Spectrophotometric Determination of Hexavalent Chromium after Complex Formation with EDTA Using H-Point Method

PRANVERA LAZO,* ALQI CULLAJ and FILIP LUBONJA

Faculty of Natural Sciences, Department of Chemistry
University of Tirana, Tirana, Albania

We have applied H-point spectrophotometric method to the analysis of water and industrial discharge samples for determination of microcontent of Cr^{6+} after its complex formation with EDTA, having the aim of increasing the sensitivity, accuracy, reproducibility and minimization of the method's bias. The concentration values of Cr^{6+} are reported for Durres region, near a chemical factory. The possibility for selective determination of Cr^{6+} in water and industrial discharges sample, simplicity and rapidity of this method make it suitable for screening large number of samples for environmental monitoring.

INTRODUCTION

Chromium is an important trace metal. It is an essential element for biological systems and an important element to human beings, with average daily intake below 100 μg[1]. The biological and environmental activity of chromium depends on its oxidation state; whereas trivalent chromium is an essential nutrient for maintaining normal physiological functions, hexavalent chromium has been demonstrated to produce deleterious effects in animals and human beings[2]. The property of more toxic form of Cr^{6+} is due to its oxidizing potential and easy permeation of biological membrane[1].

The need for selective determination of Cr^{6+} in environmental monitoring has long been recognized, and due to its toxic behaviour, it has received increasing interest in recent years. The limits of detection for Cr^{3+} and Cr^{6+} in different environmental milieus published seem to be different. It is about 0.5 mg/m^3 (Cr^{3+}) and 0.05 mg/m^3 (Cr^{6+}) in airborne[3], lower than 0.1 mg/L in seawater[4] and lower than 0.4% in ground[5]. Due to different limits of Cr^{6+} in different environmental milieus, some sensitive methods are necessary to be used. Various techniques are used to determine it in the presence of Cr^{3+}, as total chromium or selectively, like spectrophotometry[2, 5] method with diphenylcarbazide, AAS[1, 3, 6, 7] or ICP-AES[8] methods. The method of the determination of Cr^{6+} by AAS suffers from the lack of selectivity[1, 3, 6, 7]. Good results are achieved only after chemical separation of Cr^{6+}, so the application of these methods is limited.

The following discussion presents an investigation to monitor dissolved forms of Cr^{6+} in water and industrial discharge samples, in the presence of Cr^{3+} and other interfering elements, after complex formation of Cr^{6+} with EDTA. H-point method to avoid constant interference of $Fe^{2, 3+}$ and Cr^{3+} is used. Except for the insoluble chromate, which is believed to be inert to change[1] in aquatic environ-

ment, it is assumed that all forms of Cr^{6+} are soluble in water at or near neutral pH.

Theoretical

H-point method[9] is applicable under the condition that spectral interference is constant in selected spectral range or equal in two different wavelengths (Fig. 1).
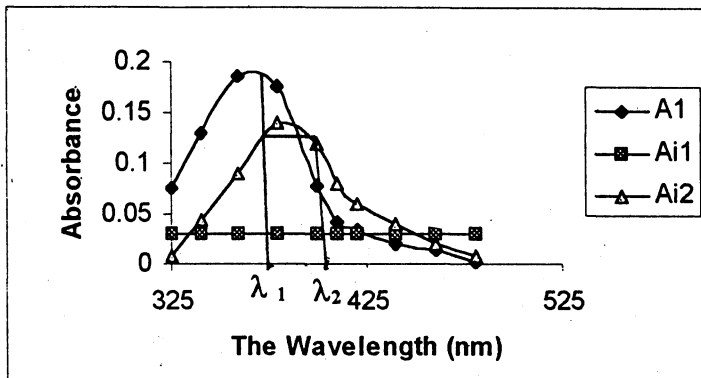

Fig. 1. The spectral curves of: (a) A_1: analyte (b) A_{i1}: constant interference (c) A_{i2}: interfering element

