

# Selective Spectrophotometric Determination of Trace Amounts of Chromium(VI) Using a Flow Injection System With a Microcolumn of Zirconium(IV) Oxide Modified Silica Gel

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Zirconium(IV) oxide coated on a silica gel surface was found to be very effective for extracting Cr<sup>VI</sup> from aqueous solutions at a pH of about 3. A microcolumn packed with this material was inserted into a flow injection system for the separation and preconcentration of Cr<sup>VI</sup>. By this process, a concentration level of 2 ppb was detected with a relative standard deviation of 2.4%. Because of the high selectivity of the immobilized substrate, it was possible to determine Cr<sup>VI</sup> in the presence of larger amounts of other ions. The analysis was also carried out on natural water spiked with Cr<sup>VI</sup>, and compared with a standard method.

**Keywords:** Zirconium(IV) oxide modified silica; silica gel surface coated with zirconium(IV) oxide; chromium(VI) separation; flow injection determination of chromium(VI)

Extraction of Cr<sup>VI</sup> from solution by using an organic ion-exchange resin is a very well-known method. However, a worsening of the sorption characteristics is observed under multi-cyclic operating conditions owing to the partial oxidation of the matrix by the sorbate. Consequently, it is more appropriate in this instance to find a sorbent based on an inorganic matrix having high stability towards the action of oxidants and exhibiting anion-exchange properties.<sup>1</sup>

In recent work, the use of zirconium(IV) oxide coated on a silica gel surface as a selective sorbent for Cr<sup>VI</sup> was described.<sup>2</sup> In this instance, the substrate and the matrix are very resistant towards oxidation; moreover, the metal oxide was not detached from the surface under multi-cyclic operation.

In general, hydrated metal oxides, obtained by a precipitation process, are normally fine powders with low mechanical resistance and, in most instances, are not useful as packing materials for column chromatography.<sup>3-5</sup> The utilization of a matrix coated with an ion-exchanger substrate could constitute an advantage, because, in the chemically modified solid, the characteristics of the original silica matrix such as rigidity, specific surface area and the average diameter of the pores are not affected.<sup>6</sup>

In the present study, a selective method is reported, involving on-line separation and preconcentration of Cr<sup>VI</sup> in a microcolumn packed with zirconium(IV) oxide coated on a silica gel surface inserted into a flow injection (FI) system. The determination of Cr<sup>VI</sup> at very low concentration levels in water is described.

## Experimental

### Preparation of Chemically Modified Silica

Silica gel having an average pore diameter of 0.60 nm and a specific surface area,  $S_{\text{BET}}$ , of 500 m<sup>2</sup> g<sup>-1</sup> was previously dried at 423 K under vacuum (0.13 Pa) before use. About 50 g of the activated silica were added to a solution containing 11.6 g (0.05 mol) of pure ZrCl<sub>4</sub> dissolved in 300 cm<sup>3</sup> of anhydrous ethanol. The mixture was heated under reflux for 8 h under a dry nitrogen atmosphere, and the resulting solid was washed by decantation and then heated at 400 K to eliminate the solvent. This dry material was hydrolysed by immersing it in de-mineralized water. The solid was washed with water to remove all the Cl<sup>-</sup> and then dried in an oven at 393 K for 5 h. The amount of Zr attached on the surface was determined by X-ray fluorescence analysis and yielded ZrO<sub>2</sub> = 3.25%.

### Preparation of Solutions

*Solution of 1,5-diphenylcarbazide (DPC).* Prepared by dissolving 0.25 g of DPC (Merck) in 20 cm<sup>3</sup> of acetone and diluting the solution to 500 cm<sup>3</sup> with de-mineralized water.

*Stock solution of Cr<sup>VI</sup> (1000 µg cm<sup>-3</sup>).* Prepared by dissolving 2.829 g of previously dried K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (Merck) in 1000 cm<sup>3</sup> of water.

*Solution of tris(hydroxymethyl)methylamine (THAM) (0.1 mol dm<sup>-3</sup>).* Prepared by dissolving 12.1 g of the substance in 1000 cm<sup>3</sup> of de-mineralized water.

### Adsorption Isotherm

The adsorption isotherm of Cr<sup>VI</sup> obtained from an aqueous solution by using the chemically modified silica was measured at 298 K. The batch technique was used.

Solutions (50 cm<sup>3</sup>) containing 4.00 × 10<sup>-4</sup> mol dm<sup>-3</sup> Cr<sup>VI</sup>, the initial pH values of which were adjusted to between 1.0 and 8.0 with HCl or NaOH, were shaken in a flask with 0.2 g of the sorbent material for 30 min. The pH of the supernatant solution in equilibrium with the solid phase in each flask was measured.

