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EDTA excess Zn(II) back-titration in the presence of 4-(2-pyridylazo)-resorcinol indicator and naphthol green β as inert dye for determining Cr(III) as Cr(III)/EDTA complex: Application of the method to a leather industry wastewater

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Abstract

The colour changes of 4-(2-pyridylazo)-resorcinol and naphthol green β as new screening metallochromic indicator in back-titration of EDTA excess with Zn(II) to determine Cr(III)/EDTA complex was investigated with the help of tristimulus colorimetry. Specific colour discrimination (SCD) and L^*, a^*, b^* 1976 parameters were successfully applied to evaluate the quality of colour transition at the end-point in non-alkaline media and in the presence of Zn(II) and Ca(II) which resulted in non-interfering species at 1×10^{-3} M and 2×10^{-3} M, respectively. The above concentrations are comparable with those used for Cr(III). Validation of the fast and accurate reported method was performed by atomic absorption spectroscopy. Moreover, the method was applied for determining Cr as Cr(III) in a wastewater effluent deriving from a leather industry.

Keywords: Chromium; Complexometric titration; 4-(2-Pyridylazo)-resorcinol; Screening agent; Leather industry effluent

1. Introduction

Nine oxidation states of chromium are described in the literature but in natural systems it occurs only as Cr(III) and Cr(VI). Cr(III), which is considered an essential nutrient for human life and is mainly present in minerals. Small amounts can be found in uncontaminated natural waters and larger amounts can be detected in human polluted environmental systems [1].

Cr(VI), the most toxic for biological systems, is a poison and a potentially carcinogenic agent and appears among the oxidation states of chromium [2]. It enters the environment from industrial effluents or waste-disposal sources such as wastewaters from steel works, tanning and electroplating industries [3–6].

In order to determine concentration and speciation of chromium species, pre-concentration and separation methods are usually required. Various techniques as, for instance, precipitation with metal hydroxides, red–ox reactions, extraction, ion exchange chromatography, digestion, separation, adsorption, filtration and centrifugation can be used [3,5–11]. The choice of the pre-concentration method will depend on the determination technique to be used and several pre-concentration systems implying different initial to final concentration ratios can be considered to perform volumetric analyses.

The main technique developed in recent years to determine Cr(VI) is based on the absorption at $\lambda_{max}(H_2O)$/nm 540 of diphenylcarbazone obtained from red–ox reaction of Cr(VI) with diphenylcarbazide. The determination of Cr(VI) is also possible after reduction to Cr(III) [3,12]. Atomic absorption spectrometry with flame (FAAS) or graphite furnace detector (AAS) [1], inductively coupled plasma mass spectrometry (ICP–MS) [13] have been often used for the determination

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of total concentration of chromium. The practical use of high performance liquid chromatography (HPLC) for determining chromium species with conventional spectrophotometric detection, or its coupling with other techniques has been also described [14–20]. At industrial level, other highly evolved techniques as, for instance, coulometry [21] or capillary zone electrophoresis (CZE) [22] can be applied.

In this paper Cr(III) was determined by exploiting the slow formation of the inert violet complex with EDTA occurring at pH 2.5–6.0 under ambient conditions [23].

In particular, the quantitative complex formation can be obtained by adding an EDTA excess to the chromium solution and boiling for 30 min under a water condenser or by microwave irradiation, 3 min at 700 W [24,25]. The Cr(III)/EDTA complex is better described in solution as a mixture of the three forms $[Cr(HEDTA)H_2O]$ (violet), $[Cr(EDTA)(OH)]^{2-}$ (blue) and $[Cr(EDTA)(OH)_2]^{3-}$ (green), the first being the predominant one in non-alkaline media [26].

Volumetric determination of the aqueous violet Cr(III)/EDTA complex at a concentration higher than 4×10^{-4} M is impracticable because the strong colour masks the end-point of the EDTA excess back-titration using different indicators in non-alkaline media [27–33]. Here, an appropriate mixture of 4-(2-pyridylazo)-resorcinol (PAR) indicator and naphthol green β (NGβ), added as inert dye, has been used to highlight the colour transition of the back-titration end-point for a concentration range of Cr(III)/EDTA complex equal to ca. $3.6 \times 10^{-4} - 2.5 \times 10^{-3}$ M at pH 6.60 [34–36]. Successful results, validated by FAAS, can be obtained by finding a compromise between PAR and NGβ concentrations used to carry out titrations. The evolution of colour changes of the new screened metallochromic indicator under the above experimental conditions has been studied by applying the specific colour discrimination (SCD) and L^*, a^*, b^* parameters reported in literature [37–45]. Moreover, an actual effluent deriving from a leather industry was successfully analyzed after a mineralization pretreatment by FAAS method and the reported EDTA back-titration.

