A STUDY OF THE FACTORS THAT INFLUENCE THE INTERFERENCE OF Fe (III) IN THE COLOURIMETRIC ANALYSIS OF Cr (VI), IN POLLUTED WATERS

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ABSTRACT

The interference of Fe(III) in the photometric determination of Cr (VI) in water using the diphenylcarbazide method was studied, and the following factors which affected it were analyzed: pH, temperature, sequence in the addition of reagents, contact time between Fe (III) and Cr (VI) before analysis, and elapsed time for colour development. The most important factor proved to be the contact time, as at least one Fe (III)-Cr(VI) species is formed, in basic, neutral or slightly acid media. This fact explains the contradictions found in literature concerning the existence and magnitude of the interference. Therefore, the separation of Fe (III) or the use of other methods to analyze Cr (VI)—polluted waters which also contain Fe (III), is recommended.

RESUMEN

Se estudió la interferencia del Fe (III) en el método de la difenilcarbazida para la determinación fotocolorimétrica del Cr (VI) en aguas; se analizaron los siguientes factores: pH, temperatura, orden de adición de reactivos, tiempo de contacto entre el Fe (III) y el Cr (VI), antes del análisis·y el tiempo de reposo para el desarrollo del color. El factor más importante resultó ser el tiempo de contacto, ya que en medio básico, neutro o ligeramente ácido, se forma al menos una especie Fe (III)-Cr(VI). Este hecho explica las contradicciones encontradas en la literatura respecto a la presencia y magnitud de la interferencia. Por lo tanto, para analizar aguas contaminadas con Cr(VI) que contengan Fe (III), se recomienda la separación de éste último o el uso de otros métodos alternativos.

INTRODUCTION

Cr (VI) is considered a very toxic species and its allowance in water is up to 0.05 ppm (Schroeder and Lee 1975).

The diphenylcarbazide method, approved by the EPA (United States Enviromental Protection Agency) (APHA *et al.* 1981) and suggested by many authors for the quantitative determination of Cr (VI) in water (Snell and Snell 1949, Serfass and Muraca 1956, Allen 1958, Jolly 1963, Furman 1975, Sandell and Onishi 1978, Vogel
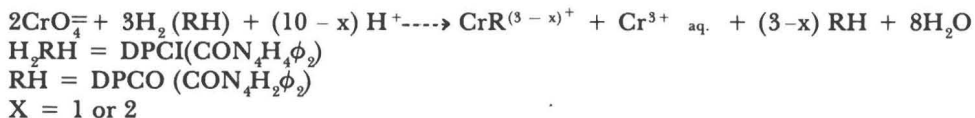
1978, APHA *et al*. 1980, Thomas and Chamberlin 1980, Rodier 1981), is based on the very sensitive colour reaction between Cr (VI) and diphenylcarbazide in mineral acid solution. Although the composition of the violet complex produced remained unknown for a long time, diverses studies (Pflaum and Howick 1956, Sano 1962, Marchart 1964, Willems *et al*. 1977) have shown that the process occurs in two steps. The first stage involves the oxidation by Cr (VI) of diphenylcarbazide (DPCI) to diphenylcarbazone (DPCP), and then the Cr (III) product of the reduction. is chelated with DPCO,

TABLE I. Fe (III) INTERFERENCE ON THE PHOTOMETRIC
DETERMINATION OF Cr (VI) IN LITERATURE

AUTHOR and YEAR	CONDITIONS	CONCLUSIONS
Snell & Snell 1949	Cr (VI) + DPCI in aq. solution pH = 1; t* = 15 min. [Cr (VI)] = 0.005-0.15 ppm	Fe does not interfere even though it yields a yellow color with DPCI
APHA, AWWA & WPCF 1971	Cr (VI) + DPCI in aq. solution pH = 1; t* = 5-20 min. [Cr (VI)] = 0-0.4 ppm [Fe (III)] > 1 ppm	Fe is a potential interferent, do not specify type of interference. In absence of Cl^- and with H_2SO_4 + H_3PO_4 no interference.
Sandell 1959	Cr (VI) + DPCI in aq. solution pH = 1-1.5; t* = seconds [Cr (VI)] = 0.4 ppm [Fe (III)] = 100, 200 ppm	Fe is disturbing element that increases or decreases absorbance of Cr depending upon t*. Recommend separation of Fe for accurate results.
Pilkington & Smith 1967	Cr (VI) + DPCI in aq. solution t* = 1-10 min [Cr] = 1 ppm [Fe] = 4 ppm	Fe interferes with decrease of absorbance of Cr, influenced by pH, temperature and kind of acid used.
Onishi & Koshima 1978	Cr (VI) + DPCI in aq. solution pH = 0.6-1.0, [Cr] = 1-10μg [Fe] = 0.1 mg	Fe interferes depending on DPCI pureness.
Vogel 1978	Cr (VI) + DPCI in aq. solution pH = 1; t* = 10-15 min. [Cr] = 0.2-0.5 ppm	Fe interferes, do not specify type of interference nor factors involved
Rodier 1981	Cr (VI) + DPCI in aq. solution pH = 1.1; t* > 10 min. [Cr] = 0.005-0.2 ppm [Fe] > 1 ppm	Same as Vogel 1978

*t = elapsed time for colour developmet.

producing the coloured ion-complex. Sano (1962) has proposed that part of the Cr (III) produced is coordinated with water molecules. The reaction can be written:

$$2CrO_4^= + 3H_2(RH) + (10 - x)H^+ \longrightarrow CrR^{(3-x)+} + Cr^{3+}{}_{aq.} + (3-x)RH + 8H_2O$$

$H_2RH = DPCI(CON_4H_4\phi_2)$

$RH = DPCO(CON_4H_2\phi_2)$

$X = 1 \text{ or } 2$

Due to its simplicity, the DPCI method is widely used in Mexican laboratories to control the chromium concentration in polluted waters. These waters may also contain other metallic ions, and generally Fe (III) is present.

The role of this ion on the colourimetric method is not clearly understood. Some authors consider Fe (III) only as a disturbing species, under certain working conditions; while others consider that iron behaves as an interfering agent. The magnitude of the interference has been related to different factors, such as pH, temperature, elapsed time for colour development, kind of acid used, etc. (Table I).

In order to define if the colourimetric method could be used for the analysis of the chromium content of ground and waste waters, which also contain Fe (III) (Gutiérrez et al. 1986), several experiments were carried out. It was especially important because the separating procedures of Cr (VI) from Fe (III) are complicated, and lower the accuracy.

In preliminary experiments, the ratio Fe/Cr was varied, but no straighforward answers were obtained, because sometimes a positive interference was observed, while in other occasions, mantaining tha same Fe/Cr ratio, it was found a negative interference or none at all (Table II).