The amount of Cr<sup>VI</sup> adsorbed by the solid was calculated by applying the equation:

$$N_f = (N_a - N_s)/m$$

where  $N_a$  is the number of moles of Cr<sup>VI</sup> added,  $N_s$  is the number of moles of Cr<sup>VI</sup> in the solution phase in equilibrium with the solid phase, and  $m$  is the mass of the solid phase.

The distribution coefficient,  $D$ , was calculated from the equation:

$$D = N_f/c$$

where  $c$  is the concentration of Cr<sup>VI</sup> in the solution phase in equilibrium with the solid phase.

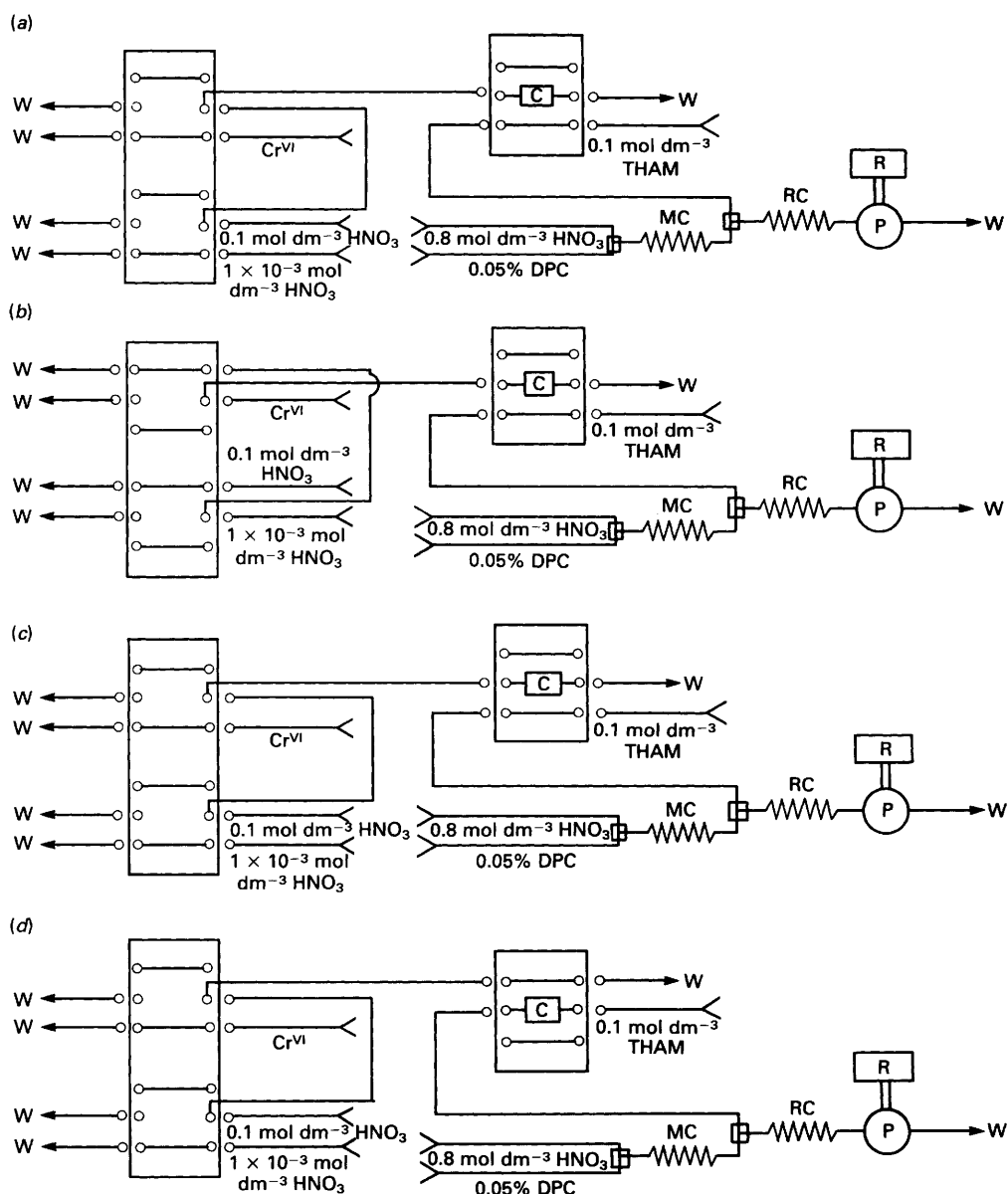
### Flow Injection

The FI configuration used is shown in Fig. 1. Two injectors were used, one for addition of Cr<sup>VI</sup> and another for addition of eluent (THAM). Time-controlled injections of the samples were used.