2. Experimental

2.1. Reagents and materials

$CrCl_3 \cdot 6H_2O$ 1003 μg/ml (Aldrich, Milwaukee, WI, USA), glacial acetic acid, nitric acid 65%, sulfuric acid 96%, hydrochloric acid 30% and hydrogen peroxide 30% (J.T. Backer, Deventer, Holland), sodium acetate and sodium hydroxide (Carlo Erba, Milan, Italy) were all of analytical grade.

The following solutions were prepared: 1 M acetic acid and 0.048 M Cr(VI) ex $K_2Cr_2O_7$ (J.T. Backer, Deventer, Holland), 1 M sodium acetate, 1.5×10^{-2} M and 5×10^{-3} M standard EDTA ex $Na_2 \cdot 2H_2O \cdot$EDTA (Carlo Erba, Milan, Italy), 3.485×10^{-3} M ethanol–water 3:1 solution of 4-(2-pyridylazo)-resorcinol, 3.415×10^{-3} M naphthol green β, 0.01 M Ca(II) by using $Ca(OAc)_2$ and 0.57 M ascorbic acid (Fluka, Milan, Italy), 0.01 M Zn(II) by diluting a 0.05 M zinc sulphate solution (Aldrich, Milwaukee, WI, USA).

A UV–vis double-beam "Shimadzu" spectrophotometer, UVPC 2401 model, equipped with 1 cm cells, an ionic chromatography (IC) "Dionex", DX-120 model, a flame atomic absorption double beam spectrophotometer (FAAS) "Varian", AA20-Plus model, a heating digester (HG), "DK" model, a pH meter WTW-340i/SET and a microwave system DAEWOO KOR-63M5A with 700 W microwave irradiation were used.

2.2. Determination of chromatic parameters

The end-point detection of metallochromic back-titration was studied as colour transition of the reaction for values of the titrant (excess EDTA concentration) and titrand (Zn(II) concentration) ratio in the range 1.06–0.94 and in step of 0.02.

From the U.V. spectra recorded during back-titrations, the tristimulus values X, Y and Z were determined by using the "weighed ordinate method" ($\Delta\lambda = 10$ nm) providing the following expressions:

$$X = \sum \bar{x}ET\,\Delta\lambda \qquad Y = \sum \bar{y}ET\,\Delta\lambda \qquad Z = \sum \bar{z}ET\,\Delta\lambda$$

where $\bar{x}E$, $\bar{y}E$ and $\bar{z}E$ (the product of the energy distribution values and tristimulus of pure spectrum colours) are values selected at different wavelengths in the range 380–770 nm for the standard illuminant C and T is the transmittance [37]. The true colour coordinates are given by:

$$x = \frac{X}{X+Y+Z} \qquad y = \frac{Y}{X+Y+Z} \qquad z = \frac{Z}{X+Y+Z}$$

The chromaticy values of the International Commission on Illumination (ICI) were chosen according to the recommendations of Reilley et al. for specifications on colour transition of visual indicators [38,39].

ICI suggested the use of absorbance instead of transmittance values in tristimulus colorimetry calculations in order to determine complementary chromaticy coordinates: Qx, Qy.

Bhuchar et al. determined the specific colour discrimination as a measure of the quality of colour changes as given by [40]:

$$\mathrm{SCD} = \frac{1}{2}1000\frac{\Delta\sigma}{\Delta(CL/CM)}$$

where

$$\Delta\sigma = [(U_2 - U_1)^2 + (V_2 - V_1)^2]^{1/2}$$

and

$$U = 0.075 - \frac{0.823(x+y-1)}{x - 7.05336y - 1.64023}$$

$$V = \frac{3.69700x - 5.07713y - 1.36896}{x - 7.05336y - 1.64023} - 0.50000$$

The $U-V$ parameters were determined by Breckenridge and Schaub; CL/CM represents the concentration of the ligand over the concentrations considered for the metal ion [40].

In 1976 the "Commission Internationale de l′Eclairage" (CIE) recommended the use of the chromaticy coordinates L^*,

a^* and b^* for the specification of colours according to the following expressions [41–45]:

$$L^* = 116\left(\frac{Y}{Yn}\right)^{1/3} - 16$$

$$a^* = 500\left[\left(\frac{X}{X_n}\right)^{1/3} - \left(\frac{Y}{Y_n}\right)^{1/3}\right]$$

$$b^* = 200\left[\left(\frac{Y}{Y_n}\right)^{1/3} - \left(\frac{Z}{Z_n}\right)\right]^{1/3}$$

where X, Y and Z are tristimulus values of the solution and $X_n = 98.041$, $Y_n = 100.000$, $Z_n = 118.103$ [37]. The chromaticy difference between two colours is given by:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

A PC computer program written in ISO C++ for the "weighed ordinate method", with coefficients of standard illuminant C and 2° standard observer chosen as reference systems, was used for determining all parameters (absorbance values were used in input and Qx, Qy, L^*, a^*, b^*, ΔE, SCD were obtained in output).

