

Flow injection spectrophotometry for speciation of Cr(VI) and Cr(III) using diphenylcarbazide and solid phase extraction with C₁₈ in-valve mini-column

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ABSTRACT Flow injection (FI) spectrophotometric sequential determination of Cr(VI) and Cr(III) has been proposed by using flow systems assembled with inexpensive and easily available components. It is based on the reaction of Cr(VI) with 1,5-diphenylcarbazide(DPC) to form a colored complex for the determination of Cr(VI). Cr(III) is oxidized in-line to Cr(VI) by Ce(IV) yielding the total Cr concentration. From the difference, Cr(III) concentration can be evaluated. Solid phase extraction with C₁₈ in-valve mini-column provides on-line pre-separation and pre-concentration. Single standard calibration is possible. Optimization for the conditions was investigated. The FI procedure developed has been applied for speciation of Cr(VI) and Cr(III) in waste water samples taken from industry in Thailand. The results obtained agree well with those obtained by ICP-AES.

KEYWORDS: flow injection, speciation, C₁₈ resin, solid phase extraction, in-valve column.

INTRODUCTION

Chromium compounds have been involved in various applications such as metal plating, pigments, leather tanning, textiles, catalysis and wood preservation.¹ Prevention and control of chromium waste have been realized. Although AAS and spectrophotometry using diphenylcarbazide (DPC) are the main analytical methods but some other methods have also been applied for the purposes,² such as XRF,³ NAA,⁴ voltammetry⁵ and ion-chromatography.⁶ Due to no established toxicity with Cr(III), the chief health problems are usually associated with Cr(VI) compounds. Thai legislation to waste water, concentration of Cr(VI) at higher than 0.25 µg ml⁻¹ is not allowed for discharge whilst the limit concentration for Cr(III) is 0.75 mg ml⁻¹.⁷

Speciation of the two species has become important. Batch procedures, which mainly make use of atomic spectrometry with off-line sample treatment for speciation of Cr(VI) and Cr(III) have been reported.⁸⁻¹¹ Flow injection analysis (FIA) was first introduced for serial assays with various advantages including making use of simple components.¹²⁻¹⁷ Flow injection (FI) techniques have proven to be very useful and powerful for on-line sample pretreatment prior

to the determination such as in-valve column,¹⁸⁻²¹ solvent extraction²² and gas diffusion.²³ And FI techniques have been coupled to various detection systems apart from spectrophotometry with various benefit, such as radiometry,²⁴⁻²⁵ ion-chromatography,²⁶ conductometry²³ or even visual.¹³

The FI pretreatment may involve on-line pre-separation and pre-concentration^{15,18-21} or dilution.^{26,38} FIA also offers the possibility of a single standard calibration^{15,18-22} and on-line speciation.²⁷ Some procedures for speciation of Cr(VI) and Cr(III) using FIA have been reported.²⁸⁻³¹ Cr(VI) reacts with diphenylcarbazide (DPC) in-line to form a colored complex which is continuously monitored spectrophotometrically. Cr(III) is in-line converted to Cr(VI) by using Ce(IV). Total Cr can then be determined. The reported system was complicated due to the temperature control at 80°C (oil bath).²⁸ FI – ETAAS system with on-line sorbent column packed with C₁₈ was used for Cr(VI) by forming complex with diethyldithiocarbamate (DDTC). Cr(III) was oxidized by peroxydisulfate for total Cr.³¹

In this work, FI systems comprising simple and low cost components have been developed for speciation of Cr (VI) and Cr(III) by sequential

determination. Cr(VI) forms complex with DPC and is sorbed onto a C_{18} in-valve column. Cr(III) is in-line oxidized to Cr(VI) so that the total Cr can be determined. Optimization of conditions was investigated, and single standard calibration was studied.

MATERIALS AND METHODS

Reagents

All chemicals were analytical-reagent grade, except where otherwise stated and de-ionized water was used.

A stock standard Cr(VI) solution ($1000 \mu\text{g ml}^{-1}$) was prepared by dissolving potassium dichromate (Merck) (2.8288 g) in water and diluted to 1.00 l with water. A stock standard Cr(III) solution was prepared similarly from chromium(III) chloride hexahydrate (Merck) (5.1123 g). Other standard solutions were obtained by dilution of the stock solution with water.

