

# On-line Oxidation of Cr(III) to Cr(VI) for Use with the Flow Injection Analysis Technique

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An on-line procedure for the oxidation of Cr(III) to Cr(VI) was developed. The extent of oxidation was followed using the 1,5-diphenylcarbazide (DPC) spectrophotometric method accommodated in a flow injection analysis (FIA) system. Cerium(IV) sulphate and potassium peroxydisulphate were tested as oxidising agents. Despite the high oxidation power of the peroxydisulphate ion in acidic solution, the use of Ce(IV) is more convenient under dynamic conditions. The best experimental conditions were obtained at 45 °C using a 0.025% *m/V* Ce(IV) solution in 0.07 M H<sub>2</sub>SO<sub>4</sub> with the Cr(III) solutions containing up to  $3.0 \times 10^{-2}$  M H<sub>2</sub>SO<sub>4</sub>.

**Keywords:** On-line oxidation; flow injection analysis; Cr(III) oxidation

The spectrophotometric determination of total chromium requires an oxidation step prior to the absorbance measurement. The procedure usually adopted involves the oxidation of Cr(III) to Cr(VI) with permanganate<sup>1,2</sup> or with Ag<sup>+</sup> catalysed peroxydisulphate (persulphate).<sup>2-4</sup> In the conventional analytical procedure an excess of permanganate is decomposed by reduction with azide or by precipitation as hydrous MnO<sub>2</sub>,<sup>2</sup> while an excess of peroxydisulphate can be decomposed by boiling the solution<sup>4</sup> or by reduction with azide.<sup>2</sup>

Considering the great analytical interest in the speciation of chromium,<sup>5</sup> the development of an inexpensive, on-line procedure for the oxidation of trace amounts of chromium should be both desirable and very useful. This would permit the use of continuous flow analysis systems in speciation studies. This paper shows that such an oxidation reaction can be followed using the flow injection analysis (FIA) approach, employing the highly sensitive and selective 1,5-diphenylcarbazide (DPC) spectrophotometric method.<sup>6,7</sup>

As permanganate absorbs near the  $\lambda_{\max}$  of the Cr - DPC complex, it cannot be used directly as an oxidising agent for chromium(III) in the proposed FIA procedure. Therefore, Ce(IV) and peroxydisulphate ions were tested as possible on-line oxidants. We found that Ce(IV) was more efficient under the experimental conditions of FIA in spite of the high oxidising power of peroxydisulphate in aqueous acidic solution.<sup>3,4</sup>

## Experimental

### Reagents

Analytical-reagent grade chemicals and de-ionised water were used to prepare all solutions, which were stored in high-density polyethylene bottles.

**Stock standard Cr(III) solution,** 1000  $\mu\text{g ml}^{-1}$ . Prepared by reduction of 2.829 g of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (G. Frederick Smith Chemical Co., 100% purity certified) with 3.5 g of sodium hydrogen sulphite (Fisher) in 2.6% *V/V* sulphuric acid (Merck). The mixture was heated to dryness and the residual solid was quantitatively transferred into a 1-l calibrated flask to which sufficient sulphuric acid was added to obtain a final analytical concentration of 0.10 M. Except where stated otherwise, working solutions were prepared daily by dilution of aliquots taken from the stock solution.

**Stock Ce(IV) solution,** 0.25% *m/V*. Prepared by dissolving 1.25 g of cerium(IV) sulphate (Carlo Erba) in sufficient concentrated sulphuric acid to obtain a final concentration of 0.20 M on completing the volume to 500 ml. This solution is stable for several weeks.<sup>8</sup> Except when previously stated,

working solutions of Ce(IV) were prepared by dilution of aliquots taken from the stock solution, adding enough sulphuric acid to obtain a final analytical concentration of 0.07 M. This procedure prevents the hydrolysis of Ce(IV).

**Potassium peroxydisulphate solution,** 2.5% *m/V*. Prepared daily by dissolving 25.0 g of potassium peroxydisulphate (Merck) in 1 l of  $2.5 \times 10^{-3}$ % *m/V* silver nitrate solution.