The following solutions were prepared to determine the chromatic parameters: an appropriate amount (4.65, 10.20, 17.00, 24.00, 32.6 ml, respectively) of 1003 μg/ml Cr(III) standard solution was added to 71.4 ml of 0.015 M EDTA solution. The pH was adjusted to 4.75 with an appropriate acetate–acetic acid buffer solution, and the Cr(III)/EDTA complex quantitatively formed after microwave, 3 min at 700 W. Sodium hydroxide and sodium acetate were added until the pH 6.60 was achieved. The volume of the solution was increased with de-ionized water up to 250 ml to obtain a total concentration of EDTA equal to 4.284×10^{-3} M and Cr(III)/EDTA complex concentrations ranging between 3.59×10^{-4} M and 2.515×10^{-3} M. NGβ (350 μl) and PAR (100 μl) were added to an aliquot (35 ml) of the above solution and, after the required volume (depending from the CL/CM ratio) of 9.765×10^{-3} M $ZnSO_4$ solution as back-titrant was added; the total volume was adjusted to 100 ml. The absorbance values at different values of CL/CM were recorded in the wavelength range 300–800 nm, while the wavelengths used for the weighed ordinate method were in the 380–770 nm range. Small amounts of sodium acetate were added during the titration with Zn(II) to maintain the pH value at 6.60.

2.3. Cr(VI) to Cr(III) reduction and determination of Cr(III) and Zn(II) in the presence of Ca(II)

An appropriate volume of $K_2Cr_2O_7$ solution 0.048 M (3.536 g of powder previously dried at 130° C for 2 h in 0.5 l of de-ionized water), 2 ml of ascorbic acid solution (10 g in 100 ml of de-ionized fresh prepared water) [25], 25 ml of $ZnSO_4$ 9.765×10^{-3} M and 50 ml of calcium acetate 0.0104 M were mixed in a 0.5 l beaker. After adjusting the pH value to 4.75, with an acetate–acetic acid buffer solution, Cr(VI) to Cr(III) reduction was completely achieved. Sodium hydroxide and sodium acetate were added up to pH 6.60. Total volume of solution was increased up to 250 ml by using de-ionized water to obtain Cr(III), Zn(II) and Ca(II) concentrations equal to 1.152×10^{-3} M, 9.76×10^{-4} M, 2.080×10^{-3} M, respectively. PAR was added (100 μl) to an aliquot of 35 ml of the above solution containing the three metal species, and only Zn(II) was straightforwardly titrated with EDTA 5×10^{-3} M (pH was held at 6.60) because both Ca(II) and Cr(III) are not complexed by EDTA at the given experimental conditions.

Another solution was prepared in the same way, with the difference that an appropriate volume of standard 0.015 M EDTA was added and 3 min microwave irradiation at 700 W was applied. Consequently Cr(III)/EDTA, Zn(II)/EDTA, Ca(II) and excess EDTA concentrations were 1.152×10^{-3} M, 9.76×10^{-4} M, 2.080×10^{-3} M, 2.156×10^{-3} M, respectively.

An aliquot of 35 ml of this second solution was back-titrated with a 9.765×10^{-3} M standard solution of Zn(II) maintaining the pH at 6.60 and by using 350 μl of NGβ and 100 μl of PAR.

From the difference between the volumes used in the two titrations above described, Cr(III) and Zn(II) concentrations were determined.

Table 1
Instrumental parameters employed to determine Cr by FAAS

Wavelength (nm)	357.9
Flame	Air–acetylene
Lamp (mA)	7
Slit width (mm)	0.2

2.4. Analyses of the synthetic samples

The chromium standard solutions prepared as above described in the determination of chromatic parameters section were diluted with distilled water in a 6:250 ratio and analyzed by FAAS. The instrumental parameters employed to determine Cr by FAAS are presented in Table 1.