Color reagent (DPC, 0.10 % (w/v)) was daily prepared by dissolving 1,5-diphenylcarbazide (Fluka) (1.0 g) in acetone (50 ml) and diluted to 1 l with nitric acid (1.0 M).

Oxidizing agent (Ce(IV) solution, 1.2 % (w/v)) was obtained from ammonium cerium(IV) sulfate dihydrate (Merck) (12.0 g) dissolved in sulfuric acid (0.3 M) and diluted to 1 l with the acid solution.

Flow Systems

Figs 1 (a) and (b) depict flow diagrams for the determination of Cr(VI) and the system for speciation of Cr(VI) and Cr(III) respectively.

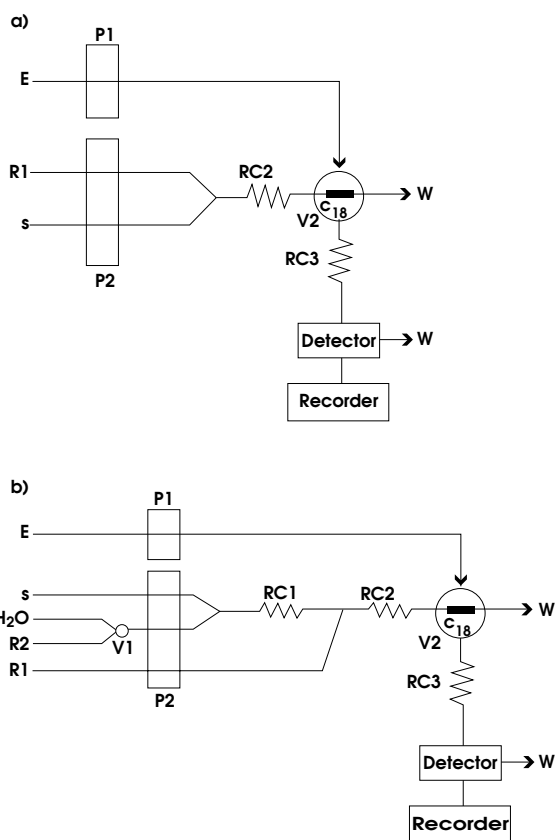


Fig 1. Flow diagrams of the systems for ; a) determination of Cr(VI) b) sequential determination of Cr(VI) and Cr(III) (P1,P2, peristaltic pumps; RC1, RC2 , RC3, reaction coils; R1, reagent (DPC in acid solution); R2, oxidizing reagent (Ce(IV) in sulfuric acid); V1, three way valve; V2, rotary injection valve; C_{18} , SPE column; S, standard / sample; E, eluent; W, waste).

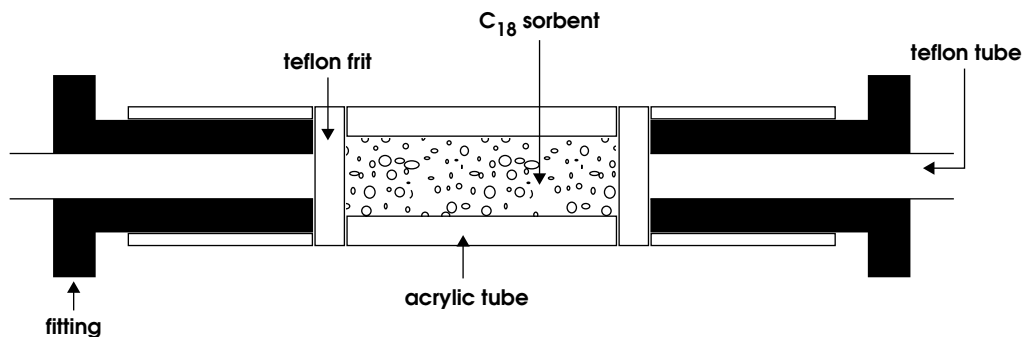


Fig 2. C_{18} SPE column (see text).

A stream of solution containing Cr (a standard or a sample) and a reagent were controlled by using a peristaltic pump (P2, FIALab-2000, Alitea). The complex formed passed through a column packed with C_{18} resin (Merck) which replaced the sample loop of an injection valve (FIALab-2000, Alitea), similarly to the one described earlier,²⁰ as represented in Fig 2. The Cr-complex adsorbed on the resin was desorbed by a stream of eluent (methanol solution) and controlled by a second peristaltic pump (P1, Eyela). Eluent flow was in the reverse direction of the loading (Fig 3) and passed a flow-through cell (30 ml, 1 cm path-length) located in a LED colorimeter (Ismatec) connected to a chart recorder (Phillip PM8521) for continuous monitoring. All the tubing used was teflon (0.8 mm id), apart from pump tubing was silicone rubber. Connections were with flexible sleeves and/or T- and Y-pieces.