TABLE II. Cr (VI) FOUND BY THE DPCI METHOD WITH Fe (III) AS AN INTERFERENT AT DIFFERENT pH VALUES Cr (VI) ADDED: 0.200 ppm

pH	Fe (III) / Cr (VI)													
	0	Δ*	20	Δ*	40	Δ*	50	Δ*	60	Δ*	80	Δ*	100	Δ*
0.8	0.200	O	0.196	-0.004	0.197	-0.003	-	-	0.195	-0.005	0.200	O	0.227	+0.027
1.0	0.201	+0.001	0.188	-0.012	-	-	0.214	+0.014	-	-	-	-	0.230	+0.030
1.2	0.200	0	0.202	+0.002	0.205	+0.005	0.171	-0.029	0.197	-0.003	0.208	+0.008	0.178	-0.022

*A = Cr(VI) detected - 0.200 ppm

Therefore, a better controlled study was needed, and the following factors were analyzed as influencing variables: pH, temperature, sequence in the addition of reagents, contact time between Cr (VI) and Fe (III) before analysis, and elapsed time for colour development. An Fe/Cr ratio of 16.0/0.200 was chosen.

MATERIAL AND METHODS

REAGENTS. The following reagents were Baker analytical grade: potassium dichromate, concentrated sulfuric acid (98%), concentrated orthophosphoric acid (86%),

concentrated nitric acid (65%) and acetone. Merck metallic iron powder from reduction (99.5%) and Merck Pro Analysi 1, 5-diphenylcarbazid zur Analyse und Redoxindikator (98% HPLC).

EQUIPMENT. Zeiss spectrophotometer, model PM2K; Bausch and Lomb u.v.-visible spectrophotometer system with X-Y recorder, model Spectronic 2000; Conductronic pH meter, modelo PH20 with Sargent-Welch electrode, model S-30072-15; Cole Parmer touch mixer, model 4721-40; and a Mettler analytical balance, model H54AR.

SOLUTIONS AND STANDARDS. Cr (VI) 100.00 ppm, from solid $K_2Cr_2O_7$; Fe (III) 1000 ppm, pH 0.8 in HCl, from a Merck Titrisol standard; Fe (III) 1000 ppm, pH 0.8 in HNO_3, from metallic Fe; Sulfuric acid 3M, from concentrated H_2SO_4; and I, 5-diphenylcarbazide (DPCI) 0.5% in acetone (Urone 1955, Allen 1958).

GENERAL METHOD. Solutions of 0.200 ppm Cr (VI) were prepared, the desired pH was achieved with H_2SO_4. In order to prepare the Fe + Cr samples, 1.6 mL of the Fe (III) standard solution in HCl were added to the 0.200 ppm Cr (VI) solution. In all cases the final volume was 100 mL. Afterwards, 2 mL of the DPCI solution were added to an aliquot of 50 mL from the previous solution, and mixed. The absorbance values were measured 10 minutes after this addition at a wavelength of 540 nm on the Zeiss spectrophotometer. Triple measurements and preparations of the solutions took place. The precision of the method was determined (Bauer 1974) with 11 solutions of Cr (VI) 0.200 ppm at a pH value of 1.2. The confidence limits were + 0.006 absorbance units (confidence level = 99%).

RESULTS AND DISCUSSION

SPECTRA OF SOLUTIONS. Spectra of 0.200 ppm Cr (VI) and 16.0 ppm Fe (III) solutions, both separated and mixed, were run after reaction with DPCI solution, according to the general method, from 400 to 600 nm, on the Bausch and Lomb Spectrophotometer and at 0.9, 1.2 and 2.0 pH values, as this interval covers the values recommended by most authors (See Table I).

All spectra showed the same general pattern with a maximum absorbance wavelength at approximately 540 nm (Fig. 1).

The curve obtained when only Fe (III) was mixed with DPCI corresponds to that of diphenylcarbazone (DPCO) (Pflaum and Howick 1956), product of the oxidation of DPCI. The shoulder corresponding to the iron complexes, product of the reaction of Fe (III) with DPCI, which should appear at 500 nm, according to Balt and Van Dalen (1963), was not observed. The absorbance value at the maximum, for the mixture Fe + Cr, was not the addtion of the individual absorbance values as could be expected, considering that the DPCI was present in excess to react with both ions.

EFFECT OF pH. The effect of the pH on the magnitude of iron interference, was studied at the following pH values: 0.5, 0.9, 1.2, 1.6, 2.0 (540 nm). It was observed, that the absorbance of the Fe + Cr solutions increases or decreases depending on pH (Fig. 2).

At pH 1.2 a positive interference was observed (this fact was confirmed throughout the whole study), while at the extreme pH values (0.5, 2.0) the absorbance values decreased considerably).
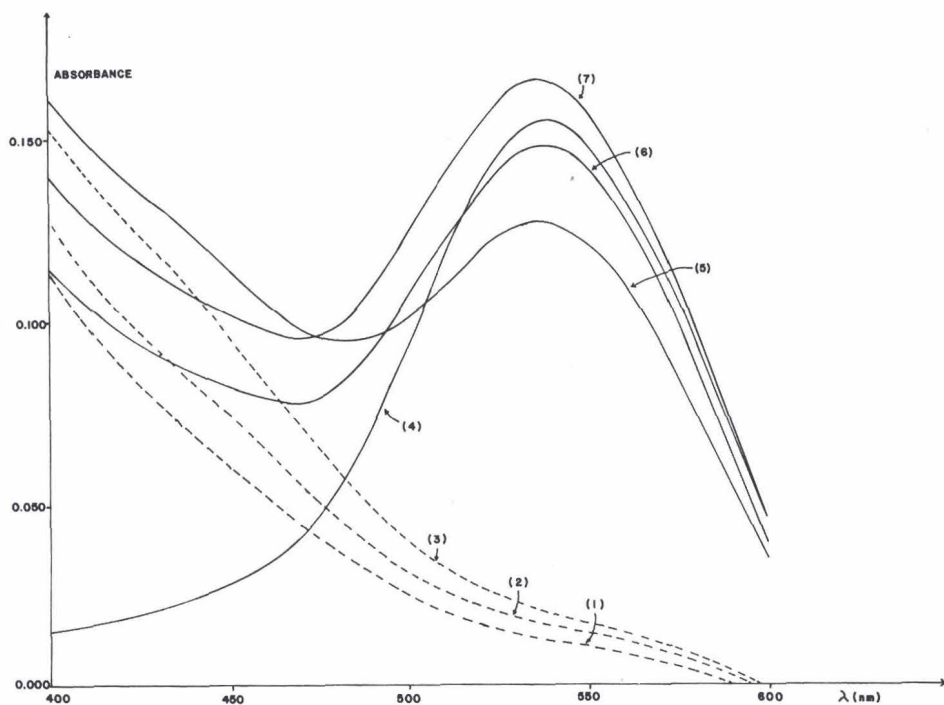
FIG. 1. Spectra of solutions:

(1) Fe (III) 16.0 ppm + DPCI at pH 0.9
(2) Fe (III) 16.0 ppm + DPCI at pH 1.2
(3) Fe (III) 16.0 ppm + DPCI at pH 2.0
(4) Cr (VI) 0.200 ppm + DPCI at pH 0.9, 1.2 and 2.0
(5) Cr (VI) 0.200 ppm + Fe (III) 16.0 ppm + DPCI at pH 2.0
(6) Cr (VI) 0.200 ppm + Fe (III) 16.0 ppm + DPCI at pH 0.9
(7) Cr (VI) 0.200 ppm + Fe (III) 16.0 ppm + DPCI at pH 1.2

It is possible that various factors are involved in the pH dependence on the interference. The following reactions of iron with chromium and DPCI are reported in literature:

— DPCI is oxidized to DPCO by Fe (III) (Balt and Van Dalen 1963).