2.5. Analyses of the wastewater

An aliquot of the diluted wastewater sample was analyzed by ionic chromatography to verify the presence of fluoride often added to this kind of effluents. The instrumental parameters employed by IC are presented in Table 2. In a heating digester, the wastewater sample (6 ml) was mineralized in two steps: (a) nitric acid and hydrogen peroxide (10 ml and 5 ml, respectively) were added and the temperature was maintained at 250 °C until the end of red-brown gas; (b) sulfuric acid (10 ml) was added, the temperature was maintained at 250 °C and when a total volume

Table 2
Instrumental parameters employed to verify the presence of fluoride by ionic chromatography (IC)

Injection volume	20 μl
Sample dilution	1:1000
Column	Ion Pac AS14A, 4 × 250 mm
Eluent	2.5 mmol/L in Na_2CO_3, $NaHCO_3$
Flow	1.0 ml/min.
Retention time of fluoride	4.3 min.

of ca. 5 ml was achieved, the solution was allowed to reach room temperature. NaOH solution was used to adjust the pH up to 3.5 and the resulting solution was prepared and analyzed by EDTA back-titration by using the newly screened metallochromic indicator.

FAAS analyses were carried out to validate the method by mineralization treatment and diluting the sample in 6:250 and 1:50 ratio with distilled water.

3. Results and discussion

The formation of EDTA–metal complexes of some bivalent and trivalent transitional elements is quantitative (metal:EDTA ratio is equal to 1:1) at ca. pH 6.5, whereas metals of IA and IIA groups virtually do not react with EDTA. 4-(2-Pyridylazo)-resorcinol shows a strong yellow-green colour in the pH range 6.6-7.0 and a maximum of absorbance at ca. 410 nm, while Cr(III)/EDTA complex shows an absorption at ca. 545 nm corresponding to a strong violet colour becoming less significant at neutral pH values.

The pH 6.60 was chosen to carry out the back-titrations as a compromise among the above factors. In fact, it is worth noting that (i) the maximum of absorbance for Cr(III)/EDTA complex at pH 6.60 is less important (ca. −10%) than at pH 5.00 [$\lambda_{max}(H_2O)$/nm 545, ε/l mol^{-1} cm^{-1}180, at pH 6.60, while $\lambda_{max}(H_2O)$/nm 545, ε/l mol^{-1} cm^{-1} 200, at pH 5.00], (ii) the used indicator 4-(2-pyridylazo)-resorcinol in non-alkaline media shows a maximum of absorbance in the pH range 6.6–7.0 ($\lambda_{max}(H_2O)$/nm 411, ε/l mol^{-1} cm^{-1} 36516, at pH 6.60), (iii) the maximum of absorbance of naphthol green β ($\lambda_{max}(H_2O)$/nm 714, ε/l mol^{-1} cm^{-1} 8373) is quite pH independent, (iv) the concentration of Ca(II) (2.918 mg in 35 ml) does not interfere and (v) the presence of 2.233 mg Zn(II) in 35 ml gives rise only to uncoloured metal–EDTA complexes in back-titrations.

The following expression derived from the Lambert–Beer law can be used when PAR, NGβ and Cr(III)/EDTA complex were simultaneously present in solution:

$$\mathrm{Abs}_\lambda = \sum_{i=1}^{n} \varepsilon_\lambda^i b c_i$$

Abs_λ and ε_λ^i represent the absorbance and the molar extinction coefficient for each species at the chosen wavelength, respectively, c_i is the molar concentration and b the optical path. Four absorbance spectra representative of the colour changes at pH 6.60 are reported in Fig. 1.

Fig. 1 shows the effect due to 350 μl of NGβ (3.415×10^{-3} M) added to a 1.312×10^{-3} M Cr(III)/EDTA solution (a plot before the addition, b plot after the addition) and the effect of the addition of Zn(II) to 1.312×10^{-3} M Cr(III)/EDTA solution in the presence of 350 μl of NGβ and 100 μl of PAR (3.485×10^{-3} M) for two different CL/CM values close to 1 (c plot before equivalent point, d plot after equivalent point). The 1.312×10^{-3} M concentration gave rise to the most appreciable blue colour because the intensity of the absorbance at $\lambda_{max}(H_2O)$/nm 545 for Cr(III)/EDTA complex