Procedure

(a) Determination of Cr(VI)

Using the manifold in Fig 1(a), a solution containing Cr(VI) (standard or sample) is merged with the color agent (DPC). A color complex is formed during the passage of the mixing coil (RC2) and passes the C_{18} in-valve column for loading. By switching the injection valve (V2), to allow eluent (methanol solution) to pass through the column to desorb the Cr-complex, which then flows through another mixing coil (RC3) before reaching the detector. Calibration graph can be obtained by either conventional way (with a series of standard solutions of various concentrations) or using a single standard calibration.

(b) Sequential determination of Cr(VI) and Cr(III) for speciation

For this flow system (Fig 1(b)), using the three-way valve (V1), oxidizing agent (R2, Ce(IV)) is selected to flow and merged with a stream of standard/sample, Cr(III) in the stream is oxidized to Cr(VI) in the mixing coil (RC1). The stream now consisting of Cr(VI) converted from Cr(III) together with the Cr(VI) containing originally in the sample, flows further and is combined with the stream of color agent (R1, DPC) to form a color complex which is then adsorbed onto and desorbed from the C_{18} resin in the in-valve column as similarly described in the above section. The signal obtained corresponds to the sum of Cr(VI) and Cr(III). When switching the valve V1, to allow water to flow (instead of the R2 stream). The signal is due to Cr(VI) only. Concentration of Cr(III) alone can then be calculated from the difference.

RESULTS AND DISCUSSION

Preliminary studies

Color formation is based on the reaction of CrO_4^{2-} with 1,5-diphenylcarbazide (DPC) in an acidic solution. The CrO_4^{2-} is reduced to Cr(III) by the DPC which is, at the same time, oxidized to 1,5-diphenylcarbazone forming a red-violet complex with the Cr(III).^{32,33} Absorption spectrum of the complex in aqueous or methanol solution was measured. Maximum absorption was observed at 540 nm at which Ce(IV) and the Ce-DPC complex in the media exhibited minimum absorption.

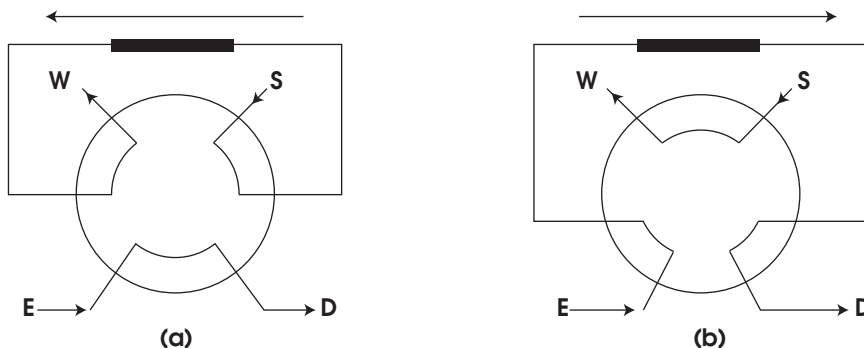


Fig 3 Positions of in-valve mini-column : a) loading and b) elution (E, eluent; D, detector; S, Cr(IV)-DPC; W, waste).

The system for determination of Cr(VI)

Optimization of the system

The parameters kept constant were : the color reagent (R2), 0.01 % (w/v) DPC in an acidic medium flowing at the same flow rate as the standard Cr(VI) solution (0.01-0.10 $\mu\text{g ml}^{-1}$); loading time, 60 s; mixing coils, 150 cm for RC2 and 75 cm for RC3; elution with 80 % (v/v) aqueous methanol at a flow rate of 3.5 ml min^{-1} . As for the effect of acidity of DPC solution, 1.0 M HNO_3 yielded a higher sensitivity than 1.0 M H_2SO_4 (from the calibration graphs: $y = 1855x + 2.41$, $r^2 = 0.995$ and $y = 1414x - 5.70$, $r^2 = 0.994$ obtained from each medium respectively). This agrees with a previous report [34].