— Fe (III) and Fe (II) react with DPCO, forming complexes (Balt and Van Dalen 1963).

— Fe (III) reacts with Cr (VI) forming an 1:1 complex in acidic medium (Espenson and Helzer 1969).

All these reactions depend on pH, in a similar manner to those of Cr (VI) with DPCI. Thus is is possible that, depending upon the particular condition, different equilibria are reached, producing positive, negative or null interferences. Some ideas about this pattern of behavior are expressed in the following paragraphs, but they should only be considered preliminarily, and further work will probably clarify them:

— At pH 1.2 the maximum absorbance is observed, probably because the complexation reaction takes place to the largest extent, as the oxidation of DPCI is favoured, and coordination reactions with iron and chromium are enhanced.

— At high pH values a hydrolysis process begins favouring the formation of Fe-Cr species.

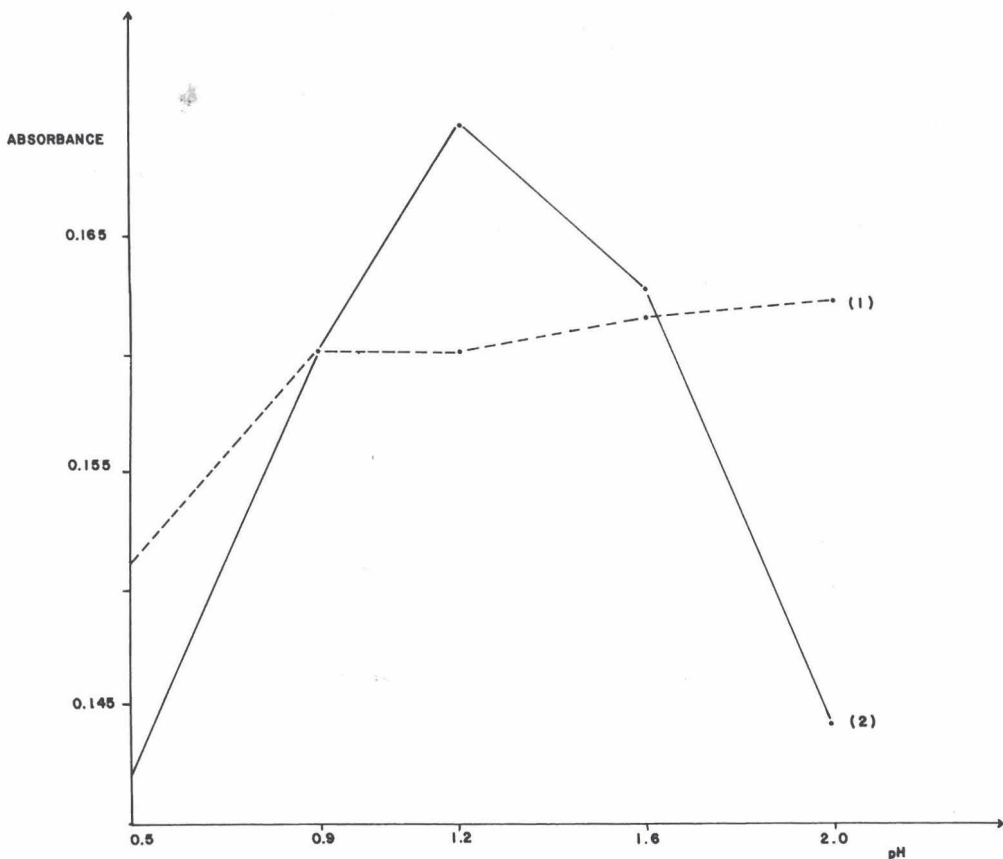— At low pH values, DPCO can be protonated therefore disfavouring the complexation reactions.

FIG. 2. Influence of the pH on the absorbance of Cr (III)-DPCO complex, at 540 nm (C.L. = + 0.006 a.u., = 1%).

(1) Cr (VI) 0.200 ppm + DPCl
(2) Cr (VI) 0.200 ppm + Fe (III) 16 ppm + PDCl

Nevertheless, the changes in the magnitude of the interference, related to the changes in pH are meaningless for the purpose of this work, because the differences in absorbance are very close to the error of the method, within the recommended interval of acidity (Table 1, Fig. 2).

TABLE III. ABSORBANCE VALUES OF Cr-DPCO COMPLEX + Fe (III) AT DIFFERENT TEMPERATURES AND SEQUENCE IN THE ADDITION OF REAGENTS: pH 1.2.

REAGENTS and SEQUENCE	TEMPERATURE	
	10°C	20°C
H_2SO_4 + Cr	0.162	0.161
H_2SO_4 + Cr + Fe	0.168	0.168
H_2SO_4 + Fe + Cr	0.169	0.170

EFFECT OF TEMPERATURE AND SEQUENCE IN THE ADDITION OF RE-AGENTS. No differences in the absorbance values were observed, between samples analyzed at 20°C or 10°C (Table III). This fact is apparently in disagreement with Pilkingston and Smith (1967), who found a decrease in the negative interference when cooling the solution. They analyzed solid samples of low chrome ilmenite at different starting conditions from those employed in this work (see conclusions).

It was also observed that changing the sequence in the addition of reagents was not relevant (Table III).

EFFECT OF CONTACT TIME BETWEEN Cr (VI) AND Fe (III) BEFORE ANALYSIS, AND OF ELAPSED TIME FOR COLOUR DEVELOPMENT. Solutions of Cr and Fe + Cr were left to age 0, 1 and 2 days, at the pH of the mixture (2.4). Just before reaction with DPCI, the acidity was adjusted with H_2SO_4, to the desired value (pH = 0.5, 0.9, 1.2, 1.6 and 2.0), according to the general method.

Stability of the colour was studied measuring the absorbance every 2 minutes for 15 minutes (elapsed time for colour development).

Only a small disturbing effect of Fe (III) on the stability of the coloured complex was observed, especially at pHs 0.9, 1.2 and 1.6. This effect is not very important because, independently of the absorbances measured during the elapsed time, were very close to the error of the method (Figs. 3, 4, 5 and 6).

