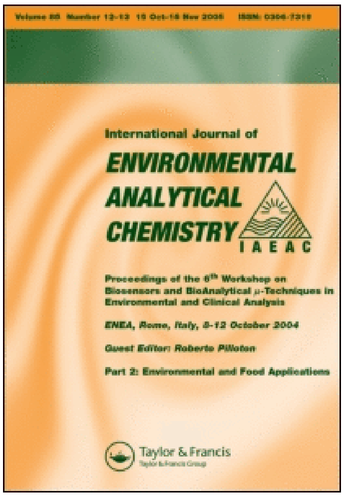

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Flores-Vélez, L. M. , Gutiérrez-Ruiz, M. E. , Reyes-salas, O. , Cram-heydrich, S. and Baeza-reyes, A.(1995) 'Speciation of Cr(VI) in Soil Extracts by Polarographic Methods', International Journal of Environmental Analytical Chemistry, 61: 3, 177 — 187

To link to this Article: DOI: 10.1080/03067319508027232

URL: http://dx.doi.org/10.1080/03067319508027232

Intern. J. Environ. Anal. Chem., Vol. 61, pp. 177–187
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Printed in the Malaysia

SPECIATION OF Cr(VI) IN SOIL EXTRACTS BY POLAROGRAPHIC METHODS

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(Received, 31 August 1994; in final form, 22 November 1994)

Polarography is very suitable to determine Cr(VI) in soil extracts. The best supporting electrolyte is NaOH 0.1 M. The detection limit (DL) of differential pulse polarography (DPP) for Cr(VI) was 1.59×10^{-5} M, and for Cr(III) was 2.85×10^{-5} M. The extraction of Cr(VI) was carried out with tris-NaOH at pH 13. Recovery of this element added to an anthrophic soil of a lacustrine zone was 98.6%. Two signals were observed by DPP in basic extracts from soils contaminated with Cr(VI) and equilibrated at pH 2 and 4. One corresponded to the Cr(VI)/Cr(III) system. The other was asymmetric and disappeared with the addition of CrO_2^{-2}. This signal can be related to a chromium-natural organic matter interaction (Cr-NOM). The soluble humic acids have the same suppressing effect of Triton-X-100, inhibiting the appearance of a polarographic maxima. The formation of a Chromium (III) oxidized organic matter chelate (Cr(III)-NOMox) is discussed.

KEY WORDS: Chromium speciation, humic acids, natural organic matter, differential pulse polarography.

INTRODUCTION

The average concentration of chromium in non-polluted soils according to Pinta and Aubert is 100 mg/kg[1]. Much higher concentrations (several thousand mg/kg) can be found in soils of old sites of chrome plating plants and "sewage farms" of the leather industry. Hexavalent chromium is toxic to animals and plants, due to its strong oxidant properties. Trivalent chromium is considered to be less toxic[2]. Differences in oxidation states affect the equilibrium of this element in the environment, especially the solubility and the adsorption to natural particles[3]. Soil is a complex system where organic and inorganic species coexist in a dynamic equilibrium between solid, liquid and gaseous phases. Therefore, speciation is very useful to assess the potential hazards of pollutants in soils and sediments.

Naturally occurring chromium in soils is mostly insoluble[1]. Anthropogenic chromium (VI) added to the soil (generally as a soluble salt), may be leached, adsorbed, reduced and/or precipitated, depending on the pH and redox conditions. In most alkaline and neutral systems, Cr(VI) species remain anionic and mobile as $HCrO_4^{-1}$ and CrO_4^{2-}. Under acidic conditions, hexavalent chromium compounds are removed from solution by adsorption into positively charged sorption sites[4,5] or are reduced. The more common reducing agents are Fe(II), organic compounds and H_2S[5–7]. Organic compounds can be expected to behave as the primary reductants for Cr(VI) species in surface soils[4].

Bartlett and Kimble[6] obtained experimental evidence of a rapid reduction of Cr(VI) in even slightly alkaline humic soils. Bloomfield and Pruden[8] refuted this result proposing that the reduction of Cr(VI) takes place during the diphenylcarbazide (DPCl) colorimetric determination, when sulfuric acid is added to the soil extract containing soluble natural organic matter (NOM). These uncertainties are mostly due to the lack of analytical methods to speciate chromium in a complex matrix. In this study polarographic methods were applied to speciate chromium in order to establish an analytical method. If the reduction of Cr(VI) with humus on neutral or basic conditions is confirmed, the use of natural organic matter to remediate polluted soils or sediments[9] can be encouraged.

EXPERIMENTAL SECTION

Reagents

Analytical grade reagents were used throughout and were prepared in acid rinsed glassware. The humic acid solution was prepared with humic acid sodium salt (Aldrich) and distilled water, resting 48 hours, until the equilibrium was reached.