The effect of the nitric acid concentration (0.10-1.5 M) of the DPC solution was examined further. 1.0 M HNO_3 gave the most sensitive calibration, with

low acid concentration being less sensitive. This indicates that the highly acidic medium needed for the oxidation of DPC by CrO_4^{2-} .^{32,33}

When DPC concentration was varied, 0.005, 0.01, 0.02, 0.03, 0.05 and 0.08 % (w/v), slopes of calibration graphs were 1832, 2087, 1940, 1832, 1826 and 1603 $\text{mV}/\mu\text{g ml}^{-1}$ respectively, 0.01 % (w/v) DPC resulting the highest slope, was then chosen for further studies. Figs 4 (a) and (b) show the effects of the lengths of the mixing coils, RC2 and RC3 respectively. The lengths of 150 and 30 cm for the RC2 and RC3 respectively were found to be suitable.

Peak heights were unchanged if the flow rates of DPC were kept in the range of 2.1-4.0 ml min^{-1} , but decreased at lower flow rates. The higher the flow rate of the Cr(VI) stream, the higher the peak heights (Fig 5). Leakage at connection was observed for flow rates of higher than 2.5 ml min^{-1} . So a flow rate of 2.5

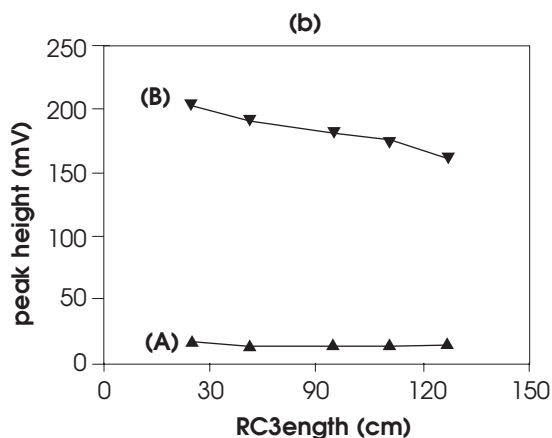
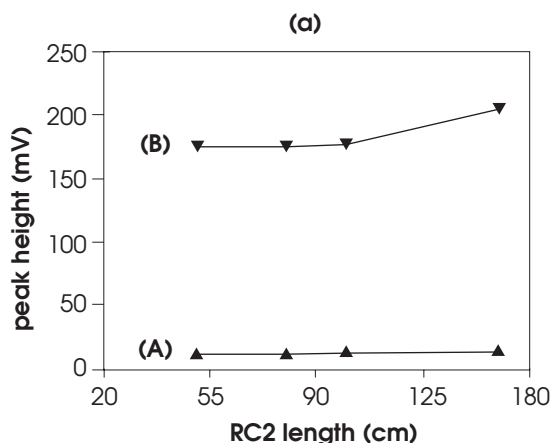


Fig 4 Effect of length of the mixing coils : (a) RC2 (the RC3 fixed at 50 cm) and (b) RC3 (the RC2 fixed at 150 cm); A) blank, B) 0.10 $\mu\text{g ml}^{-1}$ Cr(VI).

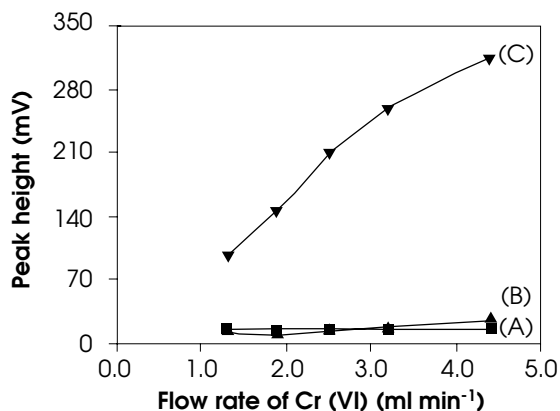


Fig 5. Effect of flow rate of Cr(VI) stream : Peak heights of (A) blank, (B) 0.01 and (C) 0.10 $\mu\text{g ml}^{-1}$. (both (A) and (B) with already blank subtraction).

