Investigation of a sensitive voltammetric method for determination of chromium (VI) in presence of chromium (III) and its application to leather

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Abstract

The determination of chromium(VI) at high concentrations can be performed spectrophotometrically with 1,5-diphenylcarbazite. The standard determination methods for chromium(VI) in leather like DIN53314 or IUC 18 have a detection limit of 3mg/kg leather. However the detection limit is not enough for lower concentrations. There is a need for lower detection limits because public awareness of hexavalent chromium has increased recently.

Voltammetry is an increasingly popular technique that in many instances offers unrivalled detection limits even when compared to vastly more expensive analytical techniques. The aim of this study is application of a very sensitive procedure of chromium(VI) determination in the presence of chromium(III) by CCAdSV (Catalytic Cathodic Adsorptive Stripping Voltammetry). The method is based on the measurement of the current obtained from the reduction of chromium(III)-DTPA (diethylentriaminepentaacetic acid) complex adsorbed at the surface of the mercury drop in the presence of nitrate.

Keywords: chromium(VI) determination, leather, CCAdSV

1.Introduction

Chromium occurs naturally in two oxidation states, chromium(VI) and chromium(III), in natural waters. The valency state distribution of dissolved chromium in naturel waters depends on the pH, the oxygen content and presence of organic matter[1]. Exposure of both forms of chromium to the environment is common and occurs from natural and industrial sources. Chromium(VI) is much more mobile, toxic and carcinogenic. Chromium(III) is considered to be essential to mammals for the maintenance of glucose, lipid, and protein metabolism, while chromium(VI) is known to damage mucous membranes and cause renal damage and has been classified as carcinogenic to humans[2]. For this reason it is useful to monitor separate species of chromium because its total content does not provide sufficient information about possible health hazards. Since there is debate on environmental convertibility of chromium(III) to the more hazardous hexavalent state, the ability to determine quantitatively hexavalent in chromium(III) substrates is of importance to many industries, especially the leather industry.

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There are numerous regulations on permissible limits of chromium(VI) in water and waste water and various upper limits of acceptability for chromium(VI) (all less than 5 $mgkg^{-1}$) have also been set for leather products by various regulatory authorities. In chrome tanned leather, the levels of chromium(III) are overwhelming with respect to chromium(VI) and methods to determine the latter in presence of the former are necessary.

Chrome tanning is the most important tanning method for the leather industry and represents over 80% of the leather production world-wide. The chemical that used in tanning processes is basic chromium(III) sulphate. Hexavalent chromium do not used in the tanning process and has no tanning effect. However, during the last years analysis of leather articles has shown traces of hexavalent chromium. This was unexpected since chromium(VI) in the presence of a high proportion of organic matter and low pH in the leather is unstable and is expected to be reduced to chrome(III).

Böhme has intensively studied the phenomenon of chromium(VI) formation in chrome tanned leather. According to the researcher's studies, formation of chromium(VI) in leather is influenced by fatliquors, especially natural products such as fish oils, drastic conditions like heating above $80^{o}C$, the process of leather production in neutral to alkaline medium, and UV exposure of finished leather[3].

Currently, quantitative analysis of leather for chromium(VI) carried out by any of four methods namely DIN 533314, IUC18, SLC22, EN 420. All these methods are photometric methods[4,5]. In these methods ground leather sample extracted for 3 hours with 0.1 M phosphate buffer solutions at pH 8.0±0.1 so that the extract pH remains within range of 7.5 to 8.0. The extract is acidified with phosphoric acid solution to mask any iron present and also to provide the acidic condition necessary for reduction of chromium(VI) with 1,5–diphenyl carbazide solution. The chromium(VI) in solution oxidizes 1,5-diphenylcarbazide to 1,5- diphenyl carbozone to give a red /violet complex with chromium which can be quantified photometrically at 540nm.

Electrochemical techniques are considered to be the most powerful methods. In particular, adsorptive stripping voltammetry (AdSV) is of interest due to its high sensitivity and selectivity. Voltammetric methods are advantageous in speciation of chromium because they offer a low detection limit and the determinations can be carried out without any additional separation step. Now polarographic and voltammetric methods have proved to be very sensitive analytical methods to determine reducible or oxidizing agents. They are widely used in the fields of pharmaceutical analysis, forensic analysis and environmental analysis due to their high sensitivity, low detection limit, easy operation and simple instrumentation.