The 0.1 M NaOH was prepared by dissolving NaOH in distilled water. Tris-NaOH (0.2 M pH 13) was made by dissolving Tris (hidroxymethyl)-aminomethan in distilled water, adjusting the pH with NaOH. Cr(VI) standards were prepared with distilled water and a stock solution of $K_2Cr_2O_7$. The solution of Cr(III) was prepared by dissolving $Cr_2(SO_4)_3$ in a basic medium (NaOH). Adjustments of the pH were made with H_2SO_4. For the polarographic measurements triply distilled mercury (Merck) was used.

Equipment

Polarograph: Metrohm 663 VA Stand series 0.5.
Atomic adsorption spectrometer: Varian model SpectrAA 400A.

Procedure

Soil characterization

The soil samples were prepared with the superficial layer of an anthropic soil from a lacustrine zone of Xochimilco, D. F. Mexico. The following routine analyses were carried out: pH, bulk density, electric conductivity and % organic carbon[10]. Total chromium in the soil was determined by adapting two acid microwave digestion techniques[9,11,12] and by atomic absorption spectrometry (Table 1).

Sample treatment

Four treatments were tested:

I) Soil at pH 8.5 + Cr(VI); II) Soil at pH 4.0 + Cr(VI); III) Soil at pH 2.0 + Cr(VI); IV) Pure humic acid at pH 2.0 + Cr(VI)

Table 1 Soil parameters.

pH water (1:5)	8.80 ± 0.02
pH $CaCl_2$ (1:5)	8.51 ± 0.01
% organic carbon	5.36 ± 0.24
% lost on ignition o.d.s	6.99 ± 0.19
elect. conduct.($dScm^{-1}$)	7.52 ± 0.02
saturation point (mL/250 g)	271.20 ± 0.02
bulk density (g/cm^3)	0.564 ± 0.007
CEC (meq/100 g)	53.29 ± 0.24
color (dry sample)	brownish grey
color (moist sample)	black
total chromium (mg/kg)	164.4 ± 4.79

Two grams of air-dried soil or humic acids were shaken with 10 mL of water overnight. The pH was adjusted with sulfuric acid. Potassium dichromate was added to get a final concentration of 3.52×10^{-3} M, and then the suspension was shaken for 48 hours. The experiments and analysis were carried out in triplicate, in 200 mL polyethylene bottles washed previously with HNO_3 and rinsed with distilled water.

Chromium extraction

Two methods were tested:

a) extraction with Tris 0.2 M at pH = 9.85 as Bloomfield and Pruden reported[8], and
b) extraction with Tris 0.2 M at pH = 13.

Each sample was extracted three times by overnight shaking with 50 mL of Tris-NaOH solution, centrifuging for 20 minutes and decanting. The final extract was made up to 100 mL with the corresponding solution (Tris pH 9.85 or Tris pH 13).

Polarographic chromium determination

Direct current polarography (DC) was used to determine the half wave potentials of Cr(VI) and Cr(III), and differential pulse polarography (DPP) was applied to quantify Cr(VI) in soil extracts (pulse E = 10 mV, t_{max}= 1 sec). The supporting electrolyte was 0.1 M NaOH, with an effective voltage range of 0.00 V to −2.10 V. The classic arrangement of three electrodes was adopted: mercury dropping as working electrode, Ag/AgCl/KCl (3M) as reference electrode and platinum as counter electrode. Dissolved oxygen in the solutions was eliminated by bubbling purified nitrogen gas during 5 minutes. Curves of Δi vs. E for the following systems (with varying chromium concentrations), were attained: Cr(III); Cr(III) + soil extract; Cr(VI); Cr(VI) + soil extract; treatment I; treatment II; treatment II + Cr(III); treatment III; treatment IV.

Electrocapillary curves cyclic voltammograms of humic acids with and without Triton-X-100 were obtained to analyze the influence of organic matter on the mercury dropping electrode.

The detection and quantification limits for chromium by DPP and AAS (flame), are: Technique DPP, Cr(VI) detection limit (3σ) 1.59×10^{-5}, quantification limit (10σ) 3.03×10^{-5} M; Technique DPP, Cr(III) detection limit (3σ) 2.85×10^{-5}, quantification limit

(10σ) 2.75×10^{-4} M; Technique AA (flame), Cr(total), detection limit (3σ) 9.15×10^{-7}, quantification limit (10σ) 2.46×10^{-6} M.

RESULTS AND DISCUSSION

Chromium extraction

The Tris solution 0.2 M at pH 9.85 did not extract the 100% of the Cr(VI) added to the soil as Bloomfield reported[8]. The recovery percentages obtained were lower than 90%. Increasing the pH to 13, the recovery percentage reached 98.6%. This means that strong alkaline media are efficient for the desorption of chromium in soils. The parental chromium of the soil was not extracted with Tris 0.2 M pH 13 (detection limit with AAS 9.15×10^{-7} M).

Recovery (%) of extractable chromium: Tris pH 9.85, 87.5 ± 2.6%; Tris pH 13, 98.6 ± 2.2%.