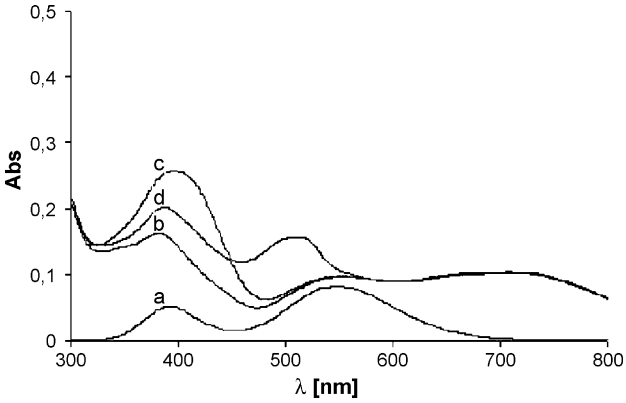

Fig. 1. Absorbance vs. wavelength (a) 1.312×10^{-3} M Cr(III)/EDTA complex, violet colour (b) 1.312×10^{-3} M Cr(III)/EDTA complex + NGβ, blue colour (c) 1.312×10^{-3} M Cr(III)/EDTA complex + NGβ + PAR + Zn(II), CL/CM = 1.02, green colour (d) 1.312×10^{-3} M Cr(III)/EDTA complex + NGβ + PAR + Zn(II), CL/CM = 0.98, red colour. These solutions were made up to 100 ml.

and the intensity of the absorbance at $\lambda_{max}(H_2O)$/nm 714 for NGβ were in ca. 1:1 ratio (see Fig. 1, a and b plots). Saturation in the visible range and a minimum at 472 nm (blue colour) can be observed in b plot, due to the addition of NGβ. From Fig. 1 it can be deduced that the addition of Zn(II) induces a transition from green (Fig. 1c plot, before the equivalent point) to red (Fig. 1d plot, after the equivalent point). In fact the intensity of the band at 411 nm decreases in d plot, while the minimum at 478 nm disappears. A new broad band at 500 nm grows and it is due to the contribution of the absorption maxima of Cr(III)/EDTA and Zn(II)/PAR complexes, at 545 and 492 nm, respectively.'

The five concentrations of Cr(III)/EDTA used for the determination of chromatic parameters were 3.59×10^{-4} M, 7.87×10^{-4} M, 1.312×10^{-3} M, 1.852×10^{-3} M and 2.515×10^{-3} M. The addition of 350 μl of NGβ induced a colour transition from violet to green for the two first concentrations, while a transition from violet to blue was observed for the other three ones. In fact, when the concentration of Cr(III)/EDTA was higher than 1.312×10^{-3} M, the violet colour of the complex was sufficiently strong to produce a blue colour in the presence of NGβ. The addition of 100 μl of PAR produced a further change to green for the three lowest concentrations, i.e. 3.59×10^{-4} M, 7.87×10^{-4} M, 1.312×10^{-3} M and to grey for the other two. It is worth noting that the optimum concentration of complex is equal to 1.312×10^{-3} M and it was selected as an example (see Fig. 1) not only because the grey colour was never observed in this case during the addition of the reagents but also because the colour changes were clearly visible.

By increasing NGβ and Cr(III)/EDTA concentrations in such a way that the ratio between the intensities of the maximum absorption peaks (blue colour) resulted 1:1 and by adding PAR, the colour of the solutions became black and the end-point titration was not appreciable when Cr(III)/EDTA concentrations were higher than 1.312×10^{-3} M. The best compromise showed to be the presence of 350 μl of the screening agent because it was possible to carry out the back-titrations also for the

Table 3
Complementary chromaticity coordinates for the colour changes of Cr(III)/EDTA with screening agent and indicator

Cr(III) [mol × l^{-1}]	Cr(III)/EDTA		Cr(III)/EDTA + naphtol green β		Cr(III)/EDTA + naphtol green β + PAR	
	Qx	*Qy*	*Qx*	*Qy*	*Qx*	*Qy*
3.59×10^{-4}	0.3381	0.4592	0.3355	0.2735	0.2740	0.1873
7.87×10^{-4}	0.3392	0.4600	0.3373	0.3125	0.2861	0.2305
1.312×10^{-3}	0.3383	0.4585	0.3368	0.3437	0.2964	0.2719
1.852×10^{-3}	0.3382	0.4608	0.3375	0.3651	0.3009	0.2956
2.515×10^{-3}	0.3393	0.4624	0.3379	0.3834	0.3064	0.3204

The reported values are the average of six determinations.

