Effect of On-line Complex Formation Kinetics on the Flow Injection Analysis Signal: the Spectrophotometric Determination of Chromium(VI)

João Carlos de Andrade,* Julio Cesar Rocha, Celio Pasquini and Nivaldi Baccan

Universidade Estadual de Campinas, Instituto de Química, C.P. 6154, 13100-Campinas, São Paulo, Brazil

The sensitivity of the flow injection analysis (FIA) method for determination of chromium(VI) using 1,5-diphenylcarbazide (DPC) depends on the concentration of the acid used in confluence with the DPC solution. At low acid concentrations slower on-line reaction kinetics are observed for Cr - DPC complex formation. Hence the chemical contribution to the over-all dispersion value cannot be ignored. This indicates that the best experimental conditions for the static procedure may not always translate directly to the dynamic conditions of FIA. In the present instance the maximum signal is obtained with acid concentrations at or above 0.80 M. Although sulphuric acid may be used, as in the conventional procedure, the best working conditions are achieved using nitric acid.

Keywords: *Flow injection analysis; on-line kinetics; chromium(VI) determination*

The reaction between chromium(VI) and 1,5-diphenylcarbazide (DPC) is the basis of the most sensitive spectrophotometric method for the determination of minute amounts of chromium.[1–3] This method is widely used for the routine determinations of chromium. On the other hand, the use of the continuous flow injection technique (FIA)[4,5] for rapid and precise analysis can make routine determinations easier and more reliable. Thus the reaction of chromium(VI) with DPC should be thoroughly studied using the flow injection approach.

Jørgensen and Regitano[6] reported the determination of chromium(VI) using DPC and 0.040 M sulphuric acid. Work in our laboratory has shown that the sensitivity of their FIA - DPC method can be improved, achieving a sensitivity closer to that of the conventional static spectrophotometric procedure.

Experimental

Reagents

All solutions were prepared using analytical-reagent grade chemicals and de-ionised water. The solutions were stored in high-density polyethylene bottles.

1,5-Diphenylcarbazide working solutions. Prepared daily by dissolving 0.250 g of DPC (Merck) in 20 ml of acetone (Carlo Erba) and diluting to 500 ml with water.

Stock standard chromium(VI) solution, 1000 μg ml^{-1}. Prepared by dissolving 2.829 g of $K_2Cr_2O_7$ (G. Frederick Smith Chemical Co., 100% purity certified) in 0.10 M sulphuric acid (Merck). The $K_2Cr_2O_7$ was heated at 160 °C for 2 h. Working solutions were prepared daily by dilution of aliquots taken from the stock solution.

Acids. Hydrochloric acid (Carlo Erba), nitric acid (Carlo Erba), perchloric acid (Carlo Erba) and sulphuric acid (Merck) of concentrations 0.10–1.5 M were prepared by diluting appropriate volumes of the concentrated acids with water.

Experimental Conditions

Fig. 1(*a*) shows the single-line FIA configuration used in this work, and also that previously reported,[6] for the determination of chromium(VI). Fig. 1(*b*) indicates the arrangement used in the stopped-flow experiments. Except where stated otherwise, the reagents and the sample

* To whom correspondence should be addressed.

were pumped at a flow-rate of 1.2 ml min^{-1} using an Ismatec Mini-S 840 peristaltic pump and Tygon peristaltic pump tubing (Technicon). Samples of 77 μl were injected into the mixed stream of acid and DPC by means of a modified home-made acrylic proportional injector.[7] Polyethylene tubing (i.d. 0.8 mm) was used for both the mixing and the reaction coils. The absorbance measurements were made in a Zeiss PM 2A spectrophotometer at 540 nm, using an 80-μl Zeiss flow cell (optical path 10 mm).