Polarographic chromium determination

DPP enables the identification of chromium species (VI) and (III) in a strong alkaline media such as is needed to extract chromium from soils. The best supporting electrolyte under these experimental conditions is NaOH (0.1 M) with a voltage range of 0.00 V to −2.10 V. Under this condition the Cr(VI)/Cr(III) and Cr(III)/Cr(II) Systems behave as non-nernstian. In the presence of soil extract and humic acid, the peak potential, Ep, for Cr(VI) = −1.11 V and for Cr(III) = −1.84 V shift slightly to more negative values [Cr(VI) = −1.13 V and Cr(III) = −1.87 V]. These are shown in Figures 1–4.

Cleven *et al.*[13] studied the Zn/HA (humic acid) and Zn/PAA (polyacrilic acid) systems and concluded that the slope of the Δi vs concentration graph is reduced as compared to the calibration graph, indicating binding of Zn^{2+}.

The complexes formed has smaller diffusion coefficients, which controlled the polarographic current. In our case similar phenomenon were observed in the presence of soil extracts and humic acid. The slope of the graphs of Δi vs concentration decreases, due to the macromolecular character of humic acid which reduces the diffusion coefficient. Also the apparent half wave potentials of both system: Cr(VI)/Cr(III) and Cr(III)/Cr(II) shift to more negative values. Ernst *et al.*[14] an Cleven[15] explained such shifts as being a results of complexation, but it requires the following conditions to be satisfied: the electrode reaction should be electrochemically reversible and the values of the $E_{1/2}$ should be sufficiently large, at least more than 25 mV. These conditions are no satisfied in CrVI-DOM associations. The system is irreversible and the shifts are smaller than 5 mV.

Cr(VI) in soil treatment

The Cr(VI) recovery of the amount initially added to the soil at pH 8.5 was 98.6%. In the pH 4 sample the recovery was only 47.3% and for the pH 2 sample, 42.5%. In this case the polarograms were different from those obtained for the soil at pH 8.5.