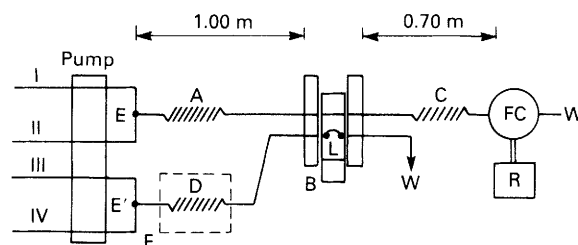
Nitric acid, sulphuric acid and DPC solutions used for optimum colour development were prepared as previously described.<sup>7</sup>

### Experimental Conditions

The FIA arrangement used to follow the on-line oxidation of Cr(III) is shown in Fig. 1. An oxidation line has been added to the configuration previously reported,<sup>6,7</sup> in which Cr(III) is oxidised to Cr(VI) prior to injection of the sample into the main FIA reaction line. The oxidation coil is immersed in a thermostated bath (Ultra Thermostat MTA KUTESZ, Model 606) in which the temperature of oxidation was controlled to within  $\pm 0.1$  °C. The reagents and the sample were pumped at a flow-rate of 1.2 ml min<sup>-1</sup> using an Ismatec Mini-S 840 peristaltic pump and Tygon peristaltic pump tubing (Technicon). Polyethylene tubing (i.d. 0.8 mm) was used for the oxidation, mixing and reaction coils. The absorbance measurements were made in a Zeiss PM 2A spectrophotometer at 540 nm, using an 80- $\mu\text{l}$  Zeiss flow cell (optical path length 10 mm).

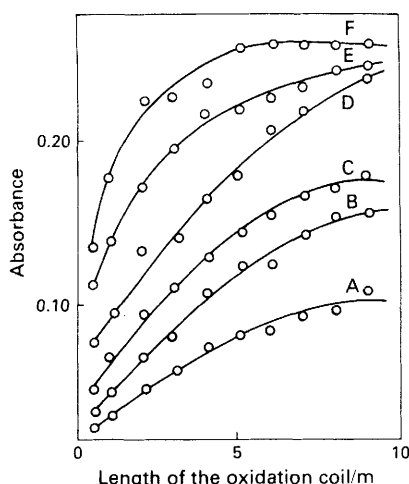
## Results and Discussion

Screening experiments on the on-line oxidation of Cr(III) to Cr(VI) were carried out using the FIA arrangement shown in Fig. 1. The effect of the length of the oxidation coil and the

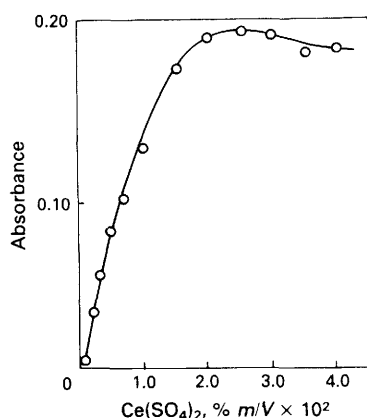


**Fig. 1.** FIA system used for the on-line oxidation of Cr(III). A, Mixing coil, length 1.0 m; B, proportional injector; C, reaction coil, length 0.7 m; D, oxidation coil, length variable (see text); E and E', confluence points; F, thermostatic bath, temperature variable (see text); L, injection loop; W, waste; FC, spectrophotometric flow cell. I, 0.80 M HNO<sub>3</sub> or 0.80 M H<sub>2</sub>SO<sub>4</sub> (see text); II, 0.05% *m/V* DPC; III, Cr(III) or Cr(VI); and IV, 0.025% *m/V* Ce(SO<sub>4</sub>)<sub>2</sub> or 2.50% *m/V* K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in  $2.5 \times 10^{-3}$ % *m/V* AgNO<sub>3</sub> or Cr(VI) or water

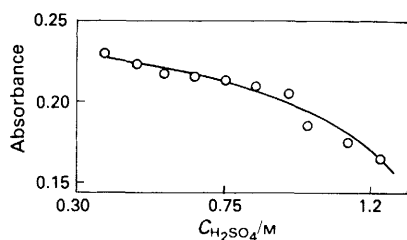
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**Fig. 2.** Oxidation of Cr(III) with Ce(IV): variation of the measured absorbance with length of oxidation coil and temperature of oxidation. Cr(III),  $3.0 \mu\text{g ml}^{-1}$ ;  $\text{Ce}(\text{SO}_4)_2$ ,  $0.01\% \text{ m/V}$  in  $0.10 \text{ M H}_2\text{SO}_4$ ; volume injected,  $77 \mu\text{l}$ . A,  $35^\circ\text{C}$ ; B,  $40^\circ\text{C}$ ; C,  $45^\circ\text{C}$ ; D,  $50^\circ\text{C}$ ; E,  $55^\circ\text{C}$ ; and F,  $60^\circ\text{C}$