Two straight lines with different slopes are obtained after the plotting of the analytical signal data at two different wavelenghts *versus* the added analyte concentration having a common point H (Fig. 2).
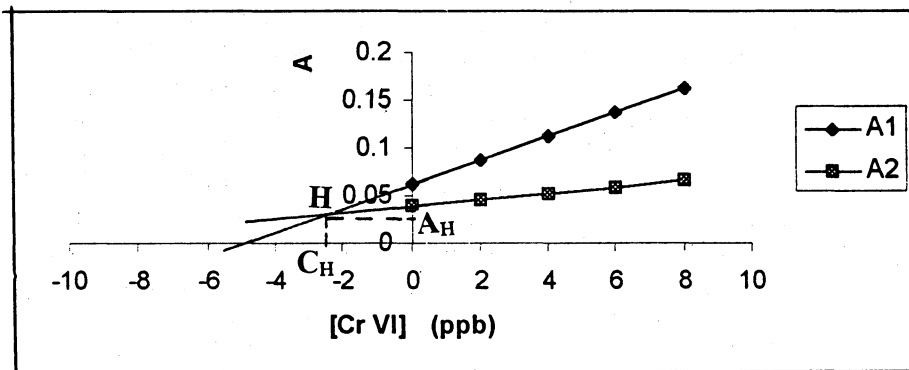

Fig. 2. The H-point calibration curves

The ordinate A_H represents the interfering signal and the abscissa C_H represents the unknown analyte concentration.

Let us carry out measuremènts in two different wavelengths λ_1 and λ_2, under the condition of some constant interference A_i:

$$A_{i1} = A_{i2} = A_i \tag{1}$$

The expression of Beer's law in each wavelength will be:

$$A_1 = K_{11} \cdot C_1 + A_i \quad \text{and} \quad A_2 = K_{21} \cdot C_1 + A_i \tag{2}$$

In the case when

$$A_1 = A_2 = A_H \tag{3}$$

we obtain

$$k_{11} \cdot C_1 - K_{12} \cdot C_1 = 0 \tag{4}$$

Let $C_1 = C_0 + C_H$ where C_0 represents the real concentration of the analyte and C_H the interfering concentration. After the transformation the expression (4) should be written as follows:

$$k_{11} \cdot (C_0 + C_H) - K_{12} \cdot (C_0 + C_H) = 0 \tag{5}$$

or

$$(k_{11} - k_{12}) \cdot (C_0 + C_H) = 0 \tag{6}$$

Finally from expression (6) we can obtain:

$$C_0 = -C_H \tag{7}$$

Finally we have demonstrated that the ordinate A_H represents the value of interfering absorbance and the abscissa C_H represents real concentration of the unknown analyte.

EXPERIMENTAL

High purity of Cr^{6+} standard solution Merck (p.a.) is used. All other reagents used in these procedures are from Merck (p.a.) reagents, too.

Water samples are filtered through a 0.45 μm filter to separate the dissolved constituents from the suspended materials, which do not contain Cr^{6+}. The sample is not acidified to avoid the reduction of Cr^{6+}. Hexavalent chromium is determined by spectrophotometry in the presence of trivalent chromium, after complex formation with EDTA. H-point method is used to avoid the constant interference of Cr^{3+} and $Fe^{2,3+}$. The sample must be stored at 4°C until the time of analysis.

Transfer 15 mL of the filtered sample to a 50 mL colorimetric tube and adjust it to pH = 7 ± 0.3 by adding 5% HCl or 5% NaOH dropwise. Add 25 mg NaF/25 mL sample. After dissolving of NaF add 5 mL 0.1 M EDTA. Dilute the content in tube with distilled water to 25 mL and stir it for homogenizing.

A Pye Unicam SP6–550 UV/Vis spectrophotometer is used for the absorbance measurements in $\lambda = 370$ and 410 nm using 1 cm cell. The instrumental parameters are optimized to achieve good analytical performance, aiming mainly to increase the sensitivity of the method.