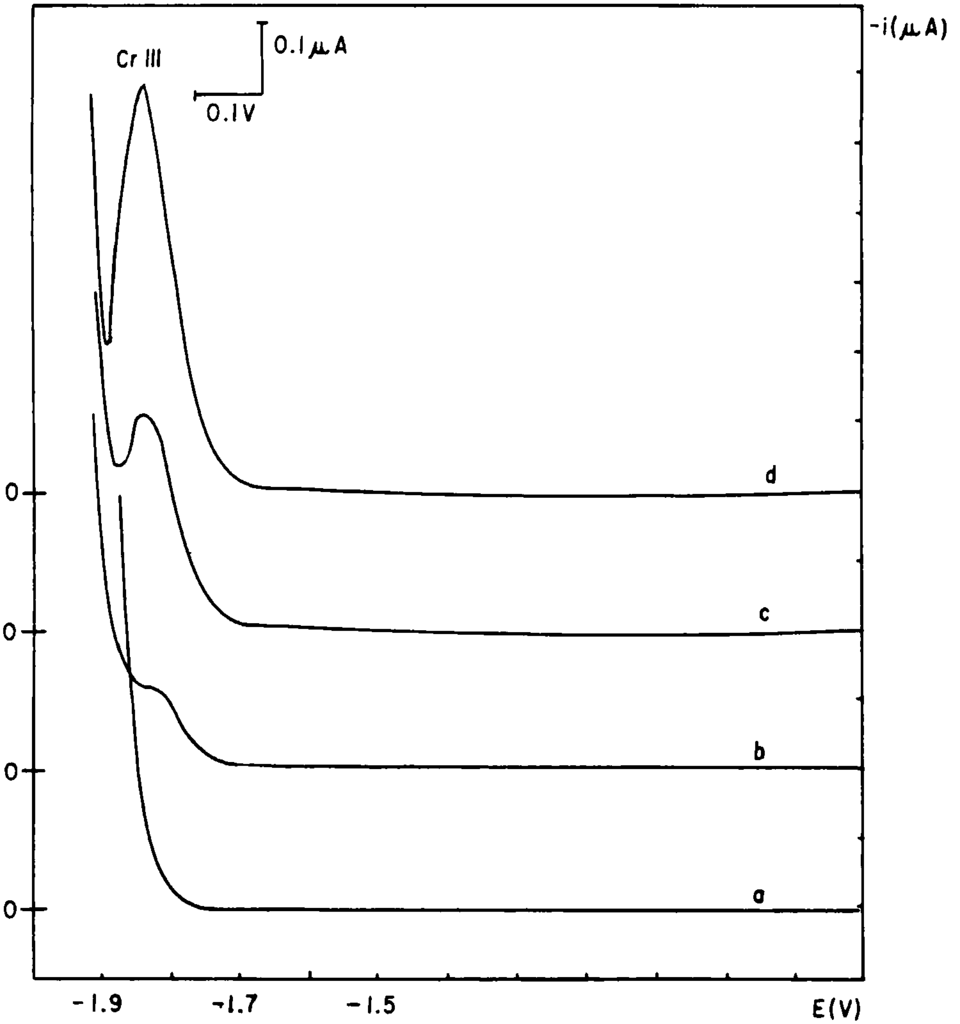

Figure 1 DPP for Cr(III) at different concentrations in 0.1 M NaOH. a) supporting electrolyte (0.1 M NaOH), b) 0.1 M NaOH plus 1.99 × 10^{-4} M Cr(III), c) 0.1 M NaOH plus 3.99 × 10^{-4} M Cr(III) and d). 0.1 M NaOH plus 4.99 × 10^{-4} M Cr(III). $\Delta E = 10$ mV; $t_{max} = 1$ sec.

Measurement of the DDP peak at 1.13 V, with and without Cr(III) gave the following results: Initial chromium (VI) concentration 3.5 × 10^{-3} M; pH 8.5, % Cr(VI) extracted with Tris pH = 13 without Cr(III) 98.6 ± 2.2, with Cr(III) 98.6; (b) pH 4, % Cr(VI) extracted with Tris pH = 13 without Cr(III) 47.3 ± 1.4, with Cr(III) 99.1; (c) pH 2, % Cr(VI) extracted with Tris pH = 13 without Cr(III) 42.5 ± 1.4, with Cr(III) 98.8.

Figure 4 illustrates the results of treatment I), in which only one signal can be seen: the reduction of Cr(VI) to Cr(III). In the treatments II) and III) two signals were observed, one corresponds to the reduction of Cr(VI)/Cr(III), and the other, asymmetric, that disappears with the addition of CrO_2^-. Simultaneously, the Cr(VI)/Cr(III) signal increases until its area corresponds to the Cr(VI) originally added, as can be seen in Figures 5 and 6.

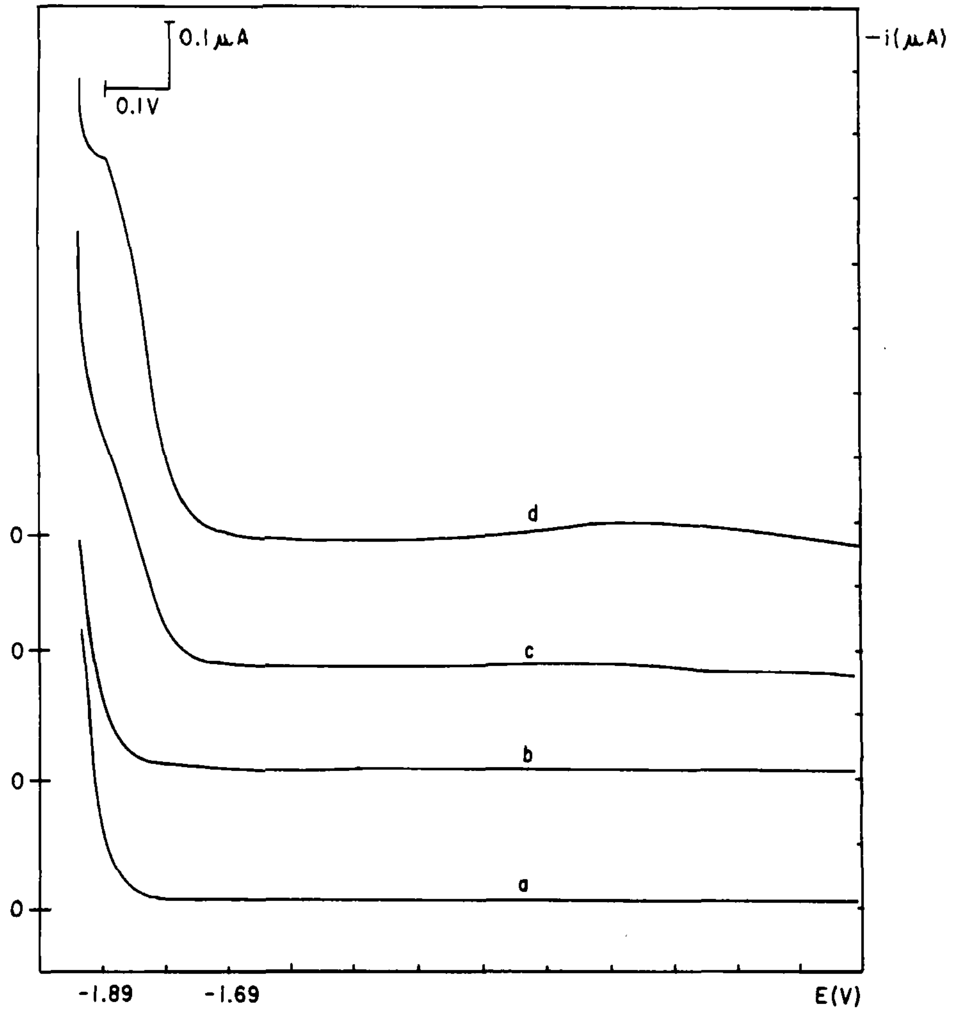

Figure 2 DPP for Cr(III) in 0.1 NaOH plus soil extract with NOM. a) supporting electrolyte alone, b) 0.1 M NaOH plus soil extract, c) solution b plus 7.5×10^{-4} M Cr(III) and d) solution b plus 1.25×10^{-3} M Cr(III). $\Delta E = 10$ mV; $t_{max} = 1$ sec.