**Fig. 3.** Oxidation of Cr(III) with Ce(IV): effect of Ce(IV) concentration on the measured absorbance of the complex Cr - DPC. Cr(III),  $3.0 \mu\text{g ml}^{-1}$ ; Ce(IV) solution, in  $1.0 \text{ M H}_2\text{SO}_4$ ; length of the oxidation coil,  $2.0 \text{ m}$ ; temperature of oxidation,  $45^\circ\text{C}$ ; and volume injected,  $77 \mu\text{l}$



**Fig. 4.** Oxidation of Cr(III) with Ce(IV): variation of the measured absorbance with analytical concentration of sulphuric acid in the Ce(IV) solution. Cr(III),  $3.0 \mu\text{g ml}^{-1}$ ;  $\text{Ce}(\text{SO}_4)_2$ ,  $0.025\% \text{ m/V}$  in  $\text{H}_2\text{SO}_4$ ; length of oxidation coil,  $2.0 \text{ m}$ ; temperature of oxidation,  $45^\circ\text{C}$ ; and volume injected,  $77 \mu\text{l}$

influence of temperature on the extent of the oxidation reaction can be followed by the variation in absorbance shown in Fig. 2. Although the oxidation yield increases with increasing temperature, at temperatures higher than  $45^\circ\text{C}$  bubbles are formed in the oxidation coil, particularly when longer coils are used. As the presence of bubbles interferes with the spectrophotometric detection, we fixed  $45^\circ\text{C}$  as the limiting working temperature for the on-line oxidation of Cr(III) by Ce(IV).

As shown in Fig. 3, the concentration of the Ce(IV) solution used in confluence with the chromium solution also has an important influence on the over-all on-line oxidation process. This observation seems to be consistent with the rate law  $d[\text{Cr}(\text{VI})]/dt = k[\text{Ce}(\text{IV})]^2[\text{Cr}(\text{III})]/[\text{Ce}(\text{III})]$ , reported by Tong and King<sup>9</sup> for the oxidation of Cr(III) by Ce(IV) in aqueous acidic sulphate media. Considering these data,  $0.025\% \text{ m/V}$  was taken as the most appropriate concentration of Ce(IV) to be used in the on-line oxidation of Cr(III).

The dependence of the oxidation yield on the analytical concentration of sulphuric acid in the Ce(IV) solution is shown in Fig. 4. The variation in the absorbance values is not so pronounced, although the rate-law coefficient for the reaction between Cr(III) and Ce(IV) contains an inverse dependence on the concentration of hydrogen sulphate ion,<sup>9</sup> indicating that the reaction proceeds more readily at lower concentration of this species. This effect of the sulphuric acid concentration on the yield may relate principally to the formation of the anionic species,  $\text{Ce}(\text{SO}_4)_3^{2-}$ , which causes a slight variation in the formal potential of the Ce(IV) - Ce(III) couple.<sup>10</sup> Hence working solutions of Ce(IV) were prepared using the minimum amount of sulphuric acid necessary to dissolve the cerium(IV) salt and to prevent its hydrolysis.

There is a marked influence of the sulphuric acid concentration in the Cr(III) solution on the oxidation yield, as indicated by Table 1. Possibly the chromium(III) - sulphate complexes that may be formed when Cr(III) is in sulphuric acid solution inhibit the oxidation reaction. In dilute solutions of sulphate and Cr(III) ion, the important chromium species is the monosulphatochromium(III) complex, present as an inert inner-sphere complex,  $[\text{Cr}(\text{H}_2\text{O})_x\text{SO}_4]^+$ , and as a labile outer-sphere association (ion-pair) complex ion,<sup>11</sup>  $[\text{Cr}(\text{H}_2\text{O})_6^{3+} \text{SO}_4^{2-}]^+$ . The species  $[\text{Cr}(\text{SO}_4)_2]^-$  appears when the sulphate ion concentration is increased.<sup>11</sup> The outer-sphere complex of sulphate and hexaquo chromium(III) ion are in rapid equilibrium with their environment but the inner-sphere chromium sulphates are not. As the rate of formation of these inner-sphere complexes is relatively slow,<sup>9</sup> they do not interfere with the oxidation when the source of sulphate ion is the cerium(IV) solution but may interfere when the Cr(III) is in a more concentrated sulphuric acid solution for some time.

