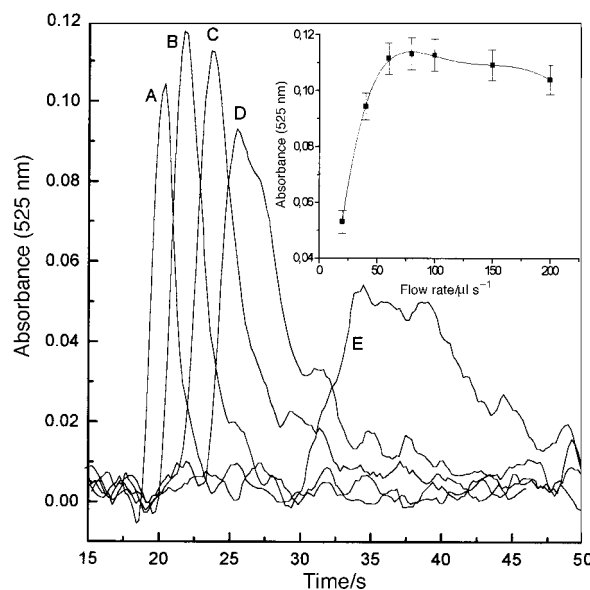| Reaction coil length/m | Relative peak height | RSD (%) |
| --- | --- | --- |
| 0.50 | 10.47 | 0.49 |
| 0.75 | 10.33 | 1.11 |
| 1.0 | 10.35 | 3.41 |
| 1.5 | 9.87 | 3.25 |



**Fig. 3** Influence of the flow rate, (A) 200, (B) 100, (C) 80, (D) 40 and (E) 20 µl s$^{-1}$, on the SI signal for a 2.0 mg l$^{-1}$ Cr(vi) solution. $S_v$ = 50 µl; reagent volume = 200 µl; carrier = de-ionized water.

waters that contain large amounts of Cr(VI) require sample dilution before analysis. This can be achieved in SIA by performing the dilution in a gradient chamber connected to a port of the selection valve,[9] but also it can be made by zone sampling from an auxiliary dilution coil, also connected to the selection valve, as proposed by Baron *et al.*[10] Control of the magnitude of dilution for a specific conduit is effected with three volume parameters: the sample volume, $S_v$, the transfer volume, $T_v$, and the analysis volume, $A_v$. The volume $S_v$ is aspirated from the sample reservoir into the holding coil, and then injected in the dilution coil using $T_v$, which consists of sample plus carrier contained in the holding coil. The size of $T_v$ determines how far the head of sample zone inside the dilution coil is from the selection valve. The volume $A_v$ is aspirated from the tail of the sample zone inside the dilution coil into the holding coil, and the analysis follows the usual procedure. The influence of the transfer volume on the dispersion coefficient, $D$, of a 0.004% m/v bromothymol blue (in 0.01 mol $l^{-1}$ borate buffer) solution is shown in Table 2 for $S_v$ and $A_v$ of 50 µl. The values of $D$ were determined as the ratio $A^0/A$, where $A^0$ is the absorbance of the pure 0.004% BTB solution in the flow cell and $A$ is the absorbance at the peak maximum when the BTB solution is subjected to the in-line dilution procedure described above, using 0.01 mol $l^{-1}$ borate buffer as carrier.

The inset in Fig. 4 shows the Cr(VI) calibration curve in the range 20–100 mg $l^{-1}$, obtained performing the SIA in-line dilution. $S_v$, $T_v$, and $A_v$ were 50, 150 and 50 µl, respectively.
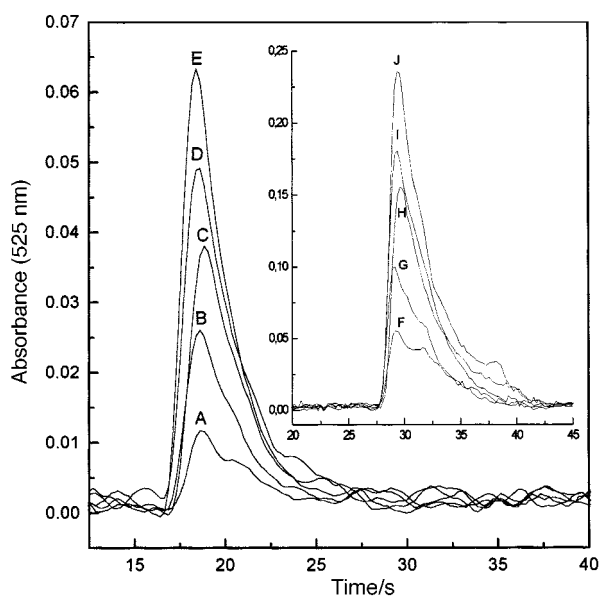