Under the working conditions of treatment II) and III), Cr(VI) was reduced in presence of humic and fulvic acids at pH 4 and 2. Skogerboe *et al.*[16] studied the reduction of Hg(II) by fulvic acids and found that at low pH values the prevailing species of fulvic acid are HFA^+ and in its presence the maximum percentage of reduction of Hg(II) occurs. They concluded that fulvic acids need to be protonated to increase their reducing character.

In our case, the reduction potential for fulvic acid has not been determined. Although there are differences, the trends are generally the same. According to Skogerboe *et al.*[16] the reduction potential at pH 2 is 0.5 V vs NHE (normal hydrogen electrode), and 0.7 V

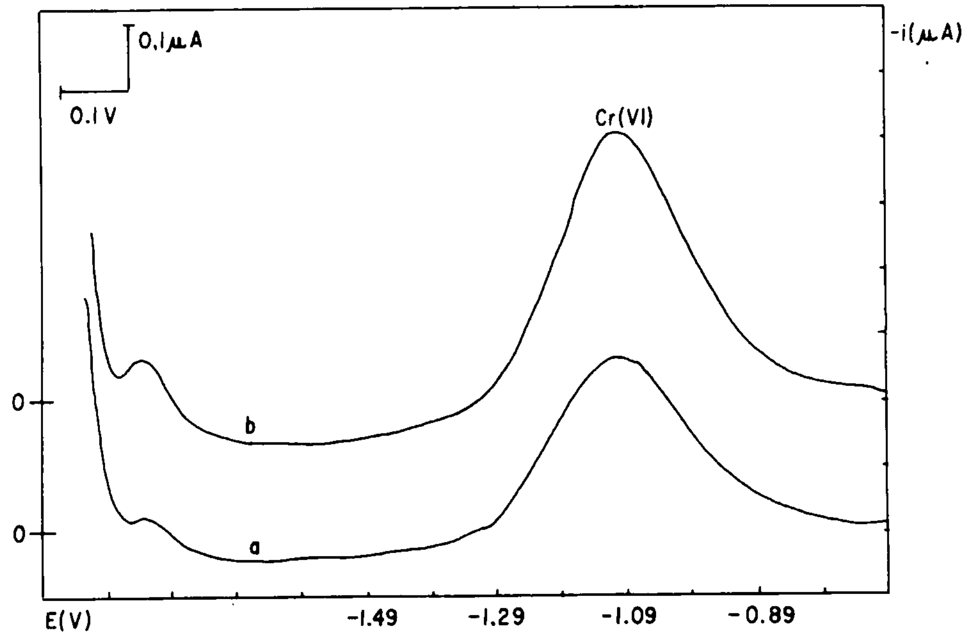

Figure 3 DPP for Cr(VI) at two concentrations in 0.1 M NaOH. a) supporting electrolyte plus 1.99×10^{-4} M Cr(VI), b) 0.1 M NaOH plus 2.99×10^{-4} M Cr(VI). $\Delta E = 10$ mV; $t_{max} = 1$ sec.