Having optimised the reagent concentrations, the variation of oxidation yield with the length of the oxidation coil was then re-investigated using the new experimental conditions. The results are given in Table 2. According to these data an oxidation coil of  $1.0 \text{ m}$  is sufficient to obtain the maximum oxidation yield. This result is very promising in terms of the application of this on-line oxidation procedure in continuous-flow determinations of total chromium.

As both the Cr(III) and Ce(IV) are in sulphuric acid solution, we again tested this acid as a medium for the formation of the Cr - DPC complex, although previous work<sup>7</sup> had indicated better results with nitric acid for the formation of this complex. As shown in Table 2, the absorbance values observed with DPC - sulphuric acid are lower than those with DPC - nitric acid, indicating that the formation of the Cr - DPC complex is more complete with nitric acid in confluence with DPC, although sulphuric acid can also be used.

The relative oxidation yield was calculated, comparing the absorbance values observed for identical concentrations of Cr(VI) and oxidised Cr(III), both measured under the same experimental conditions. The flow-rate control necessary for this comparison was effected by measuring a ratio of flow-rates,  $R_f$ , defined as the ratio between the measured absorbance of a standard solution of Cr(VI) submitted to dilution with water at the confluence point  $E'$  [see Fig. 1, feedline III, Cr(VI) standard solution; feedline IV, water] and the absorbance for the same Cr(VI) solution without on-line dilution [both feedlines III and IV pumping the Cr(VI) solution] under the same experimental conditions. This is a very convenient

**Table 1.** Variation of the relative oxidation yield with analytical concentration of sulphuric acid in the Cr(III) solution. Cr(III),  $1.50 \mu\text{g ml}^{-1}$ ;  $\text{Ce}(\text{SO}_4)_2$ ,  $0.025\% \text{ m/V}$  in  $0.07 \text{ M H}_2\text{SO}_4$ ; length of the oxidation coil,  $1.0 \text{ m}$ ; temperature of oxidation,  $45^\circ\text{C}$ ; volume injected,  $164 \mu\text{l}$ ;  $R_f$ ,  $0.433$  (see text)

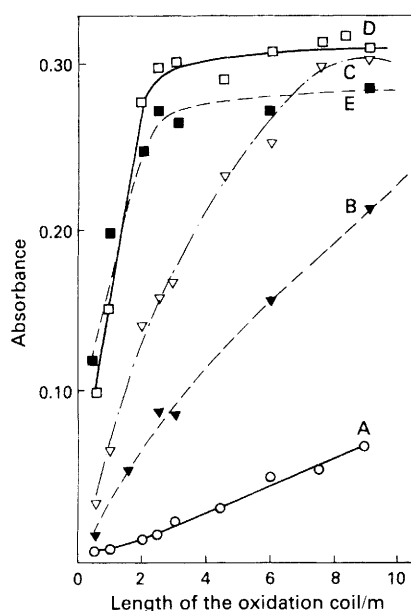
$\text{H}_2\text{SO}_4/\text{M}$	Relative oxidation yield, %
$1.0 \times 10^{-3}$	95.6
$1.0 \times 10^{-2}$	95.6
$3.0 \times 10^{-2}$	95.6
$1.0 \times 10^{-1}$	80.0
$1.8 \times 10^{-1}$	63.7
$3.0 \times 10^{-1}$	36.8
$5.0 \times 10^{-1}$	18.7
1.0	4.9
1.5	0

**Table 2.** Variation of the extent of oxidation with length of the oxidation coil. Cr(III),  $3.0 \mu\text{g ml}^{-1}$ ;  $\text{Ce}(\text{SO}_4)_2$ ,  $0.025\% \text{ m/V}$  in  $0.07 \text{ M H}_2\text{SO}_4$ ; temperature of oxidation,  $45^\circ\text{C}$ ; volume injected,  $77 \mu\text{l}$

Length/m	$A(\text{HNO}_3)^*$	$A(\text{H}_2\text{SO}_4)^\dagger$
0.50	0.212	0.202
1.00	0.215	0.202
2.00	0.215	0.204
3.00	0.215	0.207
4.00	0.217	0.213
5.00	0.220	0.213
7.00	0.226	0.213
9.00	0.224	0.199

\* Absorbance measured using  $0.80 \text{ M HNO}_3$  in confluence with  $0.05\% \text{ m/V DPC}$ .<sup>7</sup>

† Absorbance measured using  $0.80 \text{ M H}_2\text{SO}_4$  in confluence with  $0.05\% \text{ m/V DPC}$ .