**Fig. 4** SI signal for Cr(VI) concentrations of (A) 0.019 78, (B) 0.039 56, (C) 0.059 34, (D) 0.079 12 and (E) 0.0989 mg $l^{-1}$. $S_v$ = 100 µl; reagent volume = 200 µl; flow rate = 100 µl $s^{-1}$; carrier = 0.60 mol $l^{-1}$ sulfuric acid. The inset shows the SI signal for in-line dilution of Cr(VI) solutions with concentrations of (F) 19.78, (G) 39.56, (H) 59.34, (I) 79.12 and (J) 98.90 mg $l^{-1}$. Reagent volume = 200 µl; $S_v$ and $A_v$ = 50 µl; $T_v$ = 150 µl; carrier = de-ionized water.

These experiments demonstrate the adequacy of the dilution coil to perform in-line dilution, keeping a high sample throughput of 80 $h^{-1}$. In comparison with the 120 samples $h^{-1}$ that can be analyzed when no dilution is necessary, this is an impressive result that would not be possible with the gradient chamber device, which needs to be washed with large volumes of carrier between analyses to avoid carryover.

Table 3 summarizes the linear dynamic range, the limit of detection, the regression parameters and the sample throughput obtained with different approaches used in this work. The useful range of quantification above 0.1 mg $l^{-1}$ Cr(VI) and the precision of the proposed method are similar to those reported for atomic absorption spectrometry (AAS) with an air–acetylene flame.[16] The narrower linear dynamic range of the SIA method in comparison with AAS (0.25–20 and 0.4–30 mg $l^{-1}$ Cr for air–acetylene and $N_2O$–acetylene flames, respectively)[16] may be easily overcome by using different sample volumes or the in-line dilution procedure. Another advantage over AAS is the low cost of the detection system. Inexpensive miniaturized photometers are commercially available, permitting the implementation of the proposed method not only in a quality control laboratory, but also in on-line industrial process control and *in situ* environmental monitoring.

Flow injection papers[17–19] on the determination of Cr(VI) using the reaction with diphenylcarbazide report a working concentration range similar to those observed with brucine, but with a better detection limit of 0.01–0.02 mg $l^{-1}$. The brucine reagent is more stable than diphenylcarbazide, an important feature for on-line industrial process monitoring. A 2 week experiment performed by submitting a 4 mg $l^{-1}$ Cr(VI) solution to daily SIA experiments using the same reagent solution (not stored in a refrigerator) resulted in an average absorbance of $0.12_8 \pm 0.01_1$ ($n$ = 30).

Table 4 presents the results for real samples. The *t*-test for comparison of the SIA results with the certified Cr concentration resulted in *t* values of 1.18, 0.86 and 0.51 for steels AISI 440A, 4340 and 1005, respectively. At the 95% confidence level and two degrees of freedom (three replicates for each sample), the critical value of *t* is 4.3, suggesting that there is no evidence of systematic errors in the results.[15] For the washing water from an electroplating bath collected before the treatment plant, the results obtained by SIA and AAS differed by 1.0%. The experimental *t* value was 0.755, indicating that there are no

**Table 2** Influence of the transfer volume on the dispersion coefficient, $D$, for the SIA in-line dilution procedure using the dilution coil. $S_v$ = $A_v$ = 50 µl

| $T_v$/µl | Absorbance[a] (620 nm) | RSD (%)[b] | $D$ |
|---|---|---|---|
| 50 | 0.107 | 2.8 | 8.0 |
| 75 | 0.094 | 2.5 | 9.1 |
| 100 | 0.049 | 2.0 | 17.5 |
| 150 | 0.022 | 2.3 | 39.3 |
| 200 | 0.012 | 33.3 | 71.3 |

[a] Measured at the peak maximum. [b] Relative standard deviation of five experiments.