Voltammetry comprises a group of electroanalytical methods in which information about the measurement of applied potential obtained under conditions that encourage polarization of indicator or working electrodes. Generally, the working electrodes in voltammetry are characterized by their small surface area (usually a few square millimeters), which enhances polarization. Such electrodes are generally referred to as microelectrodes.

Mercury electrodes are most widely used microelectrodes for voltammetry because of their unique features. The first feature is unusually high overvoltage associated with the reduction of hydrogen ions. The second advantage is that a new

metal surface is generated continuously; thus the behavior of the electrode is independent of its past history. A third unusual feature of dropping electrode is that reducible average currents are immediately realized at any given potential regardless of whether this potential is approached from lower or higher settings. Another important advantage is nonfaradaic residual or charging current which limits the sensitivity of the classical method to concentrations about 10^{-5} M. [6].

Stripping methods involve a preconcentration step before analysis, either by forming an amalgam or complex with the particular analyte and the electrode material, or by adsorbing the substrate on the electrode surface. Following this, the potential is swept in either anodic or cathodic direction so that the preconcentrated species reacts at the electrode surface and the resulting current potential plot is recorded. When the potential is held at a negative potential followed by scanning in a positive direction, the technique is known as anodic stripping voltammetry(ASV). When the potential is held at a positive value followed by scanning in a negative direction, this technique is cathodic stripping voltammetry(CSV). When the preconcentration step is adsorption, the technique is adsorptive stripping voltammetry (AdSV). In general the stripping process is either applied at a hanging mercury drop electrode (HMDE) or mercury film electrode (MFE) deposited in situ[7].

Stripping methods are prime importance in trace work because the concentrating aspects of the electrolysis permit the determination of minute amounts of an analyte with reasonable accuracy. Thus the analysis of the solutions in the 10^{-6} to 10^{-9} M range becomes feasible by methods that are both simple and rapid [4].

Since different chromium species have different electrochemical properties in aqueous solution, electroanalytical methods have also been advocated for speciation based on an oxidation state. Adsorptive stripping voltammetry would once again appear to be a very attractive method for chromium determination in low concentration range in water and in solutions prepared from a variety of environmental samples.

Several adsorptive stripping procedures have been reported in the literature. The adsorptive preconcentration of Cr(III)-diethylentriaminepentaacetic(DTPA) complexes at hanging mercury drop electrode(HMDE) in DTPA-CH_3COONa-$NaNO_3$ solutions pH6.2 was studied by Golimowski[8]. They applied to determination of chromium at concentrations down to determinations 4. 10^{-9} $molL^{-1}$ in various water types using the method of adsorption differential pulse(AdDPV) exploiting in addition catalytic action of nitrate

$$Cr(III) \xrightarrow{e^-} Cr(II) \xrightarrow{NO_3^-} Cr(III)$$

Broussemart [9] also used DTPA for chromium in sea water, using catalytic cathodic stripping voltammetry. After chromium(VI) was determined with DTPA, the total dissolved chromium concentration was determined following the UV irradiation of the sample. The chromium (III) concentration was then calculated by the difference. The reported detection limit for chromium (VI) was 1.10^{-10} M after deposition for 2 min on a large HMDE (surface area =0,38 mm^2).

Grabarczyk [10] presented a selective and sensitive method for determination of traces of chromium(VI) in presence of a large excess of chromium(III) by DPCAdSV.

They reported that nitrilotriacetic acid (NTA) can be used as masking agent of chromium(III) for minimization of its interferences.

2. Experimental

2.1 Reagents and Apparatus

2.1.1. Reagents

Sodium nitrate, suprapur sodium hydroxide, dipotassium hydrogen phosphate, phosphoric acid, nitrilotriacetic acide,1,5 diphenylcarbazide,acetone, methonol were obtained from Merck. Diethylentriamine pentaacetic acide (DTPA) was purchased from Sigma.

Stock standard solutions of chromium(VI) were prepared by dissolving the adequate amount of $K_2Cr_2O_7$ (analytical reagent grade, Merck). From these solutions, other diluted standard solutions were prepared daily.

Stock solutions of chromium(III) and standard solutions of chromium(III) were prepared from $CrCl_3.6H_2O$ and were diluted with pH:2 HCl.