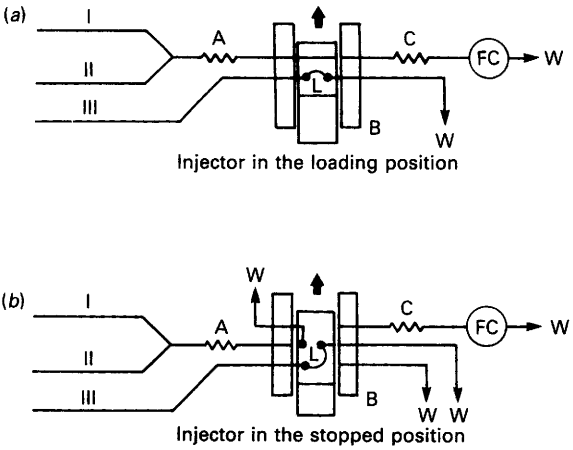

Fig. 1. The FIA system used for the determination of Cr(VI): (*a*) the single-line configuration; and (*b*) the stopped-flow configuration. A = Mixing coil, length 1.00 m; B = proportional injector; C = reaction coil, length 0.70 m; L = injection loop; W = waste; FC = flow cell, λ = 540 nm. I = Acid solution or water; II = DPC solution or water; III = Cr(VI) or pre-formed Cr - DPC.

Results and Discussion

The reaction between chromium(VI) and DPC is highly dependent on the pH.[1] The conventional procedure[1,2] uses sulphuric acid at 0.05–0.10 M (pH $\approx$ 1) as the medium for the full colour development of the Cr - DPC complex. According to the literature,[1] at acid concentrations of less than 0.05 M the colour does not develop immediately and at acid concentrations above 0.10 M the complex is less stable.

Fig. 2 shows the influence of the concentration of the nitric acid used in confluence with the DPC solution on the FIA signal. The shapes of the curves for perchloric, sulphuric and hydrochloric acids are the same as those observed for nitric acid. However, the sensitivity observed with nitric acid is better, although sulphuric acid is the acid specified in the conventional procedure.[1,2] For example, at an acid concentration of 0.80 M with nitric acid, the FIA - DPC procedure is about 5% more sensitive than with sulphuric acid. Lower sensitivity is noted at lower acid concentrations, more pronounced for hydrochloric acid than the other acids.

The best results were obtained using nitric acid of concentration at least 0.80 M (see Fig. 2) in confluence with 0.05% *m/V* DPC solution, in a single line FIA approach. The use of a higher DPC concentration is not compensated for by a corresponding gain in signal, as shown by Fig. 3.

The calibration graph obtained using the conditions described above is linear up to 4 μg ml^{-1} [A = 0.0008 + 0.1987[Cr] (μg ml^{-1}), where A = absorbance; correlation coefficient, r = 0.999]. The relative standard deviation (RSD) of ten replicate determinations ranged from 11.0% at the 50 ng ml^{-1} level to 2.5% at the 4 μg ml^{-1} level (minimum RSD = 1.2% at 1 μg ml^{-1}). The detection limit (signal to noise ratio = 3) of 15 ng ml^{-1} was calculated from the observed sensitivity and the noise associated with the measurement of the absorbance signal of the carrier solution.[8]

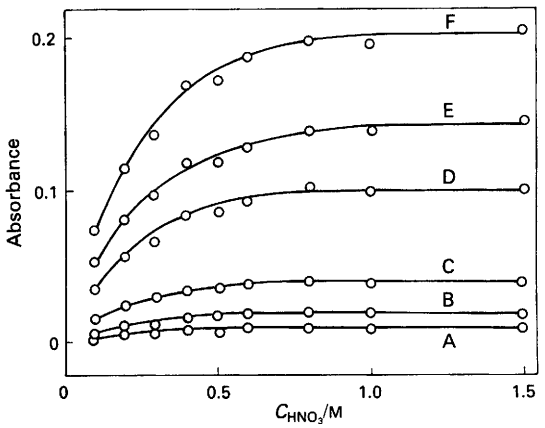

Fig. 2. Variations of the absorbances measured for various concentrations of Cr(VI) with respect to the analytical concentration of nitric acid (C_{HNO_3}) used in confluence with the DPC solution (0.05% *m/V*). Cr(VI) concentration: A, 0.05; B, 0.10; C, 0.20; D, 0.50; E, 0.70; and F, 1.00 μg ml^{-1}.