The microcolumn C (length, 2 cm; i.d., 0.3 cm) was packed with the sorbent material (about 50 mg). The operation of the FI system was carried out in four steps.

1. *Activation:* 0.1 mol dm<sup>-3</sup> HNO<sub>3</sub> was passed through the column at a flow rate of 1.7 cm<sup>3</sup> min<sup>-1</sup> for 20 s.

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**Fig. 1** Flow injection configurations: (a) activation; (b) injection; (c) washing; and (d) elution. W, Waste; MC, mixing coil; RC, reaction coil; C, microcolumn; P, spectrophotometer; and R, recorder

2. *Injection of Cr<sup>VI</sup>*: a Cr<sup>VI</sup> solution (pH 3) was passed through the column at a flow rate of  $3.4 \text{ cm}^3 \text{ min}^{-1}$  for a pre-determined time (1–6 min).

3. *Washing*: the column was washed with  $1 \times 10^{-3} \text{ mol dm}^{-3}$  HCl at a flow rate of  $2 \text{ cm}^3 \text{ min}^{-1}$  for 10 s.

4. *Elution*: Cr<sup>VI</sup> was eluted from column C in a reversed flow with  $0.1 \text{ mol dm}^{-3}$  THAM at a flow rate of  $2 \text{ cm}^3 \text{ min}^{-1}$ . A solution of DPC (0.05% m/v) was previously mixed in MC (Fig. 1) with  $0.8 \text{ mol dm}^{-3}$  HNO<sub>3</sub>. The resulting solution was allowed to react in RC with Cr<sup>VI</sup> carried by the THAM solution. The absorbance of the complex formed was measured at 540 nm in the spectrophotometer P, and the signal was recorded at R.

#### Interference Study

Stock solutions ( $1000 \mu\text{g cm}^{-3}$ ) of Cr<sup>3+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, Fe<sup>3+</sup>, Ce<sup>3+</sup>, Ce<sup>4+</sup>, Mo<sup>6+</sup>, V<sup>5+</sup>, SO<sub>4</sub><sup>2-</sup>, MnO<sub>4</sub><sup>-</sup> and PO<sub>4</sub><sup>3-</sup> were prepared for interference studies. An appropriate aliquot of each of these stock solutions was added to the Cr<sup>VI</sup>

solution ( $0.1 \mu\text{g cm}^{-3}$ ), and the resulting mixtures were analysed in the FI system as described above.

#### Chromium(vi) in Natural Water

Samples of natural water were collected from a lake on the university campus, and to each sample was added a few drops of concentrated HNO<sub>3</sub> to bring the pH of the solution to about 3. Each solution was allowed to stand overnight and then passed through a fine pore filter of  $0.45 \mu\text{m}$ . The determination of Cr<sup>VI</sup> was carried out as described above.

## Results and Discussion

#### Characteristics of the Material

Hydrated zirconium(IV) oxide adsorbs either cations or anions, depending on the solution pH. At low pH, anion exchange can occur by a mechanism in which OH<sup>-</sup> is displaced from the surface of the solid phase.<sup>1,7</sup> For zirconium(IV) oxide

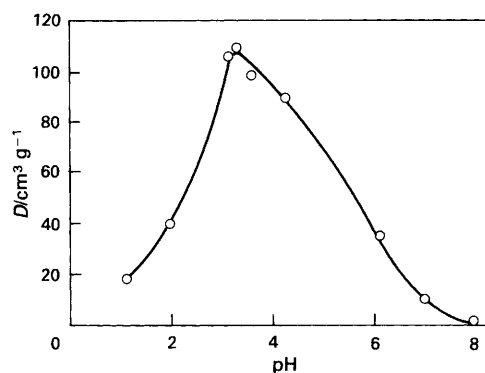


Fig. 2 Plot of distribution coefficient ( $D$ ) of  $\text{Cr}^{\text{VI}}$  versus pH of the solution.  $[\text{Cr}^{\text{VI}}] = 4.00 \times 10^{-4} \text{ mol dm}^{-3}$