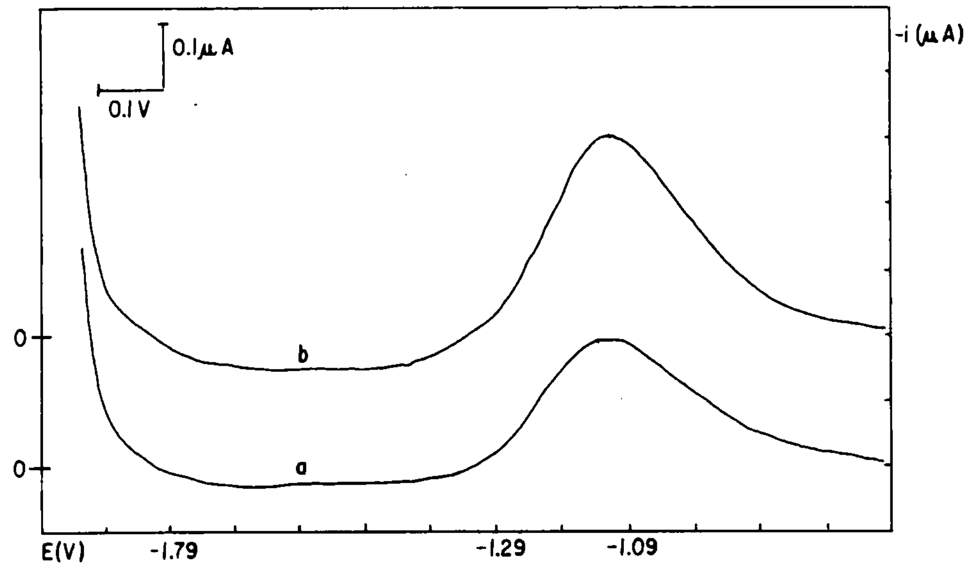

Figure 4 DPP for Cr(VI) at two concentrations in 0.1 M NaOH plus soil extract. a) supporting electrolyte plus soil extract and 1.99×10^{-4} M Cr(VI), b) 0.1 M NaOH plus soil extract and 2.99×10^{-4} M Cr(VI). $\Delta E =$ 10 mV; $t_{max} = 1$ sec.

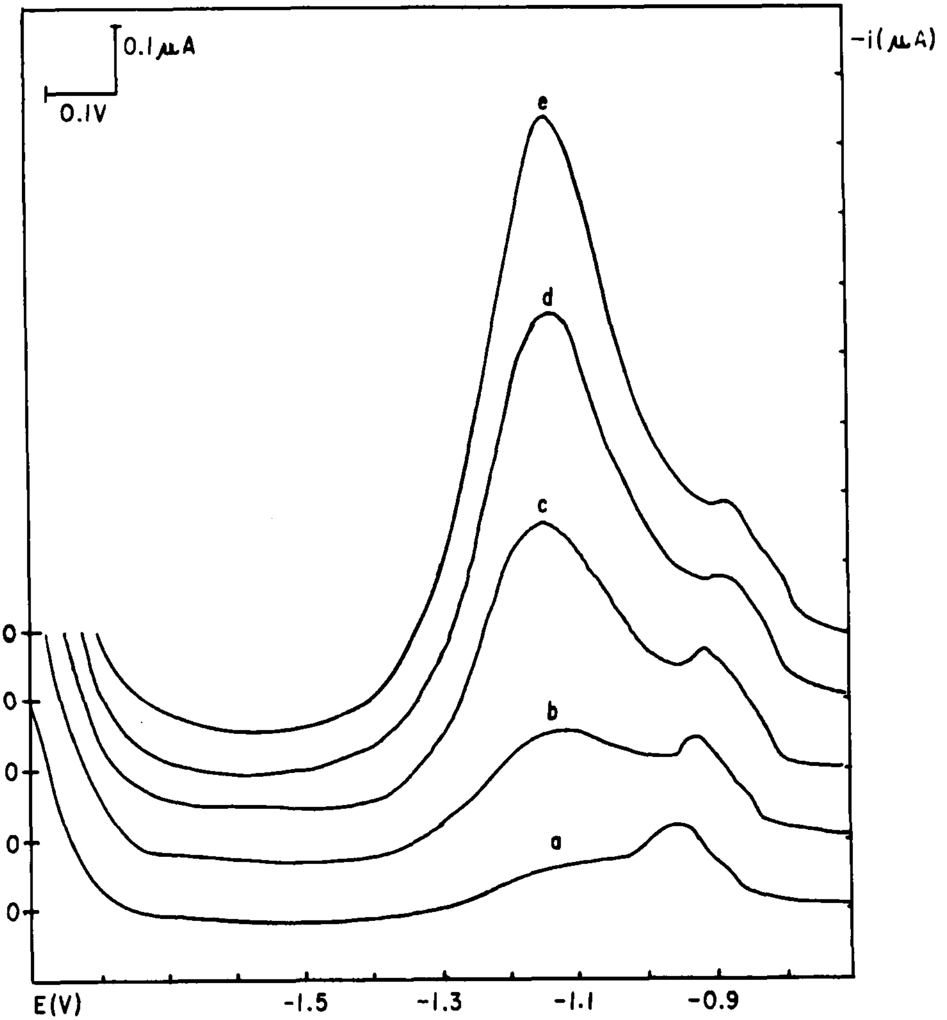

Figure 5 DPP for the extract of soil at pH 4 in 0.1 M NaOH. a) supporting electrolyte plus soil extract, b), c), d) and e) Cr(VI) standard addition in solution a: b) 9.99×10^{-4} M, c) 2.99×10^{-3} M, d) 4.99×10^{-3} M y e) 6.99×10^{-3} M. $\Delta E = 10$ mV; $t_{max} = 1$ sec.

vs NHE for humic acid. With this potential the reduction reaction of Cr(VI) is possible and can be represented by:

$$3\ \text{FAred} = 3\ \text{FAox} + 3\ \text{mH}^+ + 3\ e^-$$

$$\text{HCrO}_4^- + 3\ e^- + 7\ \text{H}^+ = \text{Cr}^{3+} + 4\ \text{H}_2\text{O}$$

$$3\ \text{FAred} + \text{HCrO}_4^- + 7\ \text{H}^+ = 3\ \text{FAox} + 3\ \text{mH}^+ + \text{Cr}^{3+} + 4\ \text{H}_2\text{O}$$

It should be stated that Wilson *et al.*[17] established, in the case of fulvic acid and vanadates, the value of m = 10. In our case we observed that to shift the equilibrium to the products, m should be larger than two.