The SPE (Solid Phase Etraction) columns were Accua Band II ODS C-18

2.1.2 Apparatus

Voltammograms of CCSV-DTPA were recorded with a 693 VA Processor (Metrohm) connected to a 694 Stand with a hanging mercury drop working electrode (Metrohm). The drop size was 4. An Ag/AgCl (3M KCl) electrode and a platinium electrode were used in the voltammetric cell as reference electrode and auxilary electrode, respectively, coupled with a PTFE stirring rod.

pH was measured with a E510 Metrohm pH meter. An Elga Pure Water System and reverse osmosis sysytem was used at all experiments.

A ICP Schimadzu and MS HP 4500 inductively coupled plasma mass spectroscopy (ICP-MS) was used to measure total chromium.

The photometric measurements were carried out using a Shimadzu 1601 UV 1601 spectrophotometer.

2.2. Procedure

2mL 0.1 M DTPA was dissolved with NaOH and pH adjusted to pH 6,2; 2 mL 2,5 M $NaNO_3$; and 2mL 0,1 M pH 6,2 phosphate buffer was added and than diluted up to 20 mL with ultrapure water. The phosphate buffer was used to minimize some metal ion interference. The voltammogram of this solution is recorded as blank. It was placed in the voltammetric cell and de-aerated for 5 minutes with nitrogen and the following program with an operation sequence and cathodic segment was performed:

OPERATION SEQUENCE

Method Cr+6

Instractions	t/s	Main Parameters		Auxillary parameters	
1 DOS/M		V.added	20.5mL		
2 REM		20Ml distile water+0.5 mLKCl 3 mol/L			
3 SMPL/M		V.fraction	mL	V.total	
4 REM		Cr 6			
5 PURGE					
6 STIR	300.0	Rot Speed		2000/min	
7 < ADD					
8 PURGE					
9 STIR	3.0				
10 0PURGE					
11 0STIR	5.0				
12 <REP		V.add	0.100 mL		
13 SEGMENT		Segm.name	katodik		
14 REP >0					
15 ADD >M		Soln.name	Cr6	V .add	20µL
16 ADD >8					
17 END					

SEGMENT KATODİK

Instractions	t/s	Main Parameters		Auxillary parameters	
1 HMDE		Drop size	4	Meas. Cell	normal
2 DPMODE		U.ampl.	-50 mV	t.meas	20.0 ms
		t.step	0,40 s	t.pulse	40.0 ms
3 STIR		Rot.speed	2000/min		
4 MEAS	30.0 s	U.meas	-900 mV		
5 0STIR	20.0s				
6 SWEEP	48.0	U.start	-900 mV	U.step	6mV
		U .end.	-1600 mV	Sweep rate	15mV/s
6 END					

This programme consists of following three steps;

1. Preconcentration with stirring at E=-0.9 V vs. Ag/AgCl electrode for 30s
2. 20 s rest time (without stirring)
3. Differential pulse scan from -0.9V vs Ag/AgCl electrode up to -1.6 V vs Ag/AgCl electrode.

In step 1 the reduced chromium(VI) accumulates as $Cr(OH)_3$ on the Hg drop and complexation of $Cr(OH)_3$ by DTPA takes place. In step 2 the stabilization of the solution occurs. And in step 3 the complexed chromium(VI) is reduced to chromium(II) on HMDE in presence of nitrate.

Standard addition of necessary volumes of chromium(VI) solutions were added and voltammograms were shown in Figure 1.

