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# Simultaneous determination of Cr(III) and Cr(VI) using differential pulse polarography and application to Gerede River

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Determination of Cr(III) in the presence of Cr(VI) from one polarogram is not easy. No such procedure was found in the literature. In polarographic studies Cr(III) had a peak only in acidic medium, while Cr(VI) had either 1 or 2 peaks in both acidic and basic solutions. In solutions that contain these 2 ions, the peak obtained in acidic medium for Cr(III) will be the sum of both ions. Thus, Cr(III) cannot be determined directly from one polarogram.

In this work, a new and simple polarographic method is established for the determination of Cr(III) and Cr(VI) by using only one polarogram. The most suitable electrolyte for this purpose was 0.1 M $KNO_3$ /$HNO_3$ (pH 2-3). The detection limits were $3 \times 10^{-7}$ M for Cr(III) and $1 \times 10^{-6}$ M for Cr(VI) in this medium. No interference was observed from most common ions. For validation, a sample containing both Cr(VI) and Cr(III) was analyzed also using 2 polarograms and good agreement was obtained. The proposed newly established direct method is applied to a real sample. For this purpose Gerede River in Turkey, which is surrounded by many leather factories, was analyzed for its chromium content, and agreement with ICP – OES was very good.

**Key Words:** Chromium speciation, Cr(VI) and Cr(III) determination, differential pulse polarography, application to wastewater

## Introduction

Determination of trace chromium and its speciation is important as it is a waste product of many factories. Thus, it will pollute the air, water, and soil. It is found in the environment as Cr(III) and Cr(VI) compounds.

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While Cr(III) is naturally found in ores, metallic chromium and Cr(VI) are mostly produced in industrial processes. These compounds are used in metallurgy, by lumber merchants, and in dye and leather factories. The toxic and carcinogen effects of Cr(VI) were realized at the end of the 19th century, while the importance of Cr(III) in living organisms, on the other hand, was discovered first in the 1960s. The International Cancer Research Institute has included Cr(VI) compounds in the first group according their carcinogenic and toxic effects.[1,2] Cr(III) is known as an essential element for carbohydrate, lipid, and protein metabolisms.[3]

Because of the opposing effects of chromium compounds, speciation plays an important role in biochemical and toxicological investigations. Since 1970 spectrophotometric methods have been used for speciation and determination of chromium compounds. In these methods usually first the total chromium content was determined and then the second compound was determined after extraction, complexation, or enrichment. These methods were applied to various water samples, wastewater, soil, and metallurgy and biological materials.[4–14] Some electroanalytical methods such as adsorptive stripping voltammetry,[15] catalytic cathodic stripping voltammetry,[16] and rotating disk electrode[17] have been used for the determination of chromium. As can be seen from a review about chromium speciation[18] very few electroanalytical methods have been used, although these methods have the advantage that they do not need any time consuming enrichment or separation procedures.[19–21] For Cr(VI) determination with differential pulse polarography (DPP) various supporting electrolytes have been tested in several investigations. Among them 0.1 M NaAc with 0.05 M ethylenediamine, pH 7; 0.2 M sodium fluoride, pH 8 $\pm$ 1; phosphate buffer, pH 10-12; and sodium citrate and ammonia buffer containing ethylenediamine, pH 10.2-10.5 are shown as the most suitable medium.[22–25] In one work borate buffer was suggested for Cr(VI) determination instead of ammonium acetate and sodium fluoride.[26] A trace amount of Cr(III) was determined in 0.05 M sodium salicylate medium by DPP.[27] In 2 separate investigations[28,29] for speciation of chromium using DPP, Cr(VI) was first reduced into Cr(III) in a medium of KSCN/HAc and total chromium was determined. In the first one,[28] Cr(III) was determined in HCl/KCl medium after Cr(VI) was reduced. In the second one,[29] on the other hand, 0.1 M $NaClO_4$ was used as electrolyte for Cr(III) determination. The Cr(VI) content was determined in the presence of Cr(III) and humic acid using DPP.[30] In this method Cr(III) and some ions present were precipitated first with $NH_4Al(SO_4)_2$ and then it was applied to synthetic and real samples.

As can be seen in most of the proposed electrochemical methods, it was not possible to determine these ions from one polarogram. Different electrolytes had to be used for the determination of each oxidation state of chromium. In most other methods time consuming procedures such as pre-concentration or pre-reduction were needed.

The objective of the present study was to develop a new and simple method for the trace determination and at the same time for the speciation of chromium compounds without any pre-reduction or separation procedure. In this work it was decided to use DPP to fulfill the above-mentioned requirements. Polarographic methods, using dropping mercury electrodes (DMEs), are useful alternatives since they allow faster, cheaper, and safer analysis. The mercury can be used continuously after washing, and thus no mercury loss is possible.

Validation can be done by working with different electrolytes and at different pH values. The results obtained with DPP are very reproducible since with the use of DME the behavior of the electrode is independent of its history.