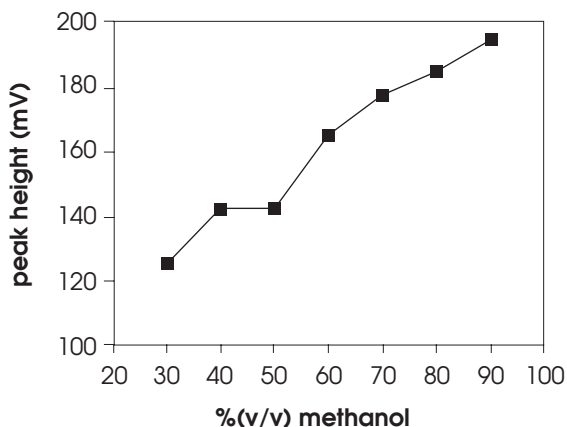


Fig 6. Effect of concentration of aqueous solution of methanol.

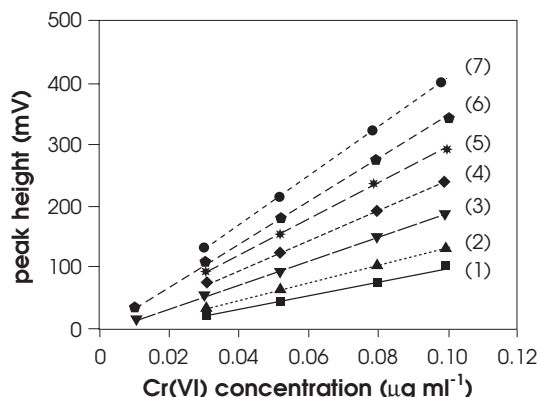


Fig 7. The calibration graph for determination of Cr(VI) (using the manifold in Fig 1(a)) different loading time; (1) 30, (2) 40, (3) 60, (4) 80, (5) 100, (6) 120 and (7) 150 s.

ml min⁻¹ was used for both the DPC and Cr(VI) stream by making use of the same pump. Constant peak heights were obtained for a flow rate of eluent (80% (v/v) aqueous solution of methanol) in the range of 3.4-4.0 ml min⁻¹. The lower flow rates led to longer elution and peak broadening. A flow rate of 3.4 ml min⁻¹ was chosen for elution. Fig 6 shows the effect of concentration of eluent. The higher methanol concentration, the higher the peaks but the concentrations of more than 90% (v/v) created more negative peaks due to Schlieren effect¹⁸ and may evolve air bubbles due to heat produced when methanol mixed with water. Elutions without quantitative recovery of Cr(IV) and/or peak broadening leading to much lower peaks were observed when methanol concentration was lower than 50% (v/v). Elution with 80% (v/v) methanol was appropriate. The optimum conditions are summarized in Table 1. Simplex optimization³⁵ was also applied and the same obtained conditions were found.

Single standard calibration

Using the optimum conditions (Table 1), a series of standards was loaded. A calibration graph was a plot of peak heights vs. different concentrations of Cr(VI) for the same loading time. Sensitivity (slope) of the plot was found to increase with loading time (Fig 7). For loading for 60 s, a detection limit (3s) was 0.02 µg ml⁻¹ (calculated from calibration data³⁶) and RSDs for 11 replicates were 11.6, 3.6 and 0.5% for 0.01, 0.05 and 0.10 µg ml⁻¹ Cr(VI) respectively. A single standard calibration was carried out by using a plot of µg Cr(VI) load, calculated from Cr(VI) solution concentration (C, mg ml⁻¹), loading flow rate (q, ml min⁻¹) and loading time (t, min) as follows: µg Cr(VI) = C.q.t., vs peak height. The plots were

Table 1. Optimum conditions for determination Cr(VI) (manifold in Fig 1 (a)).

Reagent (R1)	0.01% (w/v) DPC in 1.0 M HNO ₃
Flow rates : methanol	3.4 ml min ⁻¹
R1	2.5 ml min ⁻¹
standard/sample	2.5 ml min ⁻¹
C ₁₈ column	3.0 cm long, 3.0 mm id
Loading time on C ₁₈ SPE column	60 s
Mixing coil lengths :	RC2 150 cm
	RC3 30 cm
LED color of colorimeter	green
Sensitivity of recorder	500 mV
Chart speed of recorder	0.5 cm min ⁻¹

Table 2. The interference effects of various ions on the signal obtained from 0.05 µg ml⁻¹ Cr(VI).