RESULTS AND DISCUSSION

Spectral interference: EDTA is not a specific reagent for the determination of hexavalent chromium. In pH = 7, it forms stable complex compounds with several metal ions. Dado and Rosenthal[10] have used EDTA for simultaneous determination of Co^{2+}, Ni^{2+} and Cu^{2+} using multilinear regression method in UV-Vis region. The respective molar absorption reported is Co (462.9 nm) 14.3, Ni (378.7 nm) 12.4 and Cu (732.0 nm) 96.2 $M^{-1} cm^{-1}$. We have studied the

spectral interference of Cr^{3+}, $Fe^{2,3+}$, Co^{2+}, Ni^{2+} and Cu^{2+} complexes with EDTA for the determination of Cr^{6+} by EDTA procedure. We have plotted the absorption spectra of 0.1 mM [Cr^{3+}, Cr^{6+}, $Fe^{2,3+}$, Co^{2+}, Ni^{2+} and Cu^{2+}]–0.1 M EDTA (pH = 7) from 330 to 800 nm. Thus we found the molar absorption coefficients in various characteristic wavelengths for each element. The results are listed in Table-1.

TABLE-1

MOLAR ABSORPTIVITY OF [Cr^{3+}, Cr^{6+}, $Fe^{2,3+}$, Co^{2+}, Ni^{2+} and Cu^{2+}]-EDTA FROM 300 TO 800 nm

Compound	Wavelength (nm)					
	330	370	378	462	555	732
Fe(II, III)*	1890.0	385.0	298.0	11.8	2.4	0.06
Cr(VI)	1750.0	3744.0	3720.0	185.0	1.2	0.04
Ni(II)	9.8	1.4	13.2	0.7	6.2	3.00
Co(II)	0.3	0.9	1.1	14.9	0.8	2.30
Cr(III)	92.0	169.0	169.0	11.2	365.0	0.20
Cu(II)	54.3	1.2	5.9	0.5	10.3	98.70

*The values of the molar absorption coefficients of $Fe^{2,3+}$ are very close to each other.

From the data listed in Table-1 we can see the presence of a strong absorption value of Cr^{6+} in its characteristic wavelength (370 nm) and a strong interference of iron in both valence states. Cr^{3+} has a weak absorption peak on about 380 nm, which may be considered constant in the range 370 to 410 nm. It is shown also that the maximum absorptivity of other elements (Co^{2+}, Ni^{2+} and Cu^{2+}) on 370 nm differs significantly from the absorbence of Cr^{6+}-EDTA on 370 nm; so we can say that Co^{2+}, Ni^{2+} and Cu^{2+} do nt interfere with Cr^{6+}.

We have studied the use of NaF to avoid the interference of $Fe^{2,3+}$ with Cr^{6+} (Fig. 3).

It is clear from Fig. 3 that the strong complex compounds of iron fluoride are formed. The constant interference of $Fe^{2,3+}$ is observed on $\lambda > 360$ nm

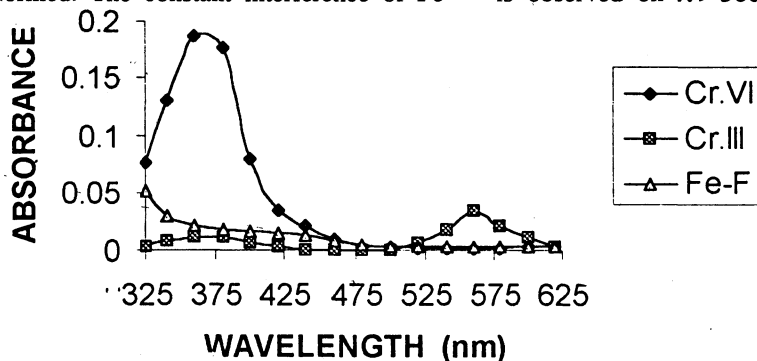Fig. 3.   The absorption curves of [Cr(IV) Cr(III), Fe(II, III)]-EDTA complexes in the presence of 1% NaF

with molar absorptivity of 62 $M^{-1} cm^{-1}$. Due to the fact that the interference of Cr^{3+} is constant in the range 370 to 410 nm, we have used this interval of wavelength for the application of H-point method, to avoid constant interference of $Fe^{2,3+}$ and Cr^{3+} on spectrophotometric determination of Cr^{6+} after its complex formation.