# Experimental

## Apparatus

A polarographic analyzer (PAR 174 A) equipped with a PAR mercury drop timer was used. The natural drop time of the electrode was in the range 2 to 3 s (2.31 mg $s^{-1}$). A Kalousek glass electrolytic cell with a saturated calomel reference electrode (SCE), separated by a liquid junction was used in the 3-electrode configuration. The counter electrode was platinum wire. The polarograms were recorded with a Linseis (LY 1600) X-Y recorder under the conditions of a drop life of 1 s, a scan rate of 2-5 mV $s^{-1}$, and a pulse amplitude of 50 mV. For the real sample analysis a DPP analyzer, a Perkin Elmer Optima 5300 DV ICP-OES, was used and for the digestion procedure a Berghof Microwave system.

## Reagents

All chemicals used were of analytical-reagent grade (pro analysis) and they were mostly nitrate salts. Triply distilled water was used in the preparation of all solutions. $KNO_3$, KCl, and sodium acetate were prepared from reagent grade salts; 0.1 M Cr(III) solution was prepared from $Cr(NO_3)_3.9H_2O$ and 0.1 M Cr(VI) was prepared from $K_2CrO_4$. The solutions of interfering ions were mostly prepared from nitrate or sulfate salts. Solutions of $10^{-3}$-$10^{-5}$ M were prepared daily from 0.1 M solutions.

The mercury used in the dropping mercury electrode was obtained from Merck (Darmstadt, Germany). Contaminated mercury was cleaned by passing it successively through dilute $HNO_3$ (3.0 M) and water columns in the form of fine droplets by using a platinum sieve. The collected mercury was dried between sheets of filter paper. Before use, a DPP polarogram of this mercury was recorded in order to confirm the absence of impurities.

## River water analysis

Gerede River, containing discharges from many leather factories and about 200 small factories along the river, was analyzed for its chromium content. Samples were collected in polyethylene bottles about 50, 300, and 2000 m from the end of the industrial region. The samples were kept in 0.1 M HCl.

# Results and discussion

## Electrochemical behavior of Cr(III)

The electrochemical behavior of Cr(III) was tested in various electrolytes. For this purpose $KNO_3/HNO_3$, $KCl/HClO_4$, KCl/HCl, NaAc/HAc, BR buffer (acetate, borate, and phosphate), NaAc/NaOH, and $K_2CO_3$ electrolytes were used at various pH values (Table 1). While no reduction peak was observed for Cr(III) in basic solutions, a sharp peak in acidic solutions (pH 2.5-6.0) varying from –0.8 V to –1.0 V, depending on the electrolyte, was observed. The most reproducible results and lowest detection limits were obtained in 0.1 M $KNO_3/HNO_3$ in pH 2.5 medium. The polarograms of Cr(III) in different concentrations taken in 0.1 M $KNO_3/HNO_3$ medium are given in Figure 1. While the detection limit was $3 \times 10^{-7}$ M in this medium, it

was $1 \times 10^{-5}$ M in $HClO_4$, $1 \times 10^{-6}$ M in HCl, $5 \times 10^{-7}$M in BR buffer, and around $5 \times 10^{-6}$ M in HAc/Ac, all at pH 2.5.

**Table 1.** DP polarographic behavior of Cr(III) and Cr(VI) in various supporting electrolytes.

| Electrolyte | pH | Cr(III), $E_{peak}$ (V) | Cr(VI), $E_{peak}$ (V) | |
|---|---|---|---|---|
| | | Cr(III) → Cr(II) | Cr(VI)→ Cr(III) | Cr(III) →Cr(II) |
| $KNO_3/HNO_3$ | 2.5 | –0.8 (sharp) | –0.3 (broad) | –0.8 (sharp) |
| $KCl/HClO_4$ | 2.5 | –0.7 (sharp) | –0.3 (broad) | –0.8 (sharp) |
| KCl/HCl | 2.5 | –0.7 (sharp) | –0.3 (broad) | –0.8 (sharp) |
| [a]BR | 2.5 | –0.7 (sharp) | –0.4 (sharp) | –0.7 (sharp) |
| NaAc/HAc | 2.0 | –0.9 (sharp) | –0.3 (broad) | –0.9 (broad) |
| NaAc/HAc | 4.0, 6.0 | –1.0 (sharp) | –0.3 (broad) | –1.0 (broad) |
| NaAc/NaOH | 12.5 | - | –1.0 (sharp) | - |
| $K_2CO_3$ | 12.5 | - | –0.4 and –0.8 (sharp) | - |
| $K_2CO_3$ | 11.0 | - | –0.4 and –0.9 (sharp) | - |
| $K_2CO_3$ | 9.0 | - | –0.2 and –1.0 (sharp) | - |