Table 4
Complementary chromaticity coordinates for the colour changes of Cr(III)/EDTA back-titrations with Zn(II) and PAR + NGβ as screened indicator

CL/CM	3.59×10^{-4} M Cr(III)/EDTA		7.87×10^{-4} M Cr(III)/EDTA		1.312×10^{-3} M Cr(III)/EDTA		1.852×10^{-3} M Cr(III)/EDTA		2.515×10^{-3} M Cr(III)/EDTA	
	Qx	*Qy*	*Qx*	*Qy*	*Qx*	*Qy*	*Qx*	*Qy*	*Qx*	*Qy*
1.06	0.2744	0.1860	0.2860	0.2303	0.2960	0.2713	0.3011	0.2957	0.3065	0.3201
1.04	0.2736	0.1850	0.2864	0.2305	0.2960	0.2713	0.3012	0.2953	0.3066	0.3202
1.02	0.2733	0.1843	0.2860	0.2300	0.2964	0.2713	0.3010	0.2953	0.3066	0.3204
1	0.2717	0.1876	0.2845	0.2324	0.2961	0.2723	0.2998	0.2978	0.3066	0.3208
0.98	0.2359	0.2516	0.2581	0.2761	0.2716	0.3045	0.2795	0.3219	0.2884	0.3424
0.96	0.2348	0.2536	0.2552	0.2812	0.2702	0.3066	0.2764	0.3260	0.2858	0.3457
0.94	0.2343	0.2547	0.2548	0.2837	0.2687	0.3090	0.2757	0.3268	0.2851	0.3465

The reported values are the average of six determinations.

1.852×10^{-3} M and 2.515×10^{-3} M concentrations. The strong colour of solutions, containing concentrations of Cr(III)/EDTA complex higher than 2.515×10^{-3} M, masks the end-point of EDTA excess back-titrations and the Lambert–Beer law cannot be used to describe their UV spectra recorded during titrations.

The complementary colour coordinates of Cr(III)/EDTA complexes in the presence of NGβ and PAR, using absorbance instead of transmittance, are presented in Table 3; back-titrations were recorded at different values of CL/CM and the results are presented in Table 4.

SCD numerical values represent a quantitative measure of quality of the colour changes of chemical indicators and SCD versus CL/CM curves are reported in Fig. 2.

The CIE L^*, a^*, b^* 1976 parameters, which provide an alternative method for comparing the quality of the colour changes

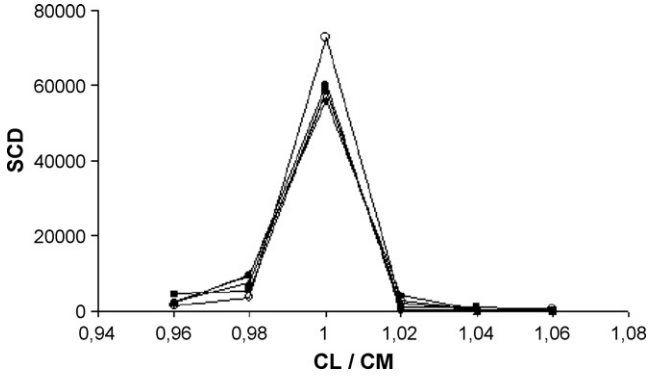

Fig. 2. SCD vs. CL/CM for Cr(III)/EDTA back-titrations with Zn(II), PAR and NGβ. The reported values are the average of six determinations. Cr(III)/EDTA: (◯) 3.59×10^{-4} M; (▲) 7.87×10^{-4} M; (■) 1.312×10^{-3} M; (♦) 1.852×10^{-3} M; (●) 2.515×10^{-3} M.

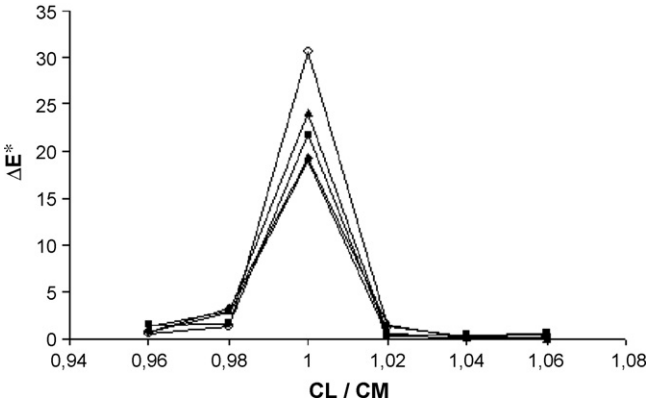

Fig. 3. ΔE^* vs. CL/CM for Cr(III)/EDTA back-titrations with Zn(II), PAR and NGβ. The reported values are the average of six determinations. Cr(III)/EDTA: (◯) 3.59×10^{-4} M; (▲) 7.87×10^{-4} M; (■) 1.312×10^{-3} M; 1.852×10^{-3} M; (●) 2.515×10^{-3} M.

of chemicals indicators, were also determined and ΔE^* versus CL/CM curves are plotted in Fig. 3. In Table 5 only the results of ΔE^* at CL/CM = 1 and SCD at CL/CM = 1 can be found.