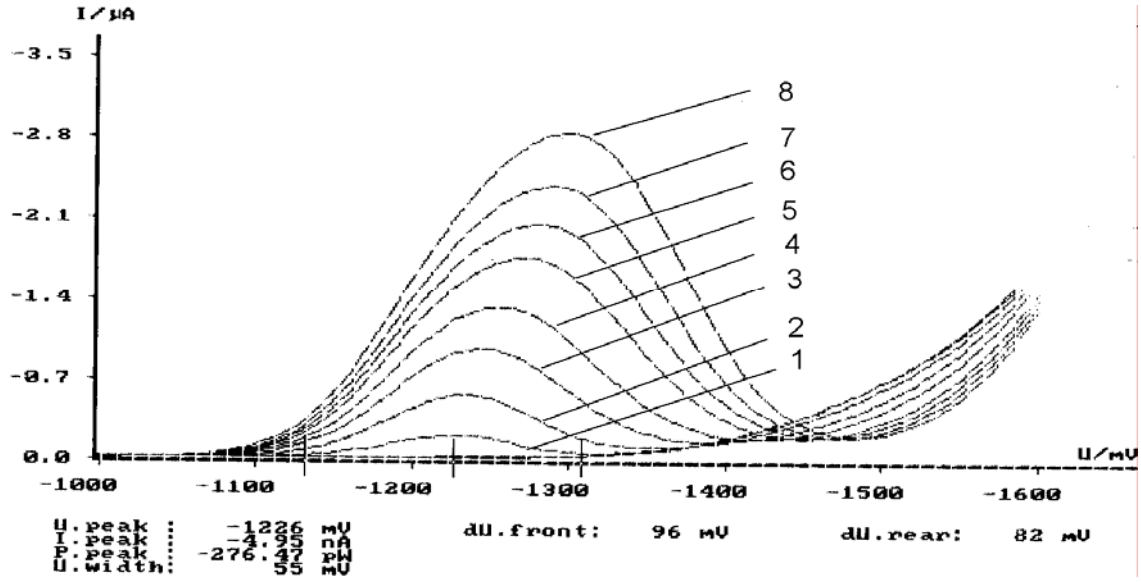

Figure 1 Dependence of peak height on chromium(VI) concentrations from 0.5-7 ppb (1 to 8)

The dependence of current on chromium(VI) concentration gives the linear calibration curve with R^2=0,9962 as shown in Figure 2. At the concentration range of 0,1 to 50 ppb chromium (VI), the linearity of calibration graph is decreased (R^2=0,9857) as also shown in Figure 3. The observed deviation from linearity can be explained by inadequateness of micro electrode's surface area as the concentration increases.

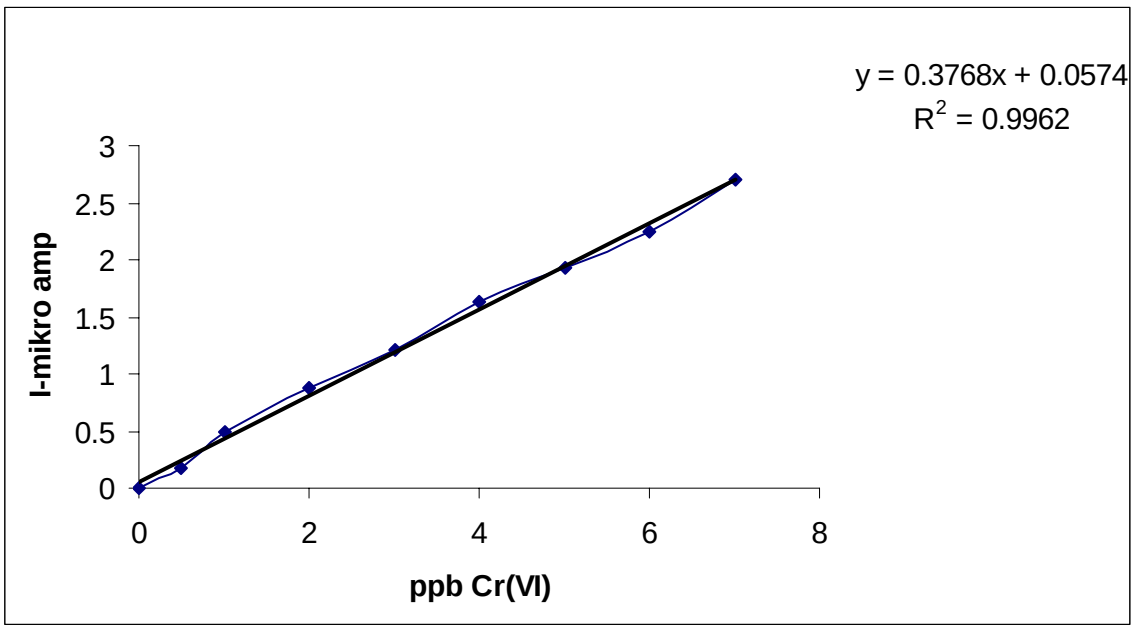

Figure 2 Dependence of peak height on chromium(VI) concentrations from 0.1 to 7 ppb