[a]Britton-Robinson buffer

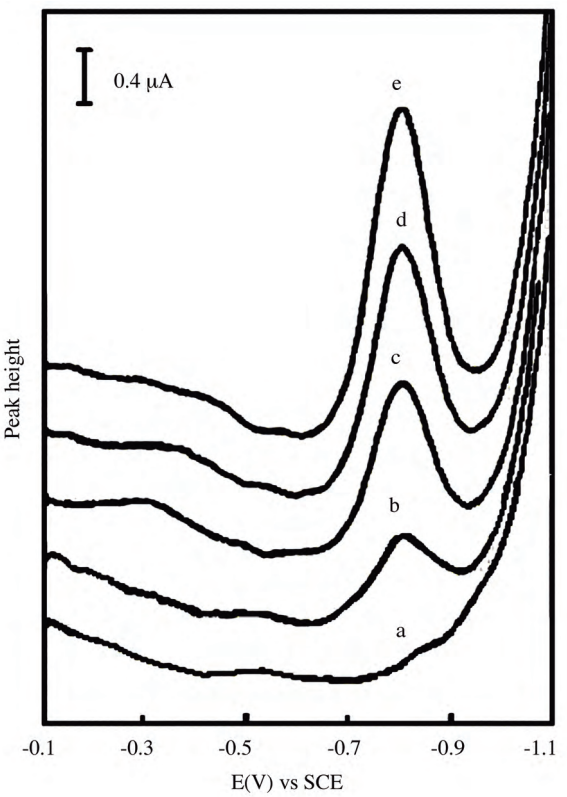


**Figure 1.** DP polarograms of Cr(III) in 0.1 M $KNO_3/HNO_3$ (pH 2.5). (a) 10 mL 0.1 M $KNO_3/HNO_3$ (pH 2.5), (b) a + 0.1 mL $1 \times 10^{-3}$ M Cr(III), (c) b + 0.1 mL $1 \times 10^{-3}$ M Cr(III), (d) c + 0.1 mL $1 \times 10^{-3}$ M Cr(III), (e) d + 0.1 mL $1 \times 10^{-3}$ M Cr(III).

## Electrochemical behavior of Cr(VI)

Chromium(VI) has at least one peak in both acidic and basic solutions either in $CrO_4^{2-}$ or $Cr_2O_7^{2-}$ form. In acidic solutions there are 2 peaks at about –0.3 V and at about –0.8 V. The first one, at –0.3 V, belongs to its reduction to Cr(III) and the second one, at –0.8 V, belongs to the reduction of Cr(III) to Cr(II).[31] The limit of detection in this medium was $1 \times 10^{-6}$ M for Cr(VI).

In basic solutions in the presence of 0.1 M NaAc/NaOH (pH 12.5) Cr(VI) has only one peak at –1.1 V, which responds well to standard additions and thus can be used for quantitative determinations (Figure 2). In 0.1 M NaAc/NaOH (pH 12.5) medium the limit of detection for Cr(VI) was $2 \times 10^{-7}$ M. In 1.0 M $K_2CO_3$ electrolyte 2 peaks were observed at about –0.4 V and –0.8 V (Figure 3). With increasing pH the peak potentials were approaching each other; at the same time, while the height of the peak at –0.4 V was decreasing, the peak at –0.8 V was increasing (Figure 4). The Cr(VI) in carbonate medium may form complex-like structures[32,33] and thus its peak shape and potential may shift with pH. This kind of behavior was observed in the presence of phosphate during the determination of chromium in wastewater using DPP.[24] In our study the detection limit

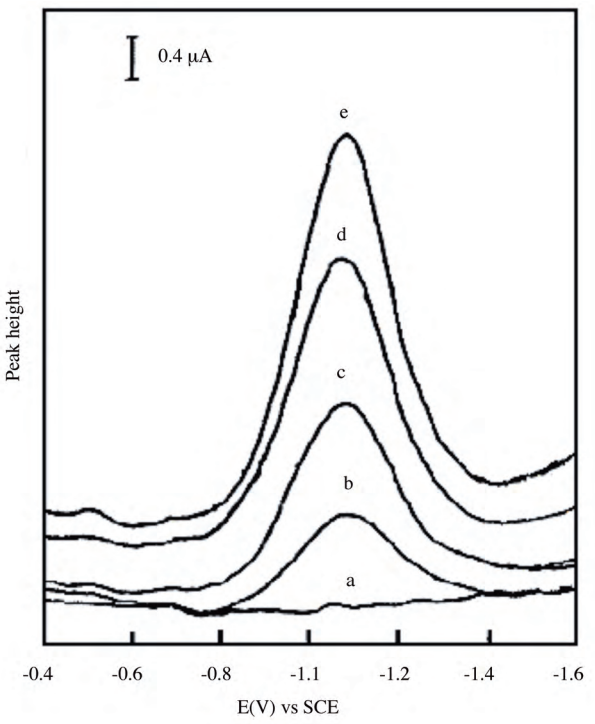


**Figure 2.** DP polarograms of Cr(VI) in 0.1 M NaAc/NaOH (pH 12.5). (a) 15 mL 0.1 M NaAc/NaOH (pH 12.5), (b) a + 0.1 mL $1 \times 10^{-3}$ M Cr(VI), (c) b + 0.1 mL $1 \times 10^{-3}$ M Cr(VI), (d) c + 0.1 mL $1 \times 10^{-3}$ M Cr(VI), (e) d + 0.1 mL $1 \times 10^{-3}$ M Cr(VI).