Table 1 Calibration graph for  $\text{Cr}^{\text{VI}}$  with use of zirconium(IV) oxide coated on a silica gel surface as sorbent

| Injection time/s | Volume injected/ $\text{cm}^3$ | Mass of $\text{Cr}^{\text{VI}}/\mu\text{g}$ | Absorbance |
|------------------|--------------------------------|---|------------|
| 10               | 0.666                          | 0.0333                                      | 0.028      |
| 40               | 2.67                           | 0.133                                       | 0.119      |
| 70               | 4.67                           | 0.233                                       | 0.201      |
| 100              | 6.67                           | 0.333                                       | 0.275      |

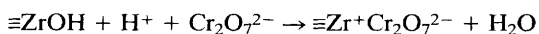
Table 2. Relative standard deviation in the determination of  $\text{Cr}^{\text{VI}}$ . Number of injections = 10 in each instance

| Time/s* | $\text{Cr}^{\text{VI}}$ concentration (ppb) | RSD (%) |
|---------|---|---------|
| 500     | 2   | 2.4     |
| 200     | 10  | 1.8     |
| 60      | 30  | 1.6     |
| 40      | 50  | 1.2     |

\* Flow rate:  $3.2 \text{ cm}^3 \text{ min}^{-1}$ .

coated on the silica surface, the exchange property of the immobilized substrate was preserved.

In Fig. 2, the distribution coefficient ( $D$ ) for  $\text{Cr}^{\text{VI}}$  is plotted against the solution pH. The maximum exchange capacity achieved by the material was  $80 \times 10^{-6} \text{ mol g}^{-1}$  at pH 3. The change of  $D$  with solution pH can be explained by the following reaction:<sup>1,7</sup>



where  $\equiv\text{ZrOH}$  denotes the metal oxide attached to the silica surface. At higher pH, the reaction is shifted towards the left-hand side whereas at lower pH ( $<3$ ), the competition reaction between  $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{Cl}^-$  (introduced as hydrochloric acid to adjust the solution pH) becomes significant. At pH 2, the concentration ratio  $[\text{Cl}^-]:[\text{Cr}_2\text{O}_7^{2-}] \approx 160$ .

### FI Experiments

In the FI experiments the microcolumn C (Fig. 1) packed with the sorbent was, in each complete cycle of operation, loaded with  $\text{Cr}^{\text{VI}}$  at a solution pH of 3, and elution was effected with THAM solution at pH 8–9. Under such conditions, the sorption and desorption operations could be repeated many times without any change in the exchange properties of the material. A  $0.1 \text{ mol dm}^{-3}$  NaOH solution was also used as an eluent, but, in this instance, after a few operations, the packing material showed changes in its sorption capacity. An attack of the surface by the strong alkali used was observed.

In order to test the possibility of using the material for the determination of  $\text{Cr}^{\text{VI}}$ , a 50 ppb solution of the ion was injected into the column at different times (from 10 to 100 s). The absorbance of the  $\text{Cr}^{\text{VI}}$ -DPC complex eluted from the column

Table 3 Interference study on the adsorption of  $\text{Cr}^{\text{VI}}$  by zirconium(IV) oxide coated on a silica gel surface

| Ion                      | Added as                                  | Concentration (ppm) | Interference factor |
|--------------------------|---|---------------------|---------------------|
| $\text{Cr}^{\text{III}}$ | $\text{Cr}(\text{NO}_3)_3$                | 5                   | 1.00                |
| $\text{Hg}^{\text{II}}$  | $\text{HgCl}_2$                           | 5                   | 0.98                |
| $\text{Mn}^{\text{II}}$  | $\text{MnCl}_2$                           | 5                   | 0.98                |
| $\text{Cu}^{\text{II}}$  | $\text{CuCl}_2$                           | 5                   | 1.02                |
| $\text{Fe}^{\text{III}}$ | $\text{FeCl}_3$                           | 1                   | 0.98                |
|                          |   | 2                   | 0.96                |
|                          |   | 3                   | 0.93                |
| $\text{Ce}^{\text{III}}$ | $\text{CeCl}_3$                           | 5                   | 1.01                |
| $\text{Ce}^{\text{IV}}$  | $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$ | 0.1                 | 0.93                |
|                          |   | 0.5                 | —                   |
| $\text{Mo}^{\text{VI}}$  | $\text{Na}_2\text{MoO}_4$                 | 0.1                 | 1.00                |
|                          |   | 1                   | 0.89                |
| $\text{V}^{\text{V}}$    | $\text{NH}_4\text{VO}_3$                  | 1                   | 0.97                |
|                          |   | 3                   | 1.01                |
|                          |   | 5                   | 1.04                |
| $\text{SO}_4^{2-}$       | $\text{H}_2\text{SO}_4$                   | 0.1                 | 0.94                |
|                          |   | 0.5                 | 0.92                |
|                          |   | 1                   | 0.83                |
| $\text{MnO}_4^-$         | $\text{KMnO}_4$                           | 1                   | 0.99                |
|                          |   | 5                   | 0.89                |
| $\text{PO}_4^{3-}$       | $\text{Na}_2\text{HPO}_4$                 | 0.01                | 0.98                |
|                          |   | 0.05                | 0.94                |
|                          |   | 0.1                 | 0.83                |
|                          |   | 1                   | 0.84                |