Table 5
SCD and ΔE^* at CL/CM = 1 of Cr(III)/EDTA back-titrations with Zn(II) and PAR + NGβ as screened indicator

Cr(III) [mol × l^{-1}]	SCD at CL/CM = 1	ΔE^* at CL/CM = 1
3.59×10^{-4}	73000	31
7.87×10^{-4}	59000	24
1.312×10^{-3}	59000	22
1.852×10^{-3}	56000	19
2.515×10^{-3}	60000	19

The reported values are the average of six determinations.

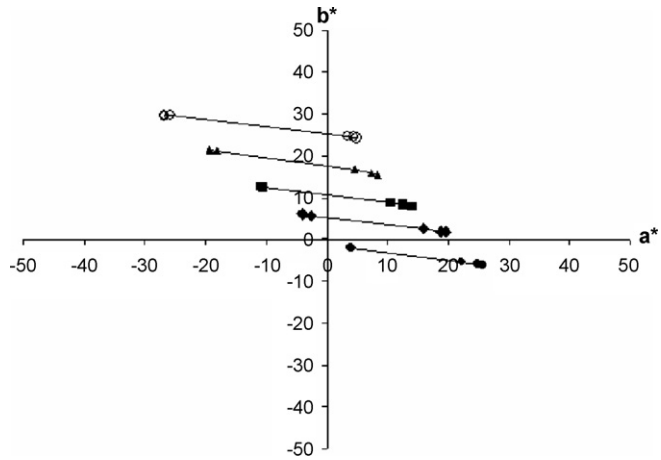

Fig. 4. Change of colour coordinates b^* vs. a^* Cr(III)/EDTA back-titrations with Zn(II), PAR and NGβ. The reported values are the average of six determinations. Cr(III)/EDTA: (◯) 3.59×10^{-4} M; (▲) 7.87×10^{-4} M; (■) 1.312×10^{-3} M; (♦) 1.852×10^{-3} M; (●) 2.515×10^{-3} M.

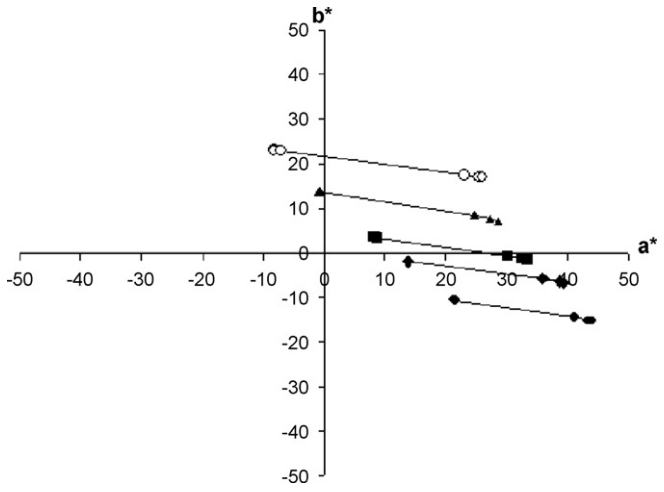

Fig. 5. Change of colour coordinates b^* vs. a^* for Cr(III)/EDTA back-titrations with Zn(II) and PAR. The reported values are the average of six determinations. Cr(III)/EDTA: (◯) 3.59×10^{-4} M; (▲) 7.87×10^{-4} M; (■) 1.312×10^{-3} M; (♦) 1.852×10^{-3} M; (●) 2.515×10^{-3} M.

The plots in Figs. 2 and 3 reporting the results at CL/CM ratio between 1.06 and 0.94, show a peak at CL/CM = 1 for all Cr(III)/EDTA concentrations but the highest quantitative colour transition of back-titrations for both methods were obtained by using the lowest concentration of complex.

Similar values were determined for SCD parameter at CL/CM = 1 when the Cr(III)/EDTA complex concentration was between 7.87×10^{-4} M and 2.515×10^{-3} M, corresponding to a colour levelling effects. On the contrary, ΔE^* parameter (at CL/CM = 1) shows a levelling effect only for 1.852×10^{-3} M and 2.515×10^{-3} M concentrations.

It is known that the best appreciable colour variation, at the back titration end point, occurs when transition curve starts from the grey zone or cross it (see Fig. 4). For this reason, although ΔE^* and SCD at CL/CM = 1 present low values for the highest concentrations of Cr(III)/EDTA complex used in this work, the titration can still be successfully carried out.

In Figs. 4 and 5 b^* versus a^* is reported, during the back-titrations, for PAR in the presence and in the absence of NGβ, respectively.