The effect of pH on the stability of the complex Cr^{6+}-EDTA: We have drafted the diagram of the variation of the absorbence of Cr^{6}-EDTA complex solution *via* the pH (Fig. 4).
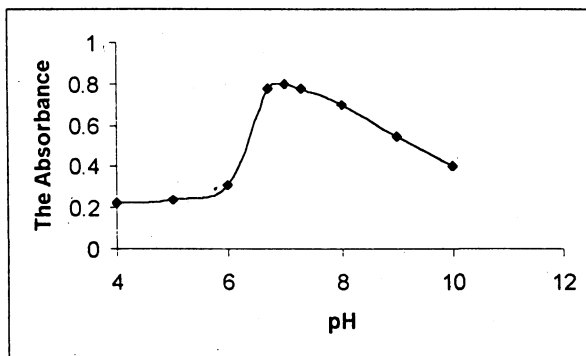

Fig. 4. The effect of pH on the stability of Cr^{6+}-EDTA complex

From Fig. 4 it can be seen that the absorbance value of Cr^{6+}-EDTA complex reaches its maximum at $pH = 7 \pm 0.3$. Maybe it is due to molar ratio of the complex formed. We have chosen this $pH = 7$ to ensure high stability of Cr^{6+}-EDTA complex and high sensitivity of the method.

Calibration curve and performance parameters: The calibration curve is obtained by linear regression of the absorbance values vs. concentration of Cr^{6+} standard solution (0 to 50 μg Cr^{6+}/L, prepared from 1 mg/L Cr^{6+} stock solution) in 370 nm. The parameters of the calibration curve, such as the slope, the intercept and correlation coefficient of the fitted values, are obtained through the method of linear regression.

The results obtained show that there is a very good relationship between concentration of chromium and the absorbance values of Cr^{6+}-EDTA system in the range from 0.1 to 10 mg of Cr^{6+}/L using 1 cm cells and 0.04 to 1.0 mg of Cr^{6+}/L using 2.5 cm cells. The correlation coefficient is higher than 0.999, the intercept is 0.0013 to 0.0019 and the slope is about 0.12 A/ppm cm. The parameters obtained are better than those obtained from the other methods used (AAS, AFS or ICP). The sensitivity achieved is comparable with biphenyl carbazide method, which is well known as the most sensitive method for the determination of Cr^{6+}.

The verification of efficiency of H-point method: Three synthetic samples are used to verify the efficiency of H-point method for the determination of Cr^{6+} in the presence of $Fe^{2,3+}$ and Cr^{3+} using EDTA as complex bounder. The composition of synthetic samples is given in Table. 2.

TABLE-2
THE COMPOSITION OF SYNTHETIC SAMPLES

No. of Sample	Content of elements (mg/L)			Cr(VI) (mg/L) (Estimated)	Rel. error (%)
	Cr(VI)	Cr(III)	Fe(III)		
N-1	0.020	50	150	0.0188	–6
N-2	0.010	30	80	0.0110	+10
N-3	0.006	20	50	0.0065	+8.3

We have used three different wavelengths (370, 385 and 410 nm) within the interval 370 to 410 nm characterized by constant interference of $Fe^{2, 3+}$ and Cr^{3+} ions, to measure the absorbance of each sample, using standard addition method in each wavelength (Fig. 5).
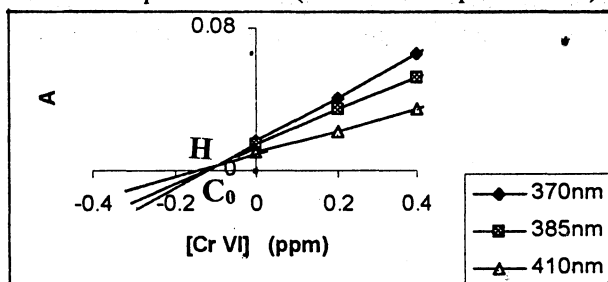
Fig. 5. shows that all calibration curves drawn for each solution in three different wavelengths have respectively a common point H, which proves the
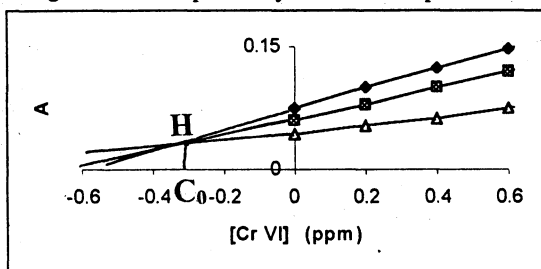
Sample N – 1* (* 20 ml sample is used)
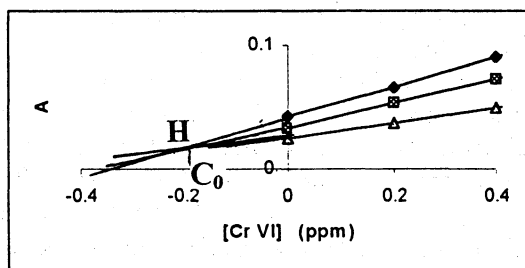
Sample N – 2* (* 20 ml sample is used)