The dispersion values for the FIA manifold used in these experiments were determined and are given in Table I. Note that as the kinetic parameters of the reaction between chromium(VI) and DPC and the chemical stability of the Cr - DPC complex are pH dependent, both the physical dispersion (D_p) and the over-all dispersion (D_o) must be calculated. The chemical contribution to the D_o value is given simply by the equation[9] $D_c = D_o - D_p$. Assuming that Beer's law is obeyed, these dispersion values (defined by Růžička and Hansen[10] as $C_0/C_{max.}$) can be calculated by the ratio $A_0/A_{max.}$. The A_0 values were obtained experimentally by pumping 0.05% *m/V* DPC solution containing 0.80 μg ml^{-1} of chromium(VI) in either sulphuric or nitric acid, prepared according to the conventional procedure,[1,2] continuously through the detector. The $A_{max.}$ values used for the calculaton of D_p were obtained by injecting 77 μl of the pre-formed Cr - DPC complex into the FIA line, using water as a carrier. Stopped-flow experiments shows that no decomposition of the complex occurs during a typical measurement, but it is convenient to measure these values using fresh solutions otherwise apparent dispersion values can be found. For the calculation of D_o, the $A_{max.}$ values are those obtained from the FIA peak maxima observed when the reaction between chromium(VI) and DPC takes place in the line.

Using 0.040 M sulphuric acid in confluence with the DPC solution, with the other experi-

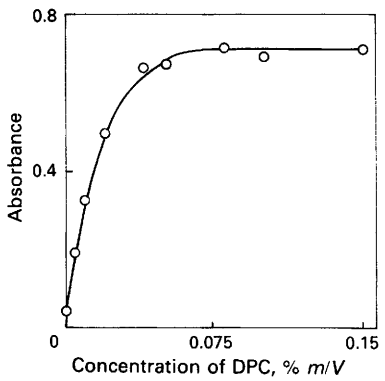

Fig. 3. Variation of the absorbance for various concentrations of DPC, in confluence with 0.80 M nitric acid. Concentration of Cr(VI): 3.0 μg ml^{-1}.

mental conditions as described above, the over-all dispersion is 11.2, which is coincidently close to the value of 11.6 found by Jørgensen and Regitano[6] for similar conditions of flow-rate and residence time.

As FIA sensitivity is related to the dispersion, it can be shown that the sensitivity of the FIA - DPC method for chromium could be improved by a factor of 2.8 only by using 0.80 M instead 0.040 M sulphuric acid (see Table I). These results are three times more sensitive than those obtained by Jørgensen and Regitano[6] under their most favourable conditions (dispersion of 9.7) and about nine times more sensitive than those obtained under their routine conditions (dispersion of 29.1).

TABLE I

DISPERSION VALUES FOUND FOR THE REACTION BETWEEN CHROMIUM(VI) AND 1,5-DIPHENYLCARBAZIDE USING A SINGLE-LINE FIA APPROACH

Working conditions as described under Experimental. Concentration of chromium(VI): 0.80 μg ml^{-1}.

Acid	Acid concentration*/M	A_o	$A_{max.}$	D_p	$A_{max.}$	D_o
		0.53				
HNO_3	0.040		—	—	0.03	17.6
	0.80		0.18	2.9	0.16	3.3
		0.56				
H_2SO_4	0.040		—	—	0.05	11.2
	0.80		0.20	2.8	0.14	4.0

* The acid concentration refers to the acid solution used in confluence with 1,5-diphenylcarbazide in the FIA system.

The dispersion values found by Jørgensen and Regitano[6] probably have a high contribution from the chemical dispersion term owing to slower reaction kinetics in the FIA line, caused by the low concentration of acid that they used . Stopped-flow experiments, as shown in Fig. 4, indicate that there is not enough time for complete formation of the complex in the FIA line when 0.040 M sulphuric acid is used in confluence with DPC. The use of a longer reaction coil might permit full colour development, but the increased contribution of the physical dispersion would be highly undesirable.