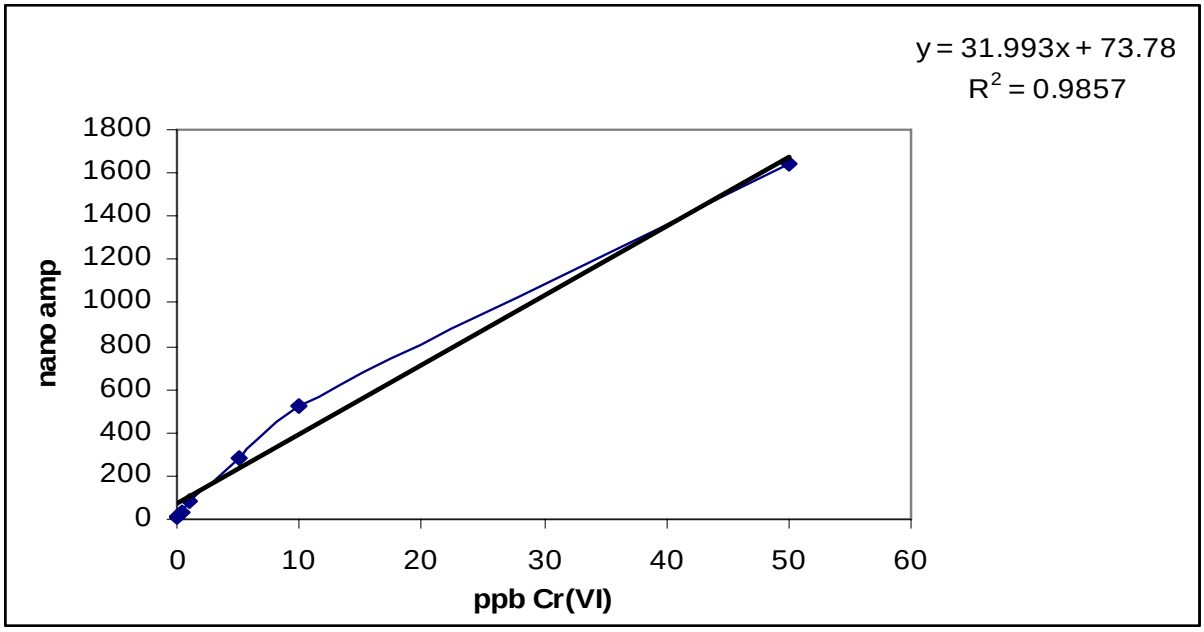

Figure 3 Dependence of peak height on chromium(VI) concentrations from 0.1 to 50 ppb chromium(VI)ppb

When the accumulation time was increased from 30 s to 60 s, peak currents increased about 30%, however the linearity of calibration curve decreased. Therefore the accumulation time was chosen as 30 s.

The catalytic CSV scan of chromium (VI) produced a peak at -1,23 V, at the bottom of hydrogen wave. The reduction current is due to the reduction of chromium(III) to chromium(II) and is enhanced by a catalytic effect in the presence of nitrate ions owing to the chemical reoxidation of chromium(II) to chromium(III) which is subsequently re-reduced at the electrode surface. The scan was preceded by adsorptive collection of chromium(III).

3. Effect of chromium(III) on this voltammetric method

Addition of chromium(III) to blank the solution, produced the same reduction peak at -1,22V indicating that adsorptive complex is also produced when chromium(III) is present in solution as shown in Figure 4. However, the reduction current of the dissolved complex of chromium(III) was not stable and gradually diminished in height, almost all disappeared in approximately 30 min.

Firstly we studied using different concentrations of 1-5-10-50-100-500 ppb chromium(III) and accumulation time of 30s. The voltammograms are shown in Figure 4.