However, there was an important fact, for all pH values, a considerable lowering of the absorbance was observed in the mixtures of Fe + Cr, aged 1 and 2 days, as compared to the absorbance of the freshly prepared mixtures (as shown by curves 5 and 6, in Figs. 3, 4, 5, 6).

In order to acquire more information about the contact time effect, wich had not been previously reported, additional experiments were carried out. Several conditions were varied, Table IV summarizes the results obtained when the following changes were made:
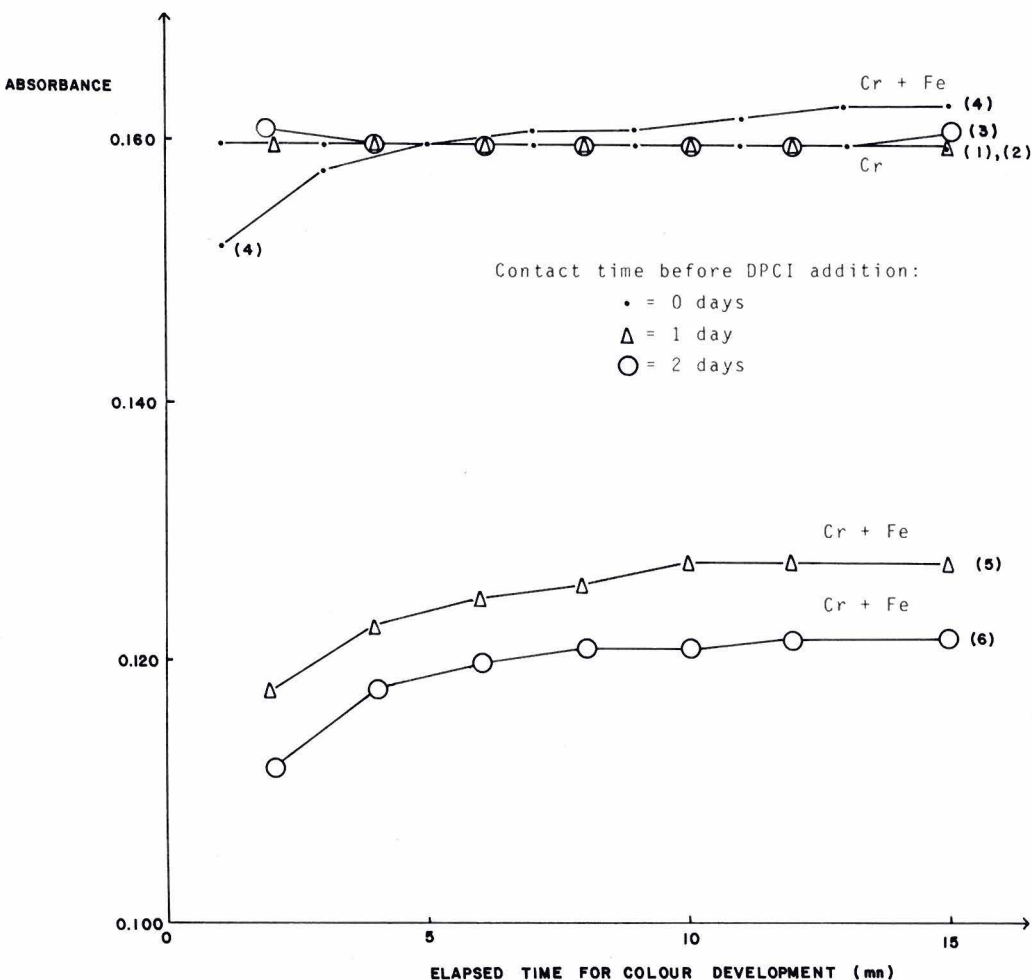
FIG. 3. Influence of the "contact time between Fe (III) and Cr (VI) before analysis" and the "elapsed time for colour development" on the absorbance of the Cr (III)-DPCO complex, at ph 0.9:

(1) Cr (VI) 0.200 ppm = DPCI at 0 days for contac time
(2) Cr (VI) 0.200 ppm + DPCI at 1 day of contact time
(3) Cr (VI) 0.200 ppm + PDCI at 2 days of contact time
(4) Cr (VI) 0.200 ppm + Fe (III) 16.0 ppm + DPCI at 0 days of contact time
(5) Cr (VI) 0.200 ppm + Fe (III) 16.0 ppm + DPCI at 1 days of contact time
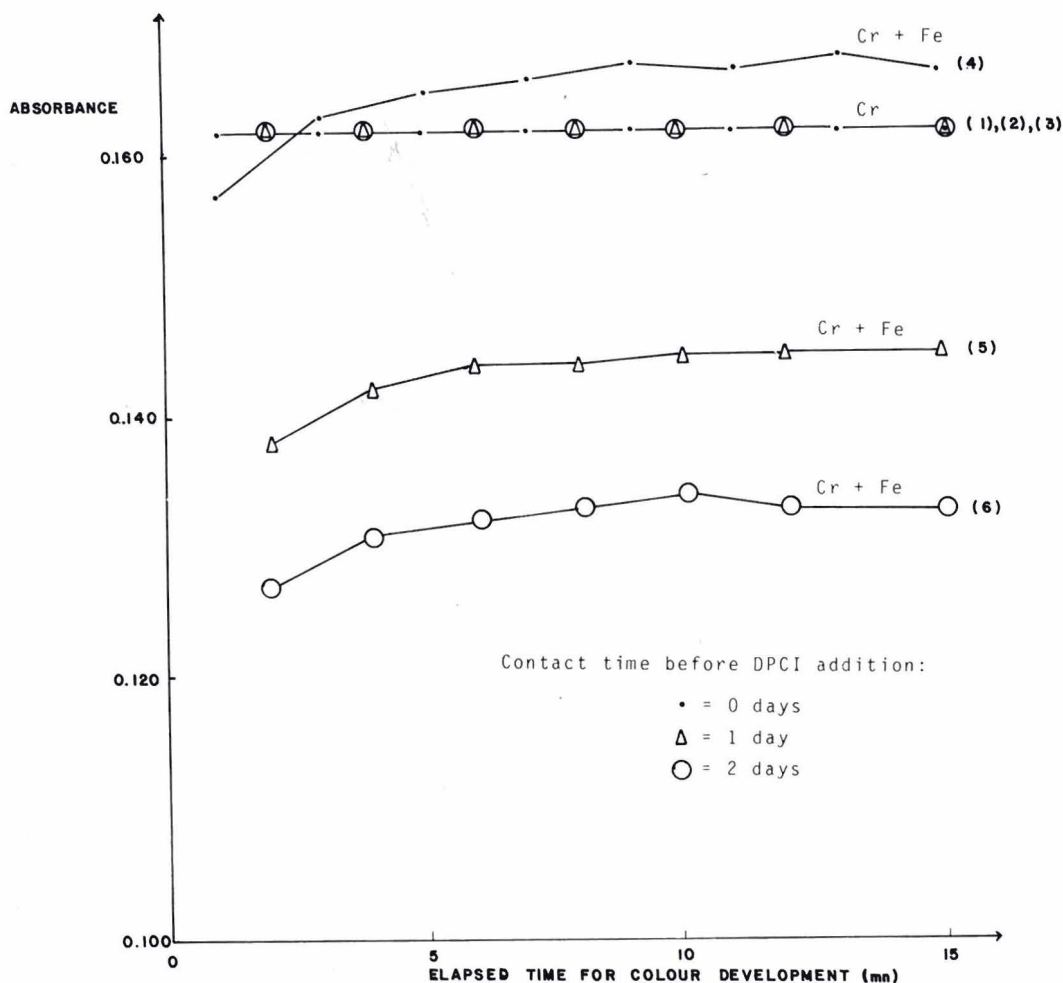(6) Cr (VI) 0.200 ppm + Fe (III) 16.0 ppm + DPCI at 2 days of contact time