Interference ions	Tolerable concentration ratio* (µg ml ⁻¹) of ion/Cr(VI)
Co ²⁺ , Ni ²⁺ , Pb ²⁺ , Mg ²⁺ , Cd ²⁺	4,000
Zn ²⁺	3,000
Fe ³⁺	2,000
Cr ³⁺ , Cu ²⁺	1,000
Fe ²⁺	3

* The concentration of an ion is considered to be interfering when causing a relative error of more than ±10% with respect to the signal of Cr(VI) alone.

found to be nonlinear. The height obtained depends not only on the Cr(VI) concentration but also on the loading time. Polynomial function was applied for the relationship:

$$\text{Peak height (mV)} = [95.77 + 34.25t - 0.06t^2] C - [17.18 - 0.20t + (7.21 \times 10^{-5})t^2].$$

Interference study

Using the optimum conditions, a 0.05 µg ml⁻¹ Cr(VI) standard solution containing the respective ion at appropriate concentrations were loaded onto the column for 60 s. Table 2 summarizes the concentration (µg ml⁻¹) ratios of potential interferences to Cr(VI) which were examined.

Sequential determination of Cr(VI) and Cr(III) for speciation

Optimization of FI condition

Using the manifold in Fig 1(b), optimization was investigated by preconcentrating for 60 s on the resin column a series of standard solutions (0.01 to 0.25

ml ml⁻¹ (Cr(VI) and/or Cr(III))). Various parameters of the manifold adjusted over the following ranges: HNO₃, 0.1-1.2 M; DPC, 0.01-0.10 % (w/v); H₂SO₄ in 1.2% (w/v) Ce(IV), 0.1-0.3 M; length of mixing coil, RC1 80-150 cm, RC2 50-200 cm, RC3 60-100 cm. It was found that 0.1% (w/v) DPC in 1.0 M HNO₃ was the most appropriate. Concentration of DPC used for this manifold condition was higher than that for the previous manifold set-up (Fig.1(a)), due to dilution effect occurring in a manifold with more lines. 1.0 M HNO₃ still provided sufficient acidity for color formation. For the oxidation of Cr(III), 1.2 % (w/v) Ce(IV) in 0.3 M H₂SO₄ was suitable. The lower the acid concentration, the higher the blank signal. At higher acid concentration, lower peaks were observed. This could possibly be due to the increase in sulfate concentration exhibiting its forming complex with Cr(III) and inhibiting the oxidation of free Cr(III) by Ce(IV) [34]. The mixing coils, RC1, RC2 and RC3 of 120, 130 and 60 cm in length respectively were found to be suitable. Using a series of standard solutions of Cr(VI) and Cr(III), and varying flow rates of the 3 lines (R1(DPC), R2(Ce(IV)) and S(standard)): 1.6, 1.6 and 1.6; 1.6, 0.7 and 1.6; 2.0, 1.2, and 2.0; 1.8, 1.2 and 1.8 ml min⁻¹ respectively, respective calibrations were obtained as follows: for Cr(VI), $y(VI) = 606.8x - 1.57$, $y(VI) = 690.9x + 3.43$, $y(VI) = 833.7x + 4.55$, $y(VI) = 758.4x + 3.89$ and for Cr(III), $y(III) = 512.3x - 9.38$, $y(III) = 682.6x - 13.7$, $y(III) = 757.4x - 10.13$, $y(III) = 740.4x - 25.39$. Ratios of the slopes of the calibrations of Cr(III) and Cr(VI) for the above conditions are 0.84, 0.98, 0.91 and 0.98 respectively. Cr(III) is thus practically quantitatively converted to Cr(VI) for the last 3 conditions as indicated by the slope ratios near unity. Using 0.25 ml ml⁻¹ of Cr(VI) standard solution, elution from the column was examined at various flow rates (2.1, 2.8, 3.6 4.0, 4.4 5.2 and 5.6 ml min⁻¹). Peak heights (subtracted for blank) and the blank values (both in mV) were 293, 308, 313, 295, 295, 310, 320 and 18, 18, 20, 20, 25, 25, 28, respectively, while analysis time (min/peak) was 3.3, 3.0, 2.4, 2.3, 2.0, 1.9, 1.8, respectively. An eluent flow rate of 4.4 ml min⁻¹ was then chosen as being optimum.

Table 3 summarizes the optimum conditions.

Calibrations for sequential determination of Cr(VI) and Cr(III).

Employing the optimum conditions (Table 3), two sets (Cr(VI) and Cr(III)) of standard solutions (0.01-0.25 mg ml⁻¹ Cr(VI), Cr(III)) were measured. For the first calibration graph (Cr(VI) standards with

Table 3. Optimum conditions for the sequential determination of Cr(VI) and Cr(III) (manifold in Fig 1 (b)).