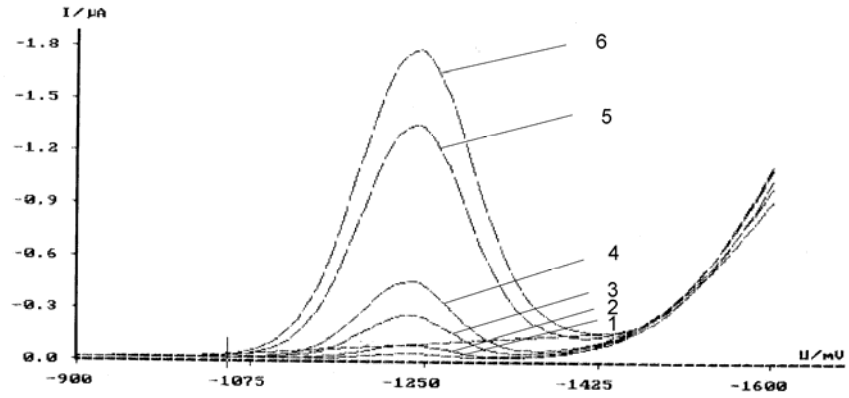

Figure 4 Dependence of peak height on chromium(III) concentrations from 1-500 ppb (1 to 6)

To investigate the effect of chromium (III) on the peak height of chromium(VI), chromium(III) was added to the constant concentration of chromium(VI) solution and the voltammograms were recorded. Figure 5 shows the standard additions of 5, 10, 25, 50 ppb chromium(III) into the 50 ppb chromium(VI) solution. Results clearly show that chromium(III) did not influence the peak height of chromium(VI). In the presence of excess of chromium(III) the reduction peak was gradually increased. To reduce this effect of chromium(III) we complexed it with NTA and proceeded voltammetric analysis.

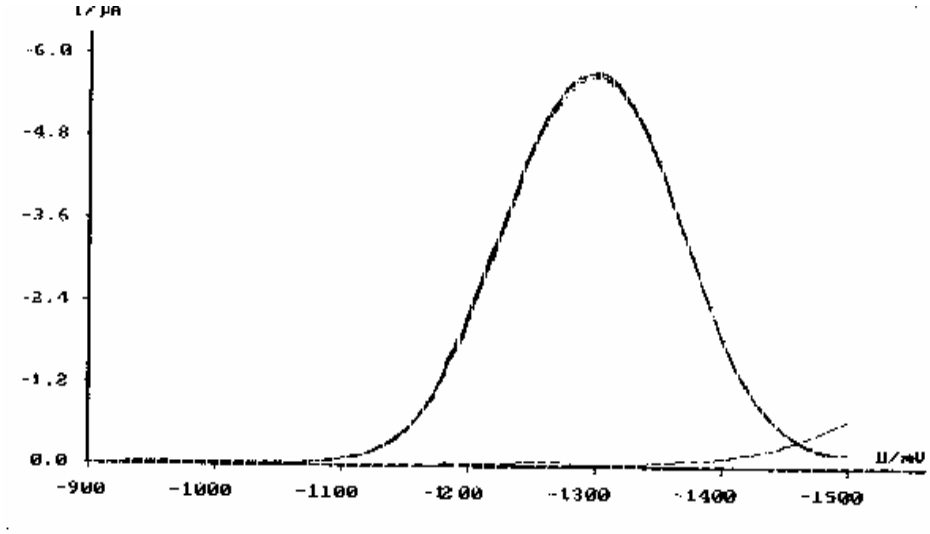

Figure 5 Voltammograms of 50 ppb chromium(VI) in the presence of 5;10;25;50 ppb chromium(III)

4. Chromium(VI) determination by AdSV with application of Nitrilotriacetic Acid (NTA) as a masking agent

For minimization of chromium(III) interference nitrilotriacetic acid was used as a masking agent. The method had three steps:

- Complexation of chromium(III) present in the sample by NTA used as a masking agent

- Accumulation of the product of chromium(VI) reduction in the form of Cr(III)-DTPA complex

- Reduction of the Cr(III)–DTPA complex in the presence of nitrates.

4.1 Procedure:

An aliquot of the sample was pippeted into a 25 mL volumetric flask. Then 0.2 M 3,0 mL NTA (was dissolved with NaOH and the pH adjusted to 6,2) was added and finally the ultra purified water was added up to 25 mL. The solution was placed in a water bath at temperature of 50^{o}C for 10 min. Then the solution was cooled to room temperature and mixed with 4mL 0,1 M DTPA, 4 mL 2,5 M $NaNO_3$, 2 mL 0,1 M phosphate buffer solution and 5mL ultrapurified water. The resulting solution was placed in the voltammetric cell and the program mentioned above was started.