FIG. 4. Influence of the "contact time between Fe (III) and Cr (VI) before analysis" and the "elapsed time for colour development" on the absorbance of the Cr (III)-DPCO complex, at pH 1.2:

(1) Cr (VI) 0.200 ppm + DPCI at 0 days of contact time
(2) Cr (VI) 0.200 ppm + DPCI at 1 days of contact time
(3) Cr (VI) 0.200 ppm + DPCI at 2 days of contact time
(4) Cr (VI) 0.200 ppm + Fe (III) 16.0 ppm + DPCI at 0 days of contact time
(5) Cr (VI) 0.200 ppm + Fe (III) 16.0 ppm + DPCI at 1 days of contact time
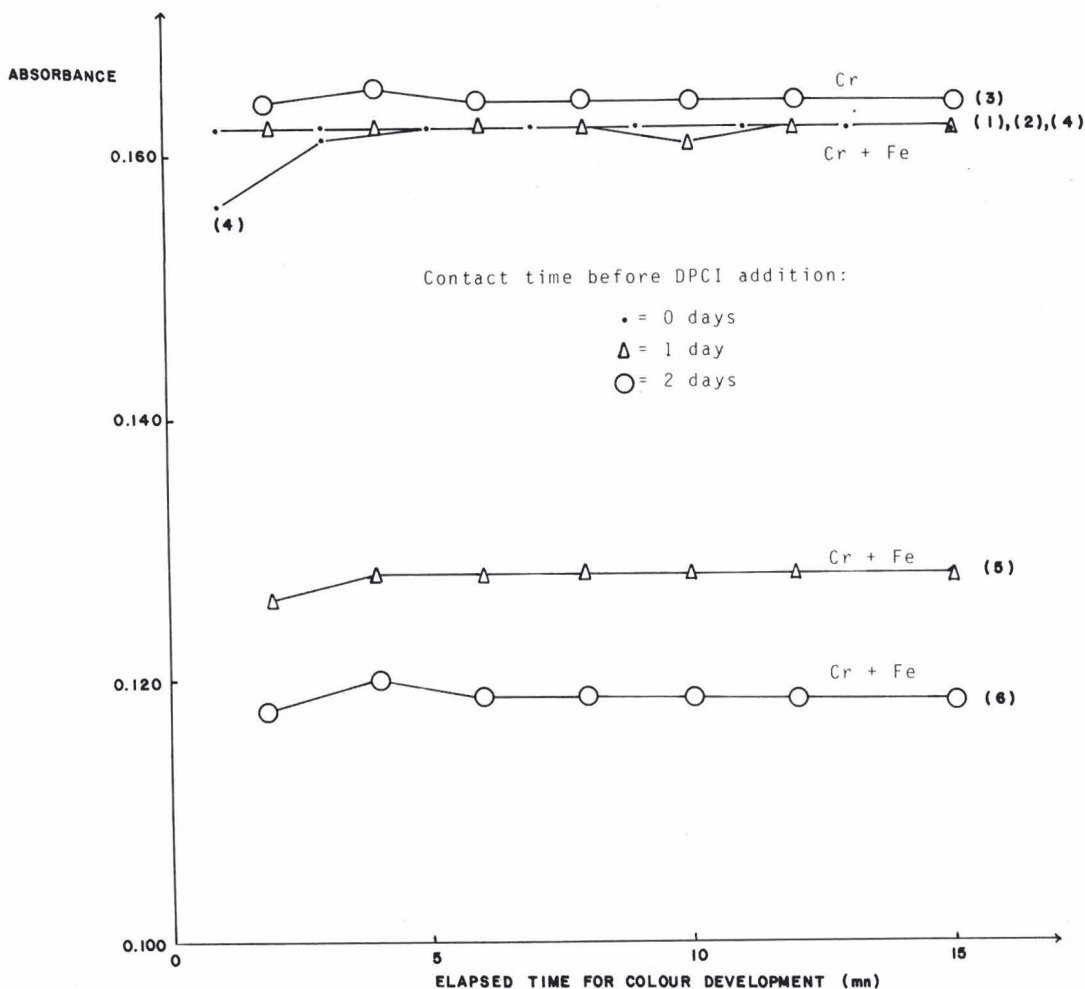(6) Cr (VI) 0.200 ppm + Fe (III) 16.0 ppm + DPCI at 2 days of contact time

FIG. 5. Influence of the "contact time between Fe (III) and Cr (VI) before analysis" and the "elapsed time for colour development" on the absorbance of the Cr (III)-DPCO complex, at pH 1.6:

(1) Cr (VI) 0.200 ppm + DPCI at 0 days of contact time
(2) Cr (VI) 0.200 ppm + DPCI at 1 days of contact time
(3) Cr (VI) 0.200 ppm + DPCI at 2 days of contact time
(4) Cr (VI) 0.200 ppm + Fe (III) 16.0 ppm + DPCI at 0 days of contact time
(5) Cr (VI) 0.200 ppm + Fe (III) 16.0 ppm + DPCI at 1 days of contact time
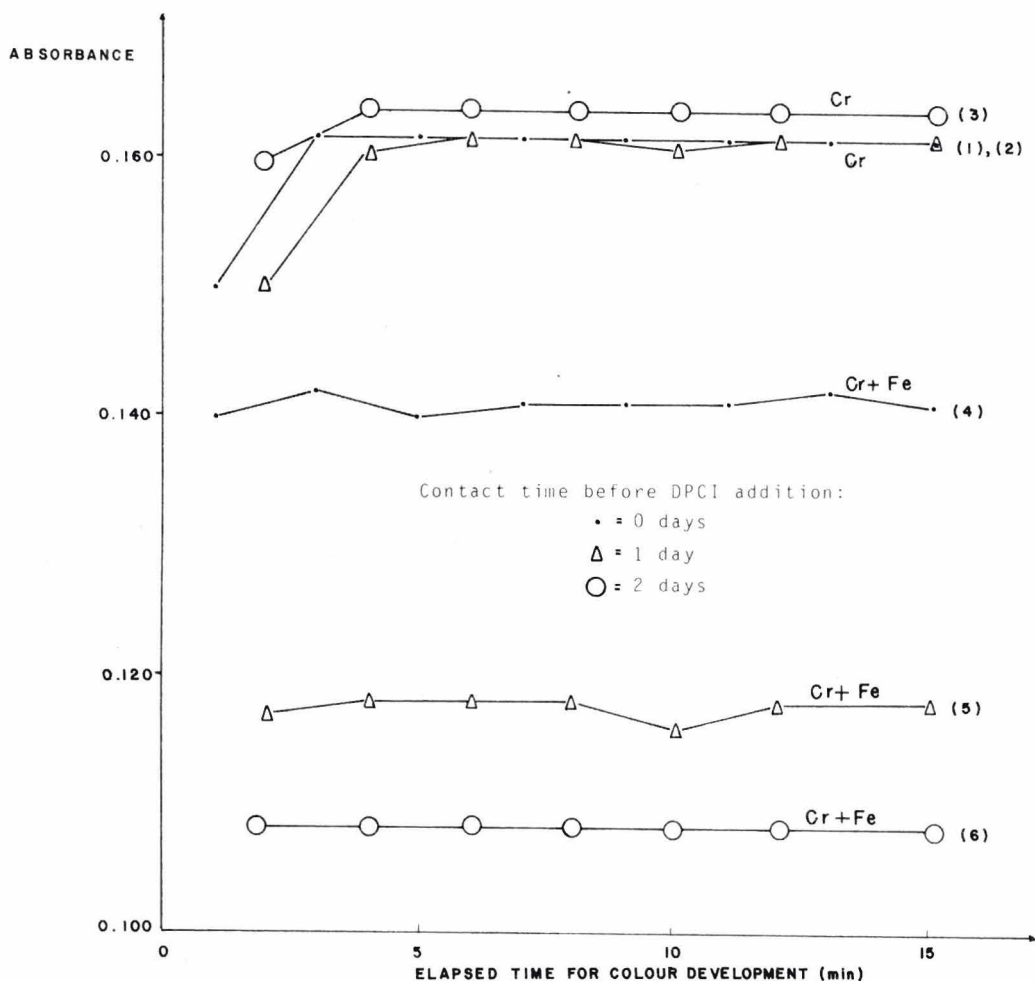(6) Cr (VI) 0.200 ppm + Fe (III) 16.0 ppm + DPCI at 2 days of contact time

FIG. 6. Influence of the "contact time between Fe (III) and Cr (VI) before analysis" and the "elapsed time for colour development" on the absorbance of the Cr (III)-DPCO complex, at pH 2:

(1) Cr (VI) 0.200 ppm + DPCI at 0 days of contact time
(2) Cr (VI) 0.200 ppm + DPCI at 1 days of contact time
(3) Cr (VI) 0.200 ppm + DPCI at 2 days of contact time
(4) Cr (VI) 0.200 ppm + Fe (III) 16.0 ppm + DPCI at 0 days of contact time
(5) Cr (VI) 0.200 ppm + Fe (III) 16.0 ppm + DPCI at 1 days of contact time
(6) Cr (VI) 0.200 ppm + Fe (III) 16.0 ppm + DPCI at 2 days of contact time

—Counter-ion of the Fe (III) standard solution: Cl^- or NO_3^- (column 1).

—Acid used for the reaction with DPCI: H_2SO_4, H_3PO_4 or the mixture (column 2).

—Contact time of Fe and Cr before analysis, 0, 2, 7 and 14 days (column 4), at pH given by the mixture (2.4).

—Contact time of Fe and Cr before analysis, 0, 2 and 7 days (column 5), at the pH recommended by the method (column 3).

TABLE IV. EFFECT OF CONTACT TIME BETWEEN 16.0 ppm Fe (III) and 0.200 ppm Cr (VI) ON THE ABSORBANCE OF THE Cr-DPCO COMPLEX, AT DIFFERENT CONDITIONS

REAGENTS + DPCI	ACID ADDED	REACTION pH	Contact t Fe-Cr at pH 2.4 (days)	Contact t Fe-Cr at reaction pH (days)	%*of ABSOR-BANCE
Fe (III) in HCl or HNO₃	H_2SO_4	1.2	0-7	0	13
			0	0-7	12
Fe (III) in HCl or HNO₃	H_3PO_4	1.2	0-7	0	0
			0	0-7	0
Fe (III) in HCl + Cr (VI)	H_2SO_4	1.2	0	0	106
			2	0	61
			0	2	92
			0	7	80
Fe (III) in HNO₃ + Cr (VI)	H_2SO_4	1.2	0	0	106
			2	0	67
			0	2	99
			7	0	13
			7	7	13
			14	0	14
Fe (III) in HCl + Cr (VI)	H_3PO_4	1.2	0	0	88
			2	0	40
			0	2	89
Fe (III) in HNO₃ + Cr (VI)	H_3PO_4	1.2	0	0	89
			2	0	50
			0	2	86
			7	0	0
			7	7	0
			14	0	0
Fe (III) in HCl + Cr (VI)	H_2SO_4 + 0.25% H_3PO_4	1.0	0	0	101
			2	0	70
			7	0	48
			0	7	38

* = Error is ± 4%

The value reported as percentase of absorbance in column 6 was obtained by considering that the absorbance from the solution of Cr (VI) + DPCI at pH 1.2 in H_2SO_4 corresponded to 100%. From this table it can be seen that:

— The absorbance at 540 nm due to the Cr (III)-DPCO complex decreases, as the contact time between Fe (III) and Cr (VI) increases, independently of the acid used as reaction medium, or the counter-ion from the Fe (III) standard solution.

— The rate of this lowering in absorbance is decreased when the mixture (pH 2.4) is left at the highest acidity (pH 1.2).

These observations suggest that a Fe (III)-Cr (VI) species is formed. It has been mentioned, that an 1:1 Fe (III): Cr (VI) complex is formed in acidic medium (Espenson and Helzer 1969, Rosseinsky 1969). Kinetic studies on the formation of this species show that the reaction is complete within tenths of a second, and it has a small stability constant.

Thus, additionally, a more stable Fe (III)-Cr (VI) compound (complex 1:1?), with a lower formation rate, must be present in the solution. The possibility of the formation of different Fe (III)-Cr(VI) species is not rejected by Espenson and King (1963).