**Table 3** Performance of the SIA system for the determination of hexavalent chromium

| $S_v$/µl | Linear range/ mg $l^{-1}$ | Regression parameters | | | | Detection limit/ mg $l^{-1e}$ | Sample throughput/ $h^{-1}$ |
| | | Slope/l $mg^{-1}$ | Intercept | $r^2$ | $n$ | | |
|---|---|---|---|---|---|---|---|
| 50[a] | 1.0–8.0 | 0.0302 ± 0.0009 | 0.0004 ± 0.0004 | 0.9986 | 5 | 0.40 | 120 |
| 100[b] | 0.2–1.0 | 0.064 ± 0.001 | −0.0005 ± 0.0009 | 0.9992 | 5 | 0.045 | 120 |
| 100[c] | 0.1–1.0 | 0.0523 ± 0.001 | −0.0009 ± 0.0009 | 0.9982 | 6 | 0.051 | 120 |
| 50 (after in-line dilution)[d] | 20–100 | 0.0021 ± 0.0001 | 0.020 ± 0.008 | 0.9948 | 5 | 11.2 | 80 |

[a] Using water as carrier. Standards in water. [b] Using 0.6 mol $l^{-1}$ sulfuric acid as carrier and as medium for standards. [c] Using 0.6 mol $l^{-1}$ sulfuric acid as carrier. Standards in water. Blank signal (Schlieren effect) subtracted. [d] Using $T_v$ = 150 µl and $A_v$ = 50 µl. [e] Calculated at three times the standard deviation of *y*-residuals plus the intercept of the calibration graph.[15]

**Table 4** Results of the determination of Cr(VI) concentration by SIA in comparison with certified values and AAS

| Sample | Chromium concentration[c] | | | Recovery Test | |
| | SI | Certified value | AAS | Added/mg | Recovered/mg |
|---|---|---|---|---|---|
| Steel AISI 440[a] | $16.3_4 \pm 0.1_9$ | 16.21 | — | — | — |
| Steel AISI 4340[a] | $0.819 \pm 0.002$ | 0.820 | — | — | — |
| Steel AISI 1005[a] | $0.081 \pm 0.001$ | 0.084 | — | — | — |
| Electroplating residual water[b] | $49.5_1 \pm 1._1$ | — | $49._5 \pm 1._1$ | — | — |
| Residual water after treatment[b] | ND[d] | — | ND | 2.00 | $2.11 \pm 0.04$ |

[a] Concentrations expressed as % m/m. [b] Concentration expressed as mg l$^{-1}$. [c] Results are the average of three experiments for each sample. [d] ND, not detected.

significant differences at the 95% confidence level between results obtained by the two techniques.[15] This result was only possible after oxidation of the sample with peroxodisulfate.

The residual water collected after the treatment plant did not contain a Cr(VI) concentration detectable by the proposed method. After oxidation with peroxodisulfate, Cr(VI) was detected at a concentration of around 100 µg l$^{-1}$. Recovery tests performed with a spiked sample showed good results, as presented in Table 4. These results indicate that the brucine oxidation is selective to the hexavalent state of oxidation, a fact that permits speciation of Cr(III) and Cr(VI).