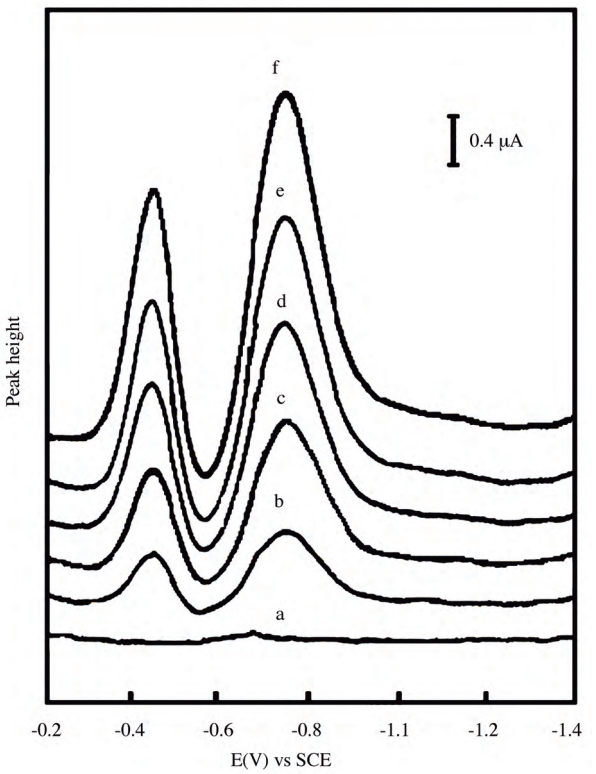


**Figure 3. DP** polarograms of Cr(VI) in 1.0 M $K_2CO_3$ (pH 12.5). (a) 10 mL 1.0 M $K_2CO_3$ (pH 12.5), (b) a + 0.1 mL $1 \times 10^{-3}$ M Cr(VI), (c) b + 0.1 mL $1 \times 10^{-3}$ M Cr(VI), (d) c + 0.1 mL $1 \times 10^{-3}$ M Cr(VI), (e) d + 0.1 mL $1 \times 10^{-3}$ M Cr(VI), (f) e + 0.1 mL $1 \times 10^{-3}$ M Cr(VI).

in 1.0 M $K_2CO_3$ medium was $5 \times 10^{-7}$ M for Cr(VI). The peak shapes and peak potentials of Cr(III) and Cr(VI) in various electrolytes are summarized in Table 1.

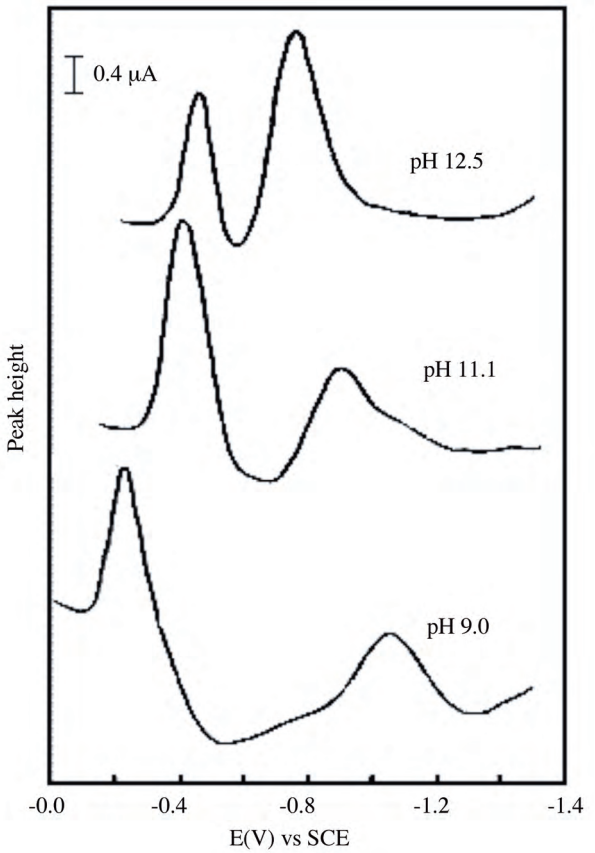


**Figure 4.** DP polarograms of Cr(VI) in 1.0 M $K_2CO_3$ at different pH values.

## Simultaneous determination of Cr(III) and Cr(VI)

Mixtures containing Cr(III) and Cr(VI) both in $1 \times 10^{-5}$ M concentrations were analyzed in various electrolytes to find the best medium for the speciation of chromium using DPP. The results obtained are summarized in Table 2. It can be seen that while for the determination of Cr(VI), 0.1 M $KNO_3/HNO_3$ pH 2.5, 0.1 M NaAc/NaOH pH 12.5, and 1 M $K_2CO_3$ pH 9-12.5 were the best electrolytes, for Cr(III) it was 0.1 M $KNO_3/HNO_3$, pH 2.5 (no peak for Cr(III) in basic solutions). It was found that in $KNO_3/HNO_3$ electrolyte, both ions could be determined with high accuracy.