When NGβ and PAR were both present, the best quality of colour change was appreciated for all of the five concentrations of Cr(III)/EDTA complex investigated because transition curves for the three lowest concentrations lie in two different quadrants and colour change at the equivalent point is easily appreciable. On the contrary the two highest concentrations showed a sharp transition from grey zone to red-wine colour at the back-titration's equivalent point.

For Cr(III)/EDTA concentrations larger than 7.87×10^{-4} M, PAR transition curves (see Fig. 5) changed only the saturation of the colour without a significant hue variation; consequently the use of PAR indicator results in a bad equivalent point.

A number of visual titrations with "single" and "screened indicator" were carried out and the results are presented in Table 6. At a 3.59×10^{-4} M complex concentration, the results were not different by using the "single" or the "screened indicator", but NGβ was necessary to carry out successfully the back-titrations for concentrations ranging between 7.87×10^{-4} M and 2.515×10^{-3} M (1.43–4.58 mg in 35 ml in Table 6). It is worth noting that the results of back-titrations to determine concentrations of Cr(III)/EDTA complex lower than 3.59×10^{-4} M (uncoloured solutions), by using the chosen volume of the "single" or "screened" indicator, were equal and the

Table 6
Visual titrations with a "single" (PAR) and "screened" (PAR + NGβ) indicator

Indicator	Cr(III) taken (mg in 35 ml)	Cr(III) found (mg in 35 ml)[a]	CV%[b]	Error %
PAR	0.65	0.66	2.70	1.5
PAR + NGβ		0.66	2.70	1.5
PAR	1.43	1.41	2.30	−1.4
PAR + NGβ		1.42	1.13	−0.7
PAR	2.39	2.33	3.10	−2.5
PAR + NGβ		2.38	0.69	−0.4
PAR	3.37	3.08	9.25	−8.6
PAR + NGβ		3.36	0.62	−0.3
PAR	4.58	3.41	15.67	−25.5
PAR + NGβ		4.57	0.55	−0.2

[a] Average of six determinations.
[b] Relative standard deviation percentage of six determinations.

Table 7
The comparison between the EDTA back-titration with Zn(II) by using the new screened metallochromic indicator and FAAS analyses of standard solutions

Cr(III) taken (mg in 35 ml)	Cr(III) found (mg in35 ml) by back-titration[a]	Cr(III) found (mg in 35 ml) by FAAS[a]
0.65	0.66 ± 0.019	0.66 ± 0.015
1.43	1.42 ± 0.017	1.44 ± 0.032
2.39	2.38 ± 0.017	2.40 ± 0.026
3.37	3.36 ± 0.022	3.39 ± 0.028
4.58	4.57 ± 0.026	4.57 ± 0.024

[a] The confidence interval ($P = 0.95$) was obtained for six determinations.

limit of quantification of all volumetric determinations reported in literature is 1×10^{-4} M [27–35].

The comparison between the proposed method and FAAS analyses of the used standard solutions is reported in Table 7. The results of back-titrations not only are very close to the figures of the chromium standard solutions but also show good agreement with FAAS.

Finally a wastewater effluent deriving from an Italian leather industry was analyzed by FAAS method and by EDTA back-titration using the newly screened metallochromic indicator. It is worth noting that a preliminary oxidation treatment (see Experimental section) was necessary to eliminate all the organic species present and the interference due to chromium fluoride complexes.

The total concentrations determined by EDTA back-titration [4653 ± 38 mg/l of Cr (confidence interval, $P = 0.95$) was obtained for six determinations] and by FAAS method [4699 ± 67 mg/l of Cr (confidence interval, $P = 0.95$) was obtained for six determinations] show good agreement.

4. Conclusions

4-(2-Pyridylazo)-resorcinol (100 μl, 3.5×10^{-3} M) and naphthol green β (350 μl, 3.4×10^{-3} M) as new screened metallochromic indicator, in the presence of Ca(II) and uncoloured metal–EDTA complexes at pH 6.60, were used to determine Cr(III)/EDTA complexes between 3.6×10^{-4} M and 2.5×10^{-3} M concentrations by means of EDTA back-titrations with Zn(II). To determine lower Cr(III)/EDTA complex concentrations (uncoloured solutions) only the above volume of indicator can be used while for higher ones the Cr(III)/EDTA complex colour masks the back-titrations end point.

A fast and accurate volumetric determination could represent a good choice to determine Zn(II) and Cr(III) in the presence of metals of IIA group, as for instance Ca(II), in wastewater showing large and variable concentrations of both Cr(VI) and Cr(III). Moreover, the method was successfully used after a preliminary mineralization treatment to inspect an actual effluent deriving from a leather Italian industry.

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