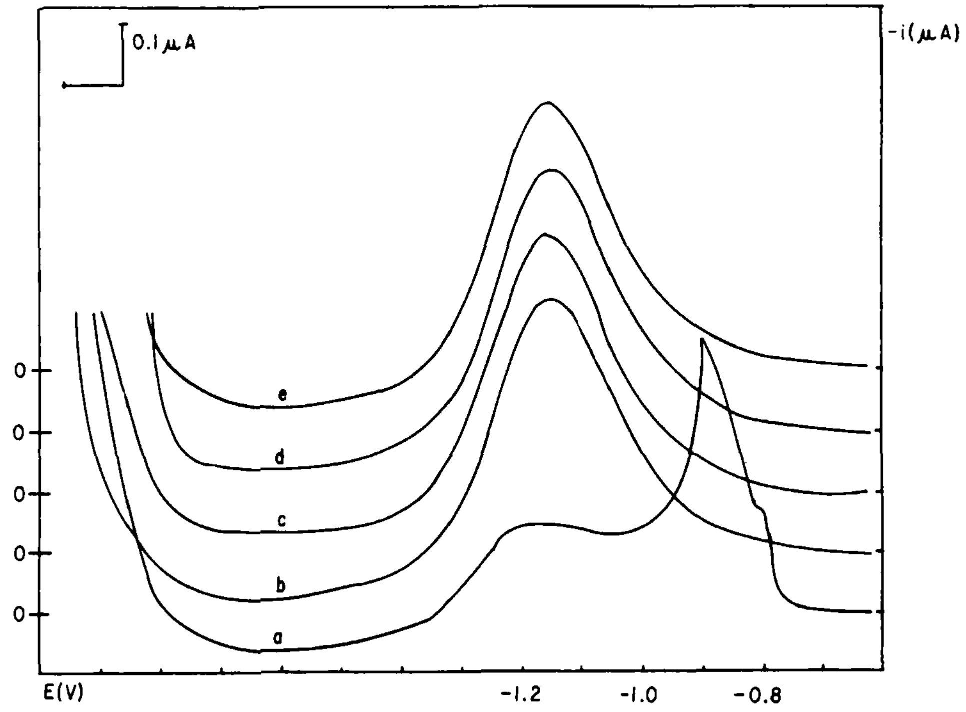

Figure 6 DPP for the extract of soil at pH 4 and addition of Cr(III). a) supporting electrolyte (0.1 M NaOH) plus soil extract, b) solution a plus 1.76 × 10^{-4} M Cr(III), c) solution a plus 3.52 × 10^{-4} M Cr(III), d) solution a plus 5.28 × 10^{-4} M Cr(III) and e) solution a plus 7.05 × 10^{-4} M Cr(III). $\Delta E = 10$ mV; $t_{max} = 1$ sec.

The reduction reaction of Cr(VI) to Cr(III) by humic and fulvic acid at pH 4 and 2, justifies the concentration decrease of Cr(VI). The Cr(III) formed could be bonded to soluble humic or fulvic acid: $(Cr(FAox)n)^{3+}$ or $(Cr(HAox)n)^{3+}$. Willems *et al.*[18] found in the case of the determination of Cr(VI) with diphenylcarbazide (DPCI) that the color reaction at pH 1.6 can be written as:

$$3\ H_4L = 3\ H_2L + 6\ H^+ + 6\ e^-$$

$$2\ CrO_4^{2-} + 6\ e^- + 16\ H^+ = 2\ Cr^{3+} + 4\ H_2O$$

$$3\ H_4L + CrO_4^{2-} + 8\ H^+ = [Cr(HL)_2]^- + Cr^{3+}\ H_2L + 8\ H_2O$$

H_4L is diphenylcarbazide (DPCI) and H_2L diphenylcarbazone (DPCO). This mechanism could be similar to the one observed in this work: the Cr(III) formed is bound to the soluble fulvic or humic acid giving place to the asymmetrical signal observed in Figures 5 and 6.