The polarograms taken in 0.1 M $KNO_3/HNO_3$, (pH 2.5) for solutions containing Cr(III) and Cr(VI) are given in Figure 5. This medium was chosen for speciation purposes since both ions can be observed in the same polarogram. As known,[31] Cr(VI) is reduced to Cr(III) at –0.3 V and Cr(III) is reduced to Cr(II) at –0.8 V; thus the peak at –0.8 V will be the sum of Cr(VI) and Cr(III) ions. In this case, Cr(III) has to be determined from this peak using the calculation given below.

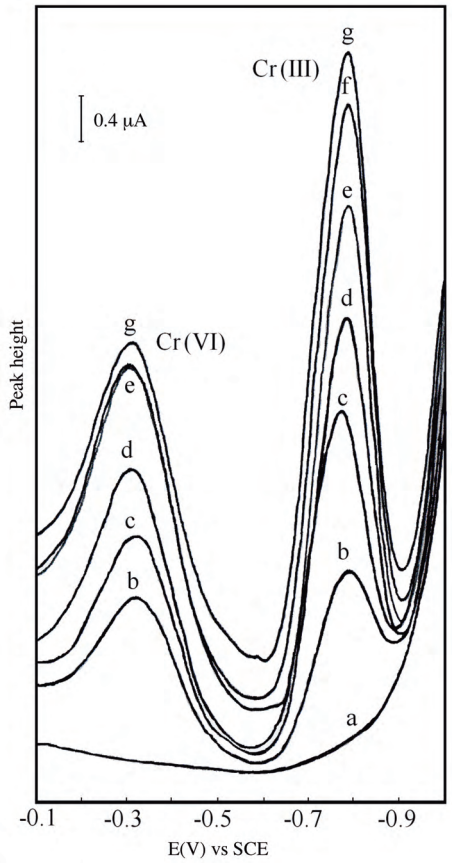


**Figure 5.** DP polarograms of Cr(III) + Cr(VI) synthetic sample in acidic medium (a) 15 mL 0.1 M $KNO_3/HNO_3$ (pH 2.5), (b) a + 0.1 mL sample of Cr(III) + Cr(VI), (c) b + 0.1 mL sample of Cr(III) + Cr(VI), (d) c + 0.1 mL $1 \times 10^{-3}$ M Cr(VI), (e) d + 0.1 mL $1 \times 10^{-3}$ M Cr(VI), (f) e + 0.1 mL $1 \times 10^{-3}$ M Cr(III), (g) f + 0.1 mL $1 \times 10^{-3}$ M Cr(III), Synthetic sample: 10 mL $1 \times 10^{-3}$ M Cr(III) and $1 \times 10^{-3}$ M Cr(VI).

For this purpose, first the unknown sample concentration of Cr(VI) has to be determined either in acidic or basic solution. While in acidic solution the peak at –0.3 V can be used for its determination, in basic solution either the peak at –1.1 V in NaOH or the peaks at about –0.2 V and –1.0 V in carbonate medium (pH 12.5-9) can be used. Basic solutions may be preferred for Cr(VI) as the peak is larger and sharper in this medium. Using the peak at –0.8 V, which is the sum of both ions, the total Cr(III) can be determined by standard additions. By subtracting the Cr(III) concentration that is formed from Cr(VI), the initial Cr(III) in an unknown sample can be determined. The results obtained in various electrolytes for a synthetic sample containing both ions are summarized in Table 2.

Here one point has to be considered, i.e. that the peak at –0.8 V, which belongs to the reduction of Cr(III) formed from the reduction of Cr(VI), is larger than the peak height of Cr(III) present in the cell. It was found that this increment in peak height was 2 times larger when their concentrations were the same. Thus a correction factor has to be used. For this purpose the equation below given was derived.