**Fig. 5.** Oxidation of Cr(III) with  $\text{Ag}^+$ -catalysed peroxydisulphate: variation of the extent of oxidation with length of the oxidation coil and temperature of oxidation. Cr(III),  $3.0 \mu\text{g ml}^{-1}$  in  $0.10 \text{ M H}_2\text{SO}_4$ ;  $\text{K}_2\text{S}_2\text{O}_8$ ,  $2.50\% \text{ m/V}$  in  $2.5 \times 10^{-3}\% \text{ m/V}$ ; volume injected,  $77 \mu\text{l}$ . A,  $40^\circ\text{C}$ ; B,  $50^\circ\text{C}$ ; C,  $60^\circ\text{C}$ ; D,  $70^\circ\text{C}$ ; and E,  $74^\circ\text{C}$

procedure for checking the extent of on-line dilution from time to time (*e.g.*, before starting a run and then after each  $2 \text{ h}$  of continuous pumping) without stopping the run. The relative oxidation yield is constant for a given  $R_f$  value.

Cr(III) does not interfere in the reaction between Cr(VI) and DPC, which was used throughout this work to follow the extent of oxidation of Cr(III) by Ce(IV). However, when Ce(IV) concentrations at or above  $0.030\% \text{ m/V}$  are used in the oxidation process, double peaks may be recorded, depending on the volume injected. These double peaks may indicate a lack of the DPC reagent in the centre of the sample zone as a result of a reaction between DPC and Ce(IV). Such double peaks are not observed when the same Cr(VI) solution is diluted with water [Fig. 1, feedline III, Cr(VI); feedline IV, water] before it is injected into the main FIA line, using the same  $R_f$  value.

The on-line oxidation can also be done using a potassium peroxydisulphate solution with  $\text{Ag}^+$  ions as a catalyst. Fig. 5 shows the results obtained for the most suitable concentrations of  $\text{S}_2\text{O}_8^{2-}$  and  $\text{Ag}^+$ . However, peroxydisulphate produces larger amounts of bubbles at lower temperatures, probably owing to  $\text{S}_2\text{O}_8^{2-}$  decomposition in acidic solution<sup>4</sup> as, with higher temperatures and longer oxidation coils, more bubbles are observed. The poorer precision at higher temperatures in Fig. 5 is a direct result of the interference of the bubbles in the absorbance measurements. Special techniques can be applied to eliminate the problem of bubbles, but this greatly increases the time required for a single analysis. Thus, the use of peroxydisulphate is not recommended for the on-line oxidation of Cr(III) using the experimental conditions described in this paper. These observations indicate, once more, that conventional procedures used in static analysis do not necessarily translate into the best conditions for FIA.<sup>7</sup>

Studies applying this on-line oxidation procedure for the sequential spectrophotometric determination of Cr(III) and Cr(VI) are in progress.

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## References

- Sandell, E. B., "Colorimetric Determination of Traces of Metals," Second Edition, Interscience, New York, 1950.
- Marzenko, Z., "Spectrophotometric Determination of Elements," Ellis Horwood, Chichester, 1976.
- Yost, D. M., *J. Am. Chem. Soc.*, 1926, **48**, 152.
- House, D. A., *Chem. Rev.*, 1962, **62**, 185.
- Florence, T. M., and Batley, G. E., *CRC Crit. Rev. Anal. Chem.*, 1980, **9**, 219.
- Storgaard Jørgensen, S., and Regitano, M. A. B., *Analyst*, 1980, **105**, 292.
- de Andrade, J. C., Rocha, J. C., Pasquini, C., and Baccan, N., *Analyst*, 1983, **108**, 621.
- Willard, H. H., and Young, P., *J. Am. Chem. Soc.*, 1929, **51**, 149.
- Tong, J. Y., and King, E. L., *J. Am. Chem. Soc.*, 1960, **82**, 3805.
- Kunz, A. H., *J. Am. Chem. Soc.*, 1931, **53**, 98.
- Fogel, N., Tai, J. M. J., and Yarborough, J., *J. Am. Chem. Soc.*, 1962, **84**, 1145.

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