Comparing the absorbances of mixtures of Fe (III)-Cr (VI), aged for the same lenght of time, at different pH values, it was observed that as the acidity of solutions increased, the interference of Fe (III) decreased, and consequently the absorbance value was enhanced (Table IV). This fact leads to the conclusion that hydrogen ions are released during the formation of the complex, in a similar way to the pausible mecha-

TABLE V. EFFECT OF CONTACT TIME ON THE ABSORBANCE VALUES
OF SOLUTION OF Cr (VI) + Fe (III) AT DIFFERENT pH VALUES

pH of solution	pH of reaction	Contact time (days)	ABSSORBANCE VALUES		COMMENTARIES
			Cr *	Fe + Cr*	
5	1	0	0.123	0.097	Absorbance values of
		1	0.123	0.082	original solution. No
		2	0.123	0.082	precipitate was observed.
7	1	0	0.122	0.670	Absorbance values of
		1	0.122	0.670	filtered solutions.
		2	0.122	0.670	
9	1	0	0.123	0.110	Absorbance values of
		1	0.123	0.110	filtered solutions.
		2	0.123	0.110	
5 - 13	1	3	0.123	0.076	2 days at pH 5; 1 day at pH 13. No precipitate was observed.
5 - 0.5	1	3	0.123	0.066	2 days at pH 5; 1 day at pH 0.5.

(*) Fe (III) = 16.0 ppm
    Cr (VI) = 0.200 ppm

nisms proposed by Epenson and Helzer (1968), where the $HCrO_4^-$ ion is in equilibrium with $CrO_4^=$, or the $Fe(H_2O)_6^{3+}$ with $Fe(H_2O)_5(OH)^{2+}$

These data also indicate that neither H_3PO_4 nor H_2SO_4 destroy the Fe-Cr complex after is has been formed, provided that the lowering of the absorbance is of the same order in magnitude for both acids.

It is important to point out that when the pH of solutions containing Fe (III) and Cr (VI) was increased, the following facts were observed (Table V):
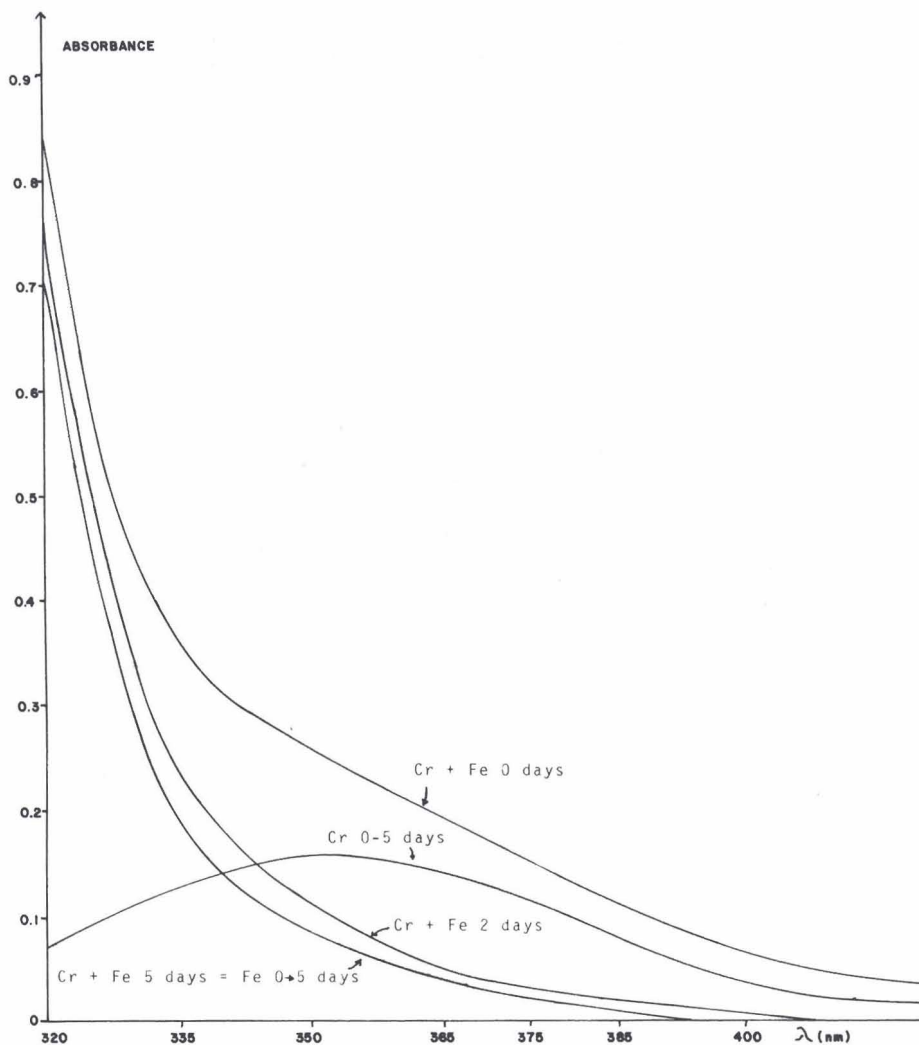

FIG. 7. Spectra of solutions of 5 ppm Cr (VI), and 400 ppm Fe (III) from the HNO_3 standard, at different contact times

— The Fe (III)-Cr (VI) species were formed more rapidly than in acidic medium.

— As pH was increased beyond and value of 5, precipitation of iron ocurred. the solid was filtered and the absorbance value of the solution was smaller than the corresponding value for Cr (VI).

— Once the Fe (III)-Cr (VI) species was formed, addition of NaOH to bring the pH slowly from 5 to 13, did not produce a precipitate.

In order to confirm the presence of Fe-Cr species, an absorption peak in the U.V.-visible region was sought for. Solutions of Cr(VI) 5 ppm and of Fe (III) 400 ppm, from the HNO_3 standard, were prepared and mixed, giving a pH of 1.1. The absorption spectra were recorded from 200-850 nm on the Bausch and Lomb Spectrophotometer, at 0, 2 and 5 days of contact (no DPCI was added). The results are shown in Figure 7.

The presence of a new absorption peak, that could be assigned to the complex, was not observed. Nevertheless the Fe (III)-Cr (VI) signal decreases with time, and after 5 days, the spectrum equals that of Fe (III). This fact indicates the formation of Fe (III)-Cr (VI) species. This new complex should absorb at low wavelegth, where the charge-transfer band of Fe (III) (in large excess) avoids its detection. The same pattern of behavior is observed in H_3PO_4.

CONCLUSIONS

Cr (VI) in solution and in contact with Fe (III), in basic, neutral, or sligthly acid media, from at least one Fe (III)-Cr(VI) species. This or these species are not destroyed by the addition of H_3PO_4, HNO_3, HCl, H_2SO_4 or DPCI, but their formation is disfavoured by a strongly acidic medium.

Procedures which recommend the use of H_3PO_4 + HNO_3 and/or cooling the solution under 15°C, (Pilkington and Smith 1967, APHA et al. 1980), might only prevent the iron interference, when the Fe (III)-Cr (VI) species have not been formed yet, as in strongly acidic solutions (i.e. samples proceeding from acid attacks on solids). However, if the particular conditions of the samples favoured the presence of Fe (III)-Cr (VI) species, then adding acid and/or cooling the solution does not eliminate the interference of Fe (III).