Here, the height of the –0.8 V peak ($h_1$) is the sum of Cr(III) and Cr(VI) peaks in the unknown. The height of the –0.8 V peak can be written as the sum of 2 terms. The first term belongs to the peak height of

unknown Cr(III) at –0.8 V and the second term belongs to the peak height of unknown Cr(VI) at –0.8 V.

$$\frac{V_1\,[Cr(III)]_1\,h_2}{V_2\,[Cr(III)]_2} + \frac{V_1\,[Cr(VI)]_1\,h_3}{V_3\,[Cr(VI)]_2} = h_1$$

**Table 2.** Results obtained from the determination of Cr(III) and Cr(VI) in a synthetic sample of $1 \times 10^{-5}$ M Cr(III) and $1 \times 10^{-5}$ M Cr(VI) in different electrolytes (N = 5, 90% confidence interval).

| Medium | $(\bar{x} \pm \frac{t.s}{\sqrt{N}}) \times 10^5$ (mol.L$^{-1}$) | |
|---|---|---|
| | Cr(VI) | [a]Cr(III) |
| pH = 12.5 NaOH/NaAc | 0.98 ± 0.06 | - |
| pH = 12.5 $K_2CO_3$ (–0.4 V) | 1.10 ± 0.11 | - |
| pH = 12.5 $K_2CO_3$ (–0.8 V) | 1.01 ± 0.08 | - |
| pH = 2.5 $KNO_3/HNO_3$ | 1.01 ± 0.10 | 0.95 ± 0.18 |
| pH = 2.5 KCl/$HClO_4$ | 1.15 ± 0.15 | Large error |
| pH = 2.5 KCl/HCl | 1.24 ± 0.50 | Large error |

[a]In calculations for Cr(VI), experimentally obtained results (at –0.3 V) were used.

In this equation, $V_1$ is the volume of sample added, $V_2$ is the volume of standard Cr(III) added, and $V_3$ is the volume of standard Cr(VI) added; $[Cr(III)]_1$ and $[Cr(VI)]_1$ are concentrations of Cr(III) and Cr(VI) in sample solution. $[Cr(III)]_2$ and $[Cr(VI)]_2$ are concentrations of their standard solutions. $h_1$, peak height of sample; $h_2$, increment of peak height after standard Cr(III) addition; $h_3$, increment of peak height obtained after standard Cr(VI) addition. After designation of $h_2$ and $h_3$, the speciation can be done simultaneously in the same electrolyte. There is no need for long and tedious separation, extraction, or pre-reduction procedures.

## Interference studies

The interference of some common ions was investigated in several electrolytes such as 0.1 M NaAc/NaOH (pH 12.5), 1 M $K_2CO_3$ (pH 9-12.5), and 0.1 M $KNO_3/HNO_3$ (pH 2.5). Most of these ions such as Zn(II), Cu(II), Fe(III), Ni(II), Se(IV), Cd(II), Pb(II), Ti(IV), and As(III) were chosen because of their peaks near to Cr(III) and Cr(VI) peaks.

### In 0.1 M $KNO_3/HNO_3$ (pH 2.5)

It was found that the above-mentioned ions, except As(III), had no interference effect in this medium on Cr(III) and Cr(VI) peaks. The peak of As(III) at –0.7 V had an overlapping effect with the peak of Cr(III) at –0.8 V when its concentration was larger than $1 \times 10^{-5}$ M (Figure 6). Cr(III) and Cr(VI) (each $1 \times 10^{-5}$ M) in a synthetic sample were determined in the presence of the above-given ions except As(III) (each $10^{-5}$ M). The Cr(III) concentration was $0.93 \times 10^{-5}$ with a 7% negative error. In a sample where all ions including As(III) (each $0.5 \times 10^{-5}$ M) were present next to Cr(III) and Cr(VI), (each $1 \times 10^{-5}$ M) the Cr(III) was $1.1 \times 10^{-5}$ M with a 10% positive error. Thus, it can be concluded that this medium can be used for the speciation

purposes in the presence of Zn(II), Cu(II), Fe(III), Ni(II), Se(IV), Cd(II), Pb(II), Ti(IV), and As(III) with high accuracy.