Electrocapillary curves

The presence of an asymmetrical signal in the soil polarograms of treatments II and III, led us to investigate the nature of this type of signal. Apparently it could be due to

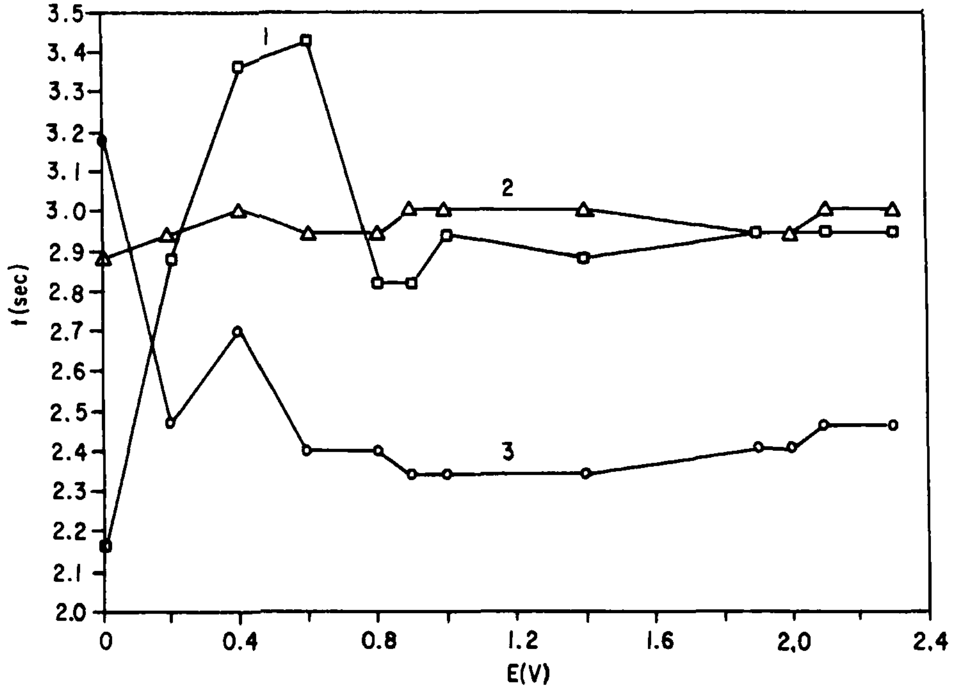

Figure 7 Electrocapillary curves of drop time versus potential at the DME. 1) supporting electrolyte alone, 2) 0.1 M NaOH plus 200 μL Triton-x-100 and 3) 0.1 M NaOH plus humic acid.

polarographic current maxima. In practice maxima are eliminated by addition of capillary active materials, (materials that change the potential of the electrocapillary maximum). The usual maximum suppressors used in aqueous solution are gelatin Triton-X-100, or other organic materials of high molecular weight[19].

Hunter *et al.*[20] found that 1 mg/L of humic acid has the same maximum suppressing effect as 1.4 mg/L of Triton-X-100. This means that in our soil extract we already had a maximum suppressor: humic acid. In order to corroborate this fact we obtained the electrocapillary curves of drop time vs potential at DME in 0.1 M NaOH for the supporting electrolyte alone, 0.2 mL Triton-X-100 1% and humic acid. The comparison of the curves in Figure 7 illustrates the change in the electrocapillary maximum, given by the peak and corresponding to the maximum in surface tension. Curves 2 and 3 in Figure 7 illustrates that humic acids are better suppressors. Humic acids are adsorbed on the mercury surface and they do not allow the adsorption of other substances. Therefore the electrochemical waves we observed in the DPP, asymmetric or not, are due to electrochemically active compounds.

CONCLUSIONS

Polarograph enables the identification of chromium species (VI) and (III) in a strong alkaline media such as needed to extract chromium from soils. Extractions with Tris-NaOH pH 13, yield 98.6% recovery percentage of Cr(VI) added to the soil.

Two signals were obtained in the soil extracts with NOM with Cr(VI), one corresponds to the reductions of Cr(VI) at −1.11 V and the other asymmetrical (−0.98 V) that disappears with the addition of CrO_2^{2-}.

The asymmetrical signal can be the result of the interaction of chromium-NOM [Cr(VI)-NOM or Cr(III)-NOM]. After the electrocapillary curves it seems that this signal is not due to the adsorption on the electrode. The study of this signal is the aim of further studies.

NOM was dissolved during the extraction covering and hindering the Cr(III) polarographic signal. With this extraction method, Cr(III) can not be determined with DPP. The reduction wave of Cr(VI) is also altered (the peak height, Δi, decreases), but it is still measurable with a detection limit of 1.59×10^{-5} M. Nevertheless the complex composition of the soil matrix and the ubiquitous organic matter present, polarography can be a successful method for the determination of anthropic chromium in soils. The extracting solution (Tris H 13) dissolves the two oxidation states. Total chromium can be determined with AAS, Cr(VI) with DPP and Cr(III) by the difference of the two. This method does not have the disadvantage of reduction due to acidification as does the DPCl-method.

Acknowledgements

This work was supported by a grant of CONACYT, (Consejo Nacional de Ciencia y Tecnología P 219CCOL891989). We are indebted to the Analytical Chemistry Department of The Chemistry College UNAM, for all the technical facilities.

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