### Interferences

Possible sources of interference are oxidizing species such as Mo(VI), Fe(III), nitrate, iodate, bromate and peroxodisulfate. According to Table 5, these ions do not oxidize either the brucine or the intermediate brucichrome, in 0.6 mol l$^{-1}$ sulfuric acid. In addition, oxalic acid does not have the catalytic role played in the oxidation by Cr(VI), so that no interference effect was observed. The above mentioned ions oxidize brucine only in sulfuric acid at a concentration 2 mol l$^{-1}$ or higher. Yamane and Mottola[6] demonstrated that heavy metals and Mn(II) have no or very little interference effect. The results in Table 5 show that Fe(III), a major component in waste waters and steels, does not interfere in the determination of Cr(IV). This is an interesting feature of the proposed method in comparison with AAS, since Fe(III) interferes when one uses an air–acetylene flame.[16]

Ions that react with $Cr_2O_7^{2-}$, such as I$^-$, NO$_2^-$, As$^{3+}$, VO$_3^-$ and Fe$^{2+}$, have a major role in chromium speciation. As Cr(III) does not react with brucine, the speciation of Cr(III) and Cr(VI) is possible, with determination of the total chromium concentration as Cr(VI) after oxidation of the sample with $S_2O_8^{2-}$. Table 5 shows that 1.68 g l$^{-1}$ $S_2O_8^{2-}$ leads to a positive error of only

4.3% in the Cr(VI) concentration. This error is minimized by boiling the solution in an acidic medium to promote the Cr(III) oxidation and further elimination of the excess of peroxodisulfate. The oxidation of Cr(III) to Cr(IV) with Ce(IV) ions is used in most speciation papers,[8,19] but it is not adequate when one uses brucine as a colorimetric reagent, as the latter is easily oxidized by Ce(IV), leading to positive errors in Cr(VI) concentration.

### Conclusion

Sequential injection is a suitable approach for automating Cr(VI) determinations based on the transient oxidation of brucine in a wide range of concentrations and different samples. The difficult mixing in SIA due to the single line system with no confluence points, which in principle would be a disadvantage, has a beneficial effect in the studied reaction. The reagent zone penetrating the sample zone as the reaction zone travels through the reaction coil produces more of the red brucichrome, compensating for the loss of signal due to the instability of the same intermediate. This permits good sensitivity of the method.

In addition, SIA has some advantages over the closed loop continuous-flow system: the reagent volume of 200 µl used per analysis is not pumped back to the reservoir, avoiding the accumulation of reaction products, which lead to baseline drift, and also the loss of sensitivity reported by Yamane and Mottola.[6] This is important for implementing an on-line Cr(VI) monitoring methodology in electroplating processes. It should be mentioned that SIA permits a significant saving of the brucine reagent, minimizing the accumulation of toxic residues.

**Table 5** Effect of possible interfering ions on the analytical signal of 2.5 mg l$^{-1}$ Cr(VI) solution spiked with the reported amounts of respective salts. Carrier = water; $S_v$ = 50 µl. Results correspond to the average of five sequential injection experiments with each solution

| Species added | Amount added/ mg l$^{-1}$ | Added as | Relative error on peak height (%) |
|---|---|---|---|
| IO$_3^-$ | 15.0 | KIO$_3$ | +0.9 |
| BrO$_3^-$ | 15.0 | KBrO$_3$ | 0 |
| NO$_3^-$ | 15.0 | NaNO$_3$ | 0 |
| NO$_2^-$ | 62.5 | NaNO$_2$ | −91.4 |
| S$_2$O$_8^{2-}$ | 1677 | K$_2$S$_2$O$_8$ | +4.3 |
| Cl$^-$ | 3550 | HCl | 0 |
| Mn(II) | 162.5 | MnSO$_4 \cdot$H$_2$O | −3.4 |
| Cu(II) | 12.5 | CuSO$_4 \cdot$5H$_2$O | 0 |
| Ce(IV) | 10.5 | Ce(SO$_4$)$_2$2(NH$_4$)$_2$SO$_4 \cdot$4H$_2$O | +45.9 |
| Mo(VI) | 43.3 | (NH$_4$)$_6$Mo$_7$O$_{24} \cdot$4H$_2$O | −1.3 |
| Mo(VI) | 86.5 | (NH$_4$)$_6$Mo$_7$O$_{24} \cdot$4H$_2$O | −3.6 |
| Fe(III) | 58.0 | Fe(NO$_3$)$_3 \cdot$9H$_2$O | +1.16 |
| Fe(III) | 116.0 | Fe(NO$_3$)$_3 \cdot$9H$_2$O | −2.3 |

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