Sample N – 3* (* 20 ml sample is used)

Fig. 5. Calibration curves of three synthetic samples performed in 370, 385 and 410 nm

hypothesis that the spectral interferences of the above samples are constant in this region of wavelength. Fig. 5 (sample N-3) shows also that the quantity of NaF used (1 mg NaF/mL) is enough to mask totally 50 mg/mL $Fe^{2, 3+}$. It could be seen very clearly through the analysis of sample N-3. The common point H of two calibration curves, performed in 370 and 410 nm, falls on the abscissa, which proves that no spectral inteference exists in this case (see Fig. 5, sample N-3). Normal measurements with calibration curves or standard addition method should be used in this case.

(e) **The analysis of real samples:** Three water samples (N-13 from the hydrovor, N-16 from the channel, N-17 before the discharge on the sea), from Durres region, near a chemical factory, are chosen for investigation. H-point method is used to calculate the content of Cr^{6+} in real samples.

To assess the reproducibility of the method we have done the analysis of the same sample three times (n = 3, P = 95%), keeping all conditions constant. The results are listed in Table-2.

TABLE-2
THE DATA OF QUALITY CONTROL OF THE ANALYSIS

No. of sample	Content of Cr^{6+} ($\overline{X}$, µg/L)		Stand. error	Sum of Squares		F-Ratio
	DC method*	H-point		Bet. Sample	With Sample	
N-13	15.0	13.5	1.09	1.07	0.20	5.33
N-16	15.3	17.1	0.43	0.14	0.45	0.93
N-17	17.0	16.6	0.05	2.80	1.25	2.25

*The results of biphenyl carbazide (DC) method.

$\overline{X}$ represents the mean of three measurements (n = 3).

Table-2 shows that the standard error is smaller than 1.09 and F-ratio value is satisfied ($F_{tab.}$ = 15.44, n = 3, P = 95%). The data of Table-2 shows too, that no significant differences exist between our results and those obtained from biphenyl carbazide method.

Conclusions

1. The proposed method of the determination of dissolved Cr^{6+} in water and industrial water samples, in the presence of $Fe^{2, 3+}$ and Cr^{3+}, using EDTA as complex formation reagent, gives good analytical performance parameters.

2. The method can be used to analyze samples containing 2 to 20 µg Cr^{6+}/L. The range of the method can be extended upward by dilution.

3. Good accuracy is obtained after the combination of spectrophotometic determination with H-point method, for the determination of Cr(VI) in water and industrial water samples, in the presence of Fe(II, III) and Cr(III). The condition of constant interference is necessary. It is achieved after complex formation of Fe(II, III) with F^- ions.

4. Direct method can be used in the absence of the interference of Fe(II, III), which are the main source of error in the determination of Cr^{6+} by spectrophotomerty, using EDTA as complex formation reagent.

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For more information, contact:
   Prof. G. KREYSA
   DECHEMA
   e.V. —c/o 11th IBS
   Theodor-Heuss-Allee 25,
   60486 Frankfurt Main, Germany
   Tel: +49 69 7564 241
   Fax:,   +49 69 7564 201
   E-mail info@dechema.de