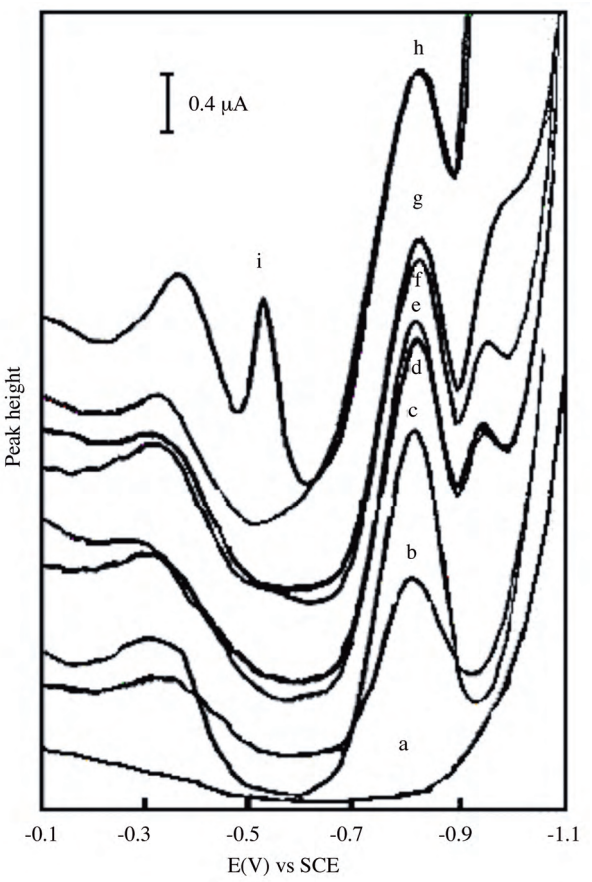


**Figure 6.** Effect of some cations on peaks of Cr(III) + Cr(VI) in a sample (a) 10 mL 0.1 M $KNO_3/HNO_3$ (pH 2.5), (b) a + 0.1 mL sample of Cr(III) + Cr(VI), (c) b + 0.1 mL sample of Cr(III) + Cr(VI), (d) c + 0.1 mL $1 \times 10^{-3}$ M Zn(II), (e) d + 0.1 mL $1 \times 10^{-3}$ M Cu(II), (f) e + 0.1 mL $1 \times 10^{-3}$ M Fe(III), (g) f + 0.1 mL $1 \times 10^{-3}$ M Ni(II), (h) g + 0.05 mL $1 \times 10^{-3}$ M As(III), (i) h + 0.05 mL $1 \times 10^{-3}$ M Se(IV).

### In 0.1 M NaAc/NaOH (pH 12.5)

In this medium since Cr(III) has no peak, only Cr(VI) determination was studied. No interference was observed in the presence of Cr(III), Ni(II), Cu(II), Zn(II), Se(IV), or Pb(II) during the determination of Cr(VI). However, the peak of cadmium at –0.74 V could overlap at higher concentrations with the peak of Cr(VI) at –0.8 V. By the addition of EDTA it was possible to eliminate this interference since the peak of Cd-EDTA complex shifted to about –1.5 V.[19] On the other hand, it was not possible to determine Cr(VI) in the presence of Fe(III) in this medium, since with the addition of Fe(III) the peak of Cr(VI) at about –1.0 V decreased and disappeared. According to previous studies[34–36] in Cr(VI)/Fe(III)/$H_2O$ systems depending on pH, various structures such as $FeOHCrO_4$, $FeOHCrO_4 \cdot 2Fe(OH)_3$, $KFe_3(CrO_4)_2(OH)_6$, and $M_2Fe_3(OH)_5(CrO_4)_3.3H_2O$ may be formed.

Their crystal structures and solubility were investigated depending on pH. The above-mentioned effect of Fe(III) may be explained by these kinds of structures.

In a synthetic sample containing Cr(III), Ni(II), Cu(II), Zn(II), Se(IV), and As(III) (each $1 \times 10^{-5}$ M) the Cr(VI) content was determined from its –1.0 V peak as $0.92 \times 10^{5}$ M with 8% relative error.

**In 1.0 M $K_2CO_3$ (pH 9-12.5)**

No interference was observed during the determination of Cr(VI) in the presence of Cr(III), Ni(II), Cu(II), Zn(II), Se(IV), As(III), Fe(III), Cd(II), and Pb(II) (each $10^{-5}$ M). In this medium none of the above given ions except Cd(II) and Pb(II) have peaks. Since Cd(II) has a peak at –0.6 V and Pb(II) has a peak at –0.5 V in this medium, there will be no interference with the peaks of Cr(VI) at –0.2 and –1.0 V. It was observed also that in this medium when pH changed from 12.5 to 9 the difference in peak potentials of Cr(VI) became larger (Figure 3).

Since some problems were observed in this medium, 2 synthetic samples in 2 different concentrations were prepared. In first sample Cr(III), Cr(VI), Ni(II), Cu(II), Zn(II), Fe(III), Se(IV), and As(III) ions were all in $1 \times 10^{-5}$ M concentration. Polarographic determination was done in 1 M $K_2CO_3$ at about pH 11.5. The Cr(VI) concentration calculated from the –0.4 V peak was $0.63 \times 10^{-5}$ M with –37% error. When it was calculated from the –1.1 V peak the result was $0.61 \times 10^{-5}$ M with –39% errors. As can be seen the results had all minus percent errors, indicating a systematic error. The reason most probably would be the precipitation of some cations at this high concentration of ions and high pH.

In the second sample where all ions were in $5 \times 10^{-6}$ M concentration, the Cr(VI) calculated from the –0.4 V peak was $4.8 \times 10^{-6}$ M (N = 4) with 4% error (Cr(III) has no peak in this medium). With the second peak at –1.1 V the result found was $3.7 \times 10^{-6}$ M with –26% error. Thus, the peak at –0.4 V was found suitable for the determination. As can be seen in more dilute solutions the error is much smaller, since precipitation cannot take place. In most polarographic methods dilute solutions are used and thus no interference effect is expected.