It was also shown that reading at a higher wavelength that 580 nm, as suggested in some standard procedures, in order to avoid the increase in absorbance caused by the presence of iron, is useless. This is because the interference was not a consequence of the formation of an Fe (III)-DPCO coloured complex (product of an Fe (III)-DPCI reaction). Indeed, as already mentioned, the most serious effect of iron, is a decrease in the absorbance. It was also demonstrated that a variation of the elapsed time was not an important factor in eliminating the iron effect.

Therefore, to analyze Cr (VI) in water samples, that contain Fe (III) in excess, in basic, neutral, or slightly acidic media, it is recommended that other methods, such as atomic absorption spectrophotometry, be used. If the colourimetric methods, have to be employed, the separation of Fe (III) has to be carried out. In the literature different techniques are recommended (Adam and Pribil 1974, Yoshimura and Ohashi, 1978, APHA et al. 1980).

Also. it is suggested that before applying colourimetric methods for the analysis of Cr (VI) in samples that contain Fe (III), under different conditions than aforementioned, their particular characteristics must be considered specially those related with the presence of Fe (III)-Cr (VI) species.

Finally, it must be pointed out that the above conclusions clarify much of the unsatisfactory nature of the existing literature, concerning iron interference on the colourimetric determinations of Cr(VI). These facts, specially explain the apparent disagreement between data related with the magnitud of iron effect, and the effectiveness of simple procedures to prevent it.

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REFERENCES

Adam J. and Pribil R. (1974). Extractions with long-chain amines VIII. Colorimetric determination of chromium (VI) with diphenylcarbazide. Talanta *21*, 616-618.

Allen T.L. (1958). Microdetermination of chromium with 1, 5-diphenylcarbohydrazide. Anal. Chem. *30*, 447-450.

APHA, AWWA and FSIWA (American Public Health Association, American Water Works Association and Federation of Sewage and Industrial Wastes). (1955). *Métodos normales para los exámenes de aguas, aguas negras y desechos industriales*. División de Salubridad, Bienestar y Habitación del Instituto de Asuntos Interamericanos, México, pp. 117-9, 402-5.

———, ——— and WPCF (Water Pollution Control Federacion) (1971). *Standard methods for the examination of water and wastewater*. APHA, Washington, 13th Ed. pp. 155-7, 426, 429.

———, ——— and ——— (1976). ———. ———, ———, 14th Ed. pp. 191-195.

———, ——— and ——— (1980). ———. ———, ———, 15th Ed. pp. 187-190.

———, ——— and ——— (1980). *Selected analytical methods approved and cited by the United States Enviromental Protection Agency*. (Supplement to the fifteenth edition of "standard methods for the examination of water and wasterwater"). S6, S17, S20 p.

Balt S. and Van Dalen E. (1963). The reactions of diphenylcarbazide and diphenylcarbazone with cations. Part IV. Cations of Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn and Pb. Anal. Chim. Acta *29*, 466-71.

Bauer E.L. (1974). *Manual de estadística para químicos*. Alhambra, Madrid, pp. 16-18, 185.

Espenson J.H. and Helzer S.R. (1969). Kinetic studies on the 1:1 complex of iron (III) and chromate ions in perchloric acid solution. Inorg. Chem. *8*, 1051-1053.

Espenson J.H. and King E.L. (1963). Kinetics and mechanism of reactions of chromium (VI) iron (II) species in acidic solution. J. Am. Chem. Soc. *85*, 3328-3333.

Furman N.H. (editor) (1975). *Standard methods of chemical analysis*. vol. I — The elements. Robert E. Krieger, Huntington, USA. pp. 356-359.

Gutiérrez M.E., Castillo S. and Bocco G. (1987). Estudio de contaminación por cromo en el norte de la Cd. de México. Un enfoque interdisciplinario. Boletín del Instituto de Geografía UNAM, México. *16*, 77-125.

Jolly S.C. (1963). Official, standardised and recommended methods of analysis. W. Heffer, Cambridge. pp. 212-214.

Marchart H. (1964). Uber die Reaktion von Chrom mit Diphenylcarbazid und Diphenylcarba-
    zon. Anal. Chim. Acta *30*, 11-17.
Onishi H. and Koshima H. (1978). Conditions for the photometric determination of chromium
    (VI) with diphenylcarbazide and effect of iron and vanadium. Bunseki Kagaku *27*, 726-
    729. (Chemical Abstracts 90:66171w).
Pflaum R.T. and Howick L.C. (1956). The chromium diphenylcarbazide reaction. J. Amer.
    Chem. Soc. *78*, 4862-4866.
Pilkington E.S. and Smith P.R. (1967). The spectrophotometric determination of chromium in
    ilmenite. Anal. Chim. Acta *39*, 321-328.
Rodier J. (1981). *Análisis de las aguas*. Omega, Barcelona. p. 269.
Rosseinsky D.R. and Nicol M.J. (1969). The iron (II)-chromium (VI) reaction: and additional
    pathway first order in iron (II). J. Chem. Soc. *19*, 2887-2890.
Sandell E.B. (1959). Colorimetric determination of traces of metals. Interscience, New York.
    Vol. II, pp. 274-276.
Sandell E.B. and Onishi H. (1978). *Photometric determination of traces of metals*. General as-
    pects. Vol. 3 Part I. Wiley, New York. pp. 389-391.
Sano H. (1962). Radioactive tracer study of the reaction between cromium (VI) and diphenyl-
    carbazide. Anal. Chim. Acta *27*, 398-399.
Schroeder D.C. and Lee G.F. (1975). Potential transformations of chromium in natural waters.
    Water, Air, and Soil Pollution *4*, 355-365.
Serfass E.J. and Muraca R.F. (1956). *The analytical chemistry of chromium: chemistry of chro-
    mium and its compounds*. (M.J. Udy, Ed.). Reinhold, New York, Vol. I. pp. 53-75.
Snell F.D. and Snell C.T. (1949). *Colorimetric methods of analysis*. Van Nostrand Reinhold,
    New York. Vol. II pp. 274-276.
Thomas L.C. and Chamberlin G.J. (1980). Colorimetric chemical analytical methods. The Tin-
    tometer Salisbury. pp. 156-157.
Urone P.F. (1955). Stability of colorimetric reagent for chromium, s-diphenylcarbazine, in va-
    rious solvents. Anal. Chem. *27*, 1354-1355.
Vogel A.I. (1978). *Vogel's textbook of quantitative inorganic analysis, including elementary ins-
    trumental analysis*. Longman Group, London. p. 738.
Willems G.J., Blaton N.M., Peeters O.M. and De Ranter C.J. (1977). The interaction of chro-
    mium (VI), chromium (III) and chromium (II) with diphenylcarbazide, diphenylcarbazone
    and diphenylcarbadiazone. Anal. Chim. Acta *88*, 345-352.
Yoshimura K. and Ohashi S. (1978). Ion-exchanger colorimetry-II. Microdetermination of
    chromium in natural waters. Talanta *25*, 103-107.