Table 4 Comparison of the results obtained for the analysis of natural water spiked with  $\text{Cr}^{\text{VI}}$

| Sample No. | $\text{Cr}^{\text{VI}}$ (ppm) |           |
|------------|-------------------------------|-----------|
|            | DPC method                    | FI method |
| 1          | 0.20                          | 0.18      |
| 2          | 0.13                          | 0.12      |
| 3          | 0.055                         | 0.050     |

was plotted against the mass of  $\text{Cr}^{\text{VI}}$  (data in Table 1). A linear relationship [ $A = 0.0049 + 0.823 (\text{Cr}^{\text{VI}})$ ; ( $\text{Cr}^{\text{VI}}$  mass in micrograms)], with a correlation coefficient ( $r$ ) of 0.999, was obtained.

The precision of the method for different  $\text{Cr}^{\text{VI}}$  concentrations was obtained by carrying out ten replicate measurements for each solution. Solution concentrations ranging from 2 to 50 ppb were injected into the column at a flow rate of  $3.2 \text{ cm}^3 \text{ s}^{-1}$ . The results are presented in Table 2. The values of the relative standard deviation (RSD) are reasonable in comparison with the results obtained with other methods for determining  $\text{Cr}^{\text{VI}}$  at approximately the same concentration level, e.g., by using electrothermal atomic absorption spectrometry.<sup>8,9</sup>

### Interference Study

The interference study was carried out by passing a binary mixture of 0.1 ppm  $\text{Cr}^{\text{VI}}$  and the interferent ion, in variable concentrations, through the column. The results are presented in Table 3. The interference factor, listed in the last column, was calculated from the ratio of the absorbance of the  $\text{Cr}^{\text{VI}}$  and interferent binary solution to that of the pure solution of  $\text{Cr}^{\text{VI}}$ . The interference of cations was studied for  $\text{Cr}^{3+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Ce}^{3+}$  until a ratio of  $[\text{interferent}]:[\text{Cr}^{\text{VI}}] = 50:1$  was reached. For  $\text{Ce}^{4+}$  and  $\text{Fe}^{3+}$ , for which the tendency to hydrolyse is greater,<sup>10</sup> the interference factor was considerably higher, mainly for the former ion.

The interference of anions was more significant because, at a solution pH of 3, the solid surface was positively charged and hence acted as an anion exchanger. Greater interference was observed for  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ , confirming the previous

observations reported by Boichinova and Tsaikov.<sup>11</sup> A high affinity for these two anions by the hydrated zirconium(IV) oxide was described.

### Chromium(VI) in Natural Water

In order to determine the amount of Cr<sup>VI</sup>, the solution was adjusted to pH 3 and then subjected to analysis in the FI system as described under Experimental. However, in the water sample collected, no Cr<sup>VI</sup> was detected (less than 2 ppb).

In order to determine the reliability of the process, the determination of Cr<sup>VI</sup> was also carried out directly in the sample, without prior separation and preconcentration, with use of DPC as the reagent. However, as the limit of detection with this reagent was 50 ppb, the samples of natural water were spiked with Cr<sup>VI</sup>. After allowing the solutions to stand overnight, the amounts of Cr<sup>VI</sup> in the solutions were determined by spectrophotometry. The same sample was also analysed by the FI technique as described previously. The results are summarized in Table 4.

The agreement between the results obtained by the two procedures is very reasonable and indicates that the material can be used for the determination of Cr<sup>VI</sup> in natural water.

### Conclusions

The high selectivity shown by zirconium(IV) oxide coated on a silica gel surface towards Cr<sup>VI</sup> represents a considerable improvement in the determination of this species in comparison with the previously described method.<sup>12-14</sup> With this methodology for the separation of Cr<sup>VI</sup>, most of the common ions usually present in water samples did not interfere. However, higher concentrations of SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> interacted with the column material, resulting in an incomplete separation of Cr<sup>VI</sup>.

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