## Application to real samples

Gerede River water was analyzed for its chromium content, since there are many leather factories and about 200 small factories along the river. For this purpose samples were collected in polyethylene bottles about 50, 300, and 2000 m from the end of the industrial region. The samples were kept in 0.1 M HCl and analyzed in various electrolytes such as 0.1 M NaAc/NaOH pH 12.5 and 1 M $K_2CO_3$ pH 12.5 for Cr(VI) and in 0.1 M $KNO_3/HNO_3$ pH 2.5 for Cr(III).

Since in 0.1 M NaAc/NaOH pH 12.5 medium Pb and Cd peaks are nearly the same potential as the Cr(VI) peak, EDTA can be used in case of the presence of Pb and Cd in river water. This probable interference was eliminated by the use of EDTA. It was surprising that in all these collected samples Cr(VI) was not detected; chromium was only in Cr(III) form. The reason might be the presence of some reducing agents used in leather tanning. When Cr(VI) was added to the river water sample it was also reduced and it could not be observed. The quantity of Cr(III) in river water was determined in 0.1 M $KNO_3/HNO_3$ (pH 2.5) electrolyte using the peak at –0.8 V. The Cr(III) content at various distances is given in Table 3. A decrease from 94 mg $L^{-1}$ to 32 mg $L^{-1}$ was observed when the distance changed from 50 to 2000 m.

**Table 3.** Results of Cr(III) determination in Gerede River (Cr(VI) was not present) (N = 5, 90% confidence interval).

| [a]Distance (m) | $\bar{x} \pm \frac{t.s}{\sqrt{N}}$(mg $L^{-1}$) | | |
|---|---|---|---|
| | DPP | [b]DPP | [b]ICP-OES |
| 50 | 94.0 ± 15.6 | 122.6 ± 6.5 | 124.2 ± 1.8 |
| 300 | 66.3 ± 16.1 | NA | NA |
| 2000 | 32.3 ± 2.1 | NA | NA |

[a]From the end of the industrial region.

[b]Microwave digested

NA: not analyzed

For validation of our method, the sample taken from the same river at 50 m distance was analyzed after microwave digestion for its chromium content using ICP-AES and the quantity found was 124.2 ± 1.8 mg $L^{-1}$. Since the result with DPP for the water sample without microwave digestion was 94 mg $L^{-1}$, the same microwave digested water sample was once more analyzed using DPP and the quantity found was 122.6 ± 6.5 mg $L^{-1}$ (for 90% CI and N = 3) instead of 94 mg $L^{-1}$. This result indicates that in river water some part of the chromium is bound as an organic constituent. Thus, without digestion the unbound chromium was determined. The agreement between the results obtained with the 2 different methods for the same digested sample indicates the reliability of our method. The results are given in Table 3. Only the result for water taken from 50 m distance could be used for ICP-OES since samples taken from 300 and 2000 m were not left.

The trace elements in Gerede River were also analyzed with ICP-OES and the results were as follows: Al: 0.2, B: 42.4, Ba: 0.1, Ca: 287.5, Cr: 124.2, Fe: 3.4, K: 23.2, Li: 0.2, Mg: 98.7, Mn: 0.2, Mo: 0.004, Na: 2994.5, Ni: 0.04, Pb: 0.2, Si: 9.7, Ti: 0.1, V: 0.5, and W: 0.4 in mg $L^{-1}$. On the other hand, Ag, Cd, Co, Cu, Ge, Sc, Sn, Tl, and Zn could not be detected.

## Conclusions

A differential pulse polarographic method is proposed for the speciation of Cr(III) and Cr(VI) compounds. In the presence of both ions, 2 methods can be applied. In the first method, only one polarogram is used for the determination of both ions in acidic medium, 0.1 M $KNO_3$ /$HNO_3$ (pH 2-3). In this medium the peak at –0.8 V is the sum of Cr(III) and Cr(VI) and the peak at –0.3 V belongs to Cr(VI). Cr(VI) will be determined from the peak at –0.3 V; Cr(III) content on the other hand can be calculated from the –0.8 V peak after subtraction of Cr(VI) content. The main advantage of this method is that the determinations can be made using only one polarogram. There is no need to change the electrolyte or pH, and there is no need for time consuming procedures such as reduction or enrichment.

In the second method 2 polarograms have to be used. Cr(VI) is determined in basic solution either in carbonate or NaOH medium and then Cr(III) in acidic medium is determined as given above from its –0.8 V peak.

The detection limit was about 2 × $10^{-7}$ M for Cr(VI) in 0.1 M NaAc/NaOH (pH 12.5) and 3 × $10^{-7}$ M for Cr(III) in 0.1 M $KNO_3$ /$HNO_3$ (pH 2.5). Gerede River in Turkey, which is surrounded by many leather factories, was analyzed for its chromium content.

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