Reagent	R1	0.1%(w/v) DPC in 1.0 M HNO ₃
	R2	1.2%(w/v) Ce(IV) in 0.3 M H ₂ SO ₄
Flow rate :	Methanol	4.4 ml min ⁻¹
	R1	1.8 ml min ⁻¹
	R2	1.2 ml min ⁻¹
	Standard /sample	1.8 ml min ⁻¹
Loading time on C ₁₈ column		60 s
Mixing coil length:	RC1	120 cm
	RC2	130 cm
	RC3	60 cm
LED color of colorimeter		green
Recorder sensitivity		500 mV
Chart speed		0.5 cm min ⁻¹

reference to H₂O) the valve V1 (Fig 1(b)) was switched for the H₂O stream. For the second calibration graph (Cr(VI) standards with reference to Ce(IV)), the valve V1 was selected to allow the Ce(IV) solution (R2) to flow. And for the third calibration (Cr(III) standards with reference to Ce(IV)), similar to the second calibration graph but using Cr(III) standards.

All the 3 linear calibrations are expressed respectively as follows:

$$y_1 = 1300 x_1 - 11.35, r = 0.999 \dots (1)$$

$$y_2 = 602 x_2 - 2.37, r = 0.996 \dots (2)$$

$$\text{and } y_3 = 603 x_3 - 0.54, r = 0.997 \dots (3)$$

where x_1, x_2, x_3 and y_1, y_2, y_3 refer to concentrations and peak heights for the above 3 conditions respectively.

Equations (2) and (3) indicate quantitative oxidation of Cr(III) to Cr(VI).

A sample to be determined for Cr(VI) and Cr(III) would replace the stream of standard. A peak height (PH1, mV) obtained by using the condition for the equation (1) leads to the Cr(VI) content: [Cr(VI), $\mu\text{g ml}^{-1}$] = (PH1 + 11.35)/1300, while a peak height (PH2) obtained by the condition used for the equation (3) represents the total content [Cr, tot] of Cr: [Cr, tot] = (PH2 + 0.54)/603. Hence, [Cr(III)] = [Cr, tot] - [Cr(VI)].

Speciation of Cr(VI) and Cr(III) for samples

Waste water samples taken from industrial areas without any sample pretreatment but cooled in 4 °C were analyzed for Cr(VI) and Cr(III) by using the above proposed procedure. Results obtained by the FIA method agreed well with those obtained by ICP-AES procedure³⁷ (Table 4). Comparative linear

Table 4. Comparison of determination of industrial waste water samples for speciation of Cr(VI) and Cr(III) by FIA and ICP-AES^(a) methods.

Sample No.	Cr(VI) ($\mu\text{g ml}^{-1}$)		Cr(III) ($\mu\text{g ml}^{-1}$)	
	FIA	CP	FIA	ICP
1	0.50	0.54	0.80	0.76
2	0.70	0.69	1.20	1.12
3	0.50	0.49	0.55	0.54
4	0.75	0.73	0.75	0.82
5	1.05	1.11	0.90	0.80
6	1.10	1.12	1.00	0.83
7	0.40	0.43	0.90	0.88
8	0.35	0.34	0.75	0.73
9	0.40	0.40	0.65	0.64
10	0.55	0.53	0.90	0.86
11	0.35	0.36	0.75	0.77
12	0.50	0.50	0.70	0.66

^(a) analyzed at the Department of Mineral Resources, Ministry of Industry using the procedure described in³⁷

regressions of all the above ICP-AES (x) versus FIA (y) values for Cr(VI) and Cr(III) are: $y = 1.1x + 0.0$, $r = 0.99$ and $y = 0.9x + 0.1$, $r = 0.97$ respectively.

CONCLUSION

FI spectrophotometric determination of Cr(VI) and Cr(III) using 1,5-diphenylcarbazine and solid phase extraction with C_{18} in-valve mini-column has been developed. The FI systems assembled with simple and easily available components can also perform on-line pre-separation and preconcentration. Single standard calibration is possible. The proposed method for sequential determination of Cr(VI) and Cr(III) leads to speciation of the species by using an inexpensive instrument, and with in-line oxidation process. The method has been applied to waste water samples taken from industries in Thailand.

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