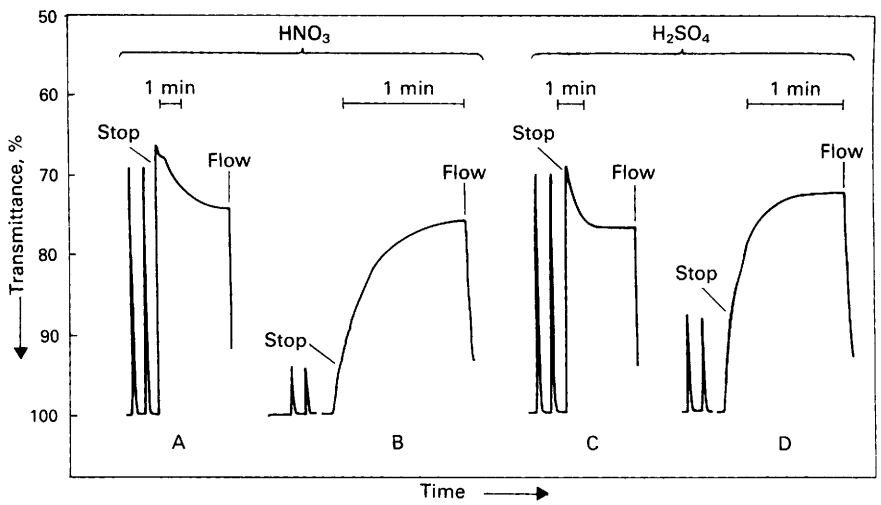

Fig. 4. Stopped-flow studies using nitric and sulphuric acids in confluence with DPC solution (0.05% *m/V*). A, 0.80 M HNO_3; B, 0.040 M HNO_3; C, 0.80 M H_2SO_4; and D, 0.040 M H_2SO_4. The first two peaks in each instance are the transient FIA peaks at the stated acidic conditions and the third signal is formed under stopped-flow conditions. Concentration of Cr(VI) = 0.80 μg ml^{-1}.

These results explain the inconsistencies found previously,[6] namely the constant sensitivity found when changing the length of the reaction coil and the large variation of the dispersion values observed on changing the flow-rate. In the first instance there is probably a compensation between an increase in D_p and a decrease in D_c. In the second instance, as a lower flow-rate means a higher residence time, more time exists for the formation of the Cr - DPC complex, which would result in a lower D_o value. Table II shows that the effect of changing the flow-rate conditions on the D_o values is small if the reaction is really completed in the FIA line.

TABLE II

OVER-ALL DISPERSION VALUES OBSERVED ON CHANGING THE FLOW-RATE IN THE SINGLE-LINE FIA APPROACH USED FOR CHROMIUM(VI) DETERMINATIONS BY THE 1,5-DIPHENYLCARBAZIDE METHOD

Concentration of chromium(VI) = 0.80 μg ml^{-1} and of DPC = 0.05% m/V.

Flow-rate/ml min^{-1}		D_o	
Nitric acid	1,5-Diphenylcarbazide	0.040 M HNO_3	0.80 M HNO_3
0.4	0.4	6.8	3.3
0.7	0.7	12.0	3.3
1.2	1.2	17.6	3.3
1.4	1.4	25.0	4.1
2.0	2.0	37.9	4.1
2.8	2.8	48.2	4.4
3.4	3.4	66.3	5.6

Fig. 4 also indicates that the use of the stopped-flow technique could improve the sensitivity of the Jørgensen and Regitano procedure,[6] but the sampling rate will decrease. Fig. 4A and C show that the Cr - DPC complex is almost completely formed in the FIA line when an acid concentration of 0.80 M is used. Although the complex is less stable when $C_{acid} \geqslant 0.80$ M, there is plenty of time to record the maximum of the FIA signal. The higher stability of the complex in 0.80 M nitric acid can also be seen on comparing Fig. 4A and C.

The over-all dispersion of our working conditions in relation to the conventional spectrophotometric procedure[1,2] is 3.5, calculated by the ratio $A_0(H_2SO_4)/A_{max.}$ (HNO_3, 0.80 M). Such a value indicates that the observed FIA sensitivity is about three times lower than that of the conventional static spectrophotometric procedure at 540 nm, mainly owing to physical dispersion. Despite this lower sensitivity, the FIA procedure still has several advantages over the conventional method, *e.g.*, better reproducibility, fast sampling rate and low cost. Under the experimental conditions described here a sampling rate of 120 samples per hour, with negligible carry-over, is possible.

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