4.2 Complexation of chromium(III) with NTA

According to literature data[9], the reaction of complexation of chromium(III) by complexones proceeds slowly and the reaction time depends on temperature of the solution and concentration of complexone. In this study the time of complex formation was fixed on 10 min., and temperature values were room temperature 18^{o}C, 40^{o}C and 50^{o}C. During the trials it was observed that at 50^{o}C chromium(III) formed a better complexation and this temperature value was selected for the complexation process. The effect of complexation temperature on chromium signal for chromium(III) at 10 and 100 ppb concentrations were given in Table 1.

Cr(III)	**NTA**	**Temperature(°C)**		
		18^{o}C	**40^{o}C**	**50^{o}C**
10	–	229.8	–	–
10ppb	0.015M	114nA	19 nA	3nA
100ppb	–	1272nA	–	–
100ppb	0.015M	663nA	166.8nA	10nA

Table 1 The effect of NTA and complexation temperature on chromium(III) peak height

The effect of NTA on the behavior of chromium(VI) was also investigated at 50°C for 10 minutes and results were shown in Table 2.

Cr(VI)	**With DTPA (procedure2.2)**	**After complexation with NTA (procedure 4.1)**
1 ppb	79.7	53.0
5 ppb	284.5	253.7
10 ppb	501.6	395

Table 2 The effect of NTA on the peak height of chromium(VI) at 50 °C for 10 minutes

These results indicate that NTA which was added as a masking agent for chromium(III) also reduced the peak height of chromium(VI) approximately 20-30%.

5. Application of the method on leather analysis

In order to apply the voltammetric method to leather samples, leather samples were extracted in accordance with IUC 18 method (2grams of leather sample was shaken in pH=8 phosphate buffer for 3 hours). Filtrate was passed through SPE column and then 10ml filtrate was taken and diluted to 25ml (S1). The voltammogram was recorded according to the procedure 2.2. Standard addition of chromium(VI) was performed as 1, 2 and 3 ppb. The results are shown in Figure 6a and 6b

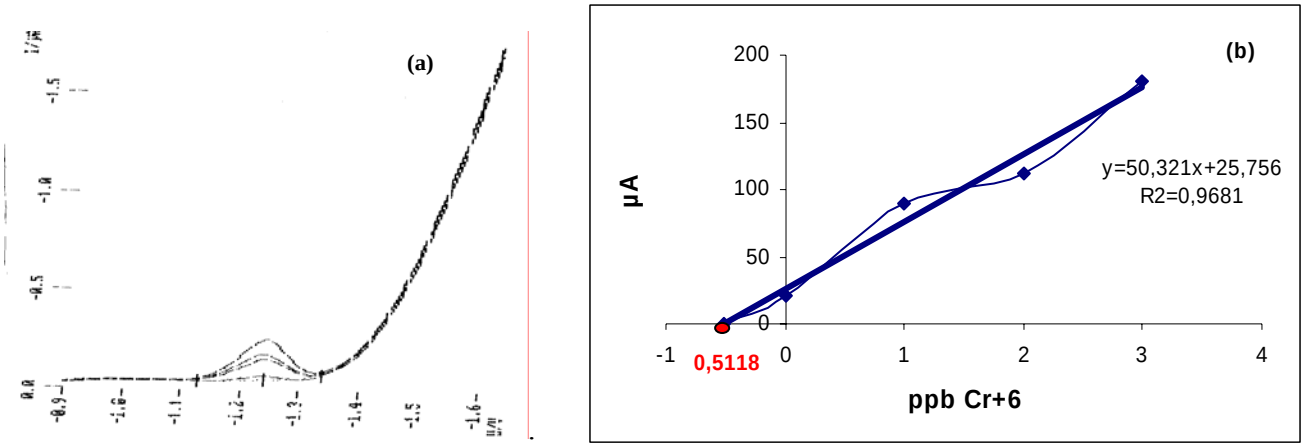

Figure 6a: The voltammograms of chromium(VI) for leather samples and 1-2-3 ppb chromium(VI) additions.

6b: The determination of chromium VI concentration by standard addition method

In this solution and in S1 solution the chromium(VI) contents were found to be 0.51 ppb and 10,5 ppb respectively by using the dilution factor of 40. The chrome content of leather was calculated as 2,63 ppm. The same leather sample was analyzed in accordance with IUC 18 method and the result was found 3,3 ppm.

In two leather samples total chrome analysis was done using ICP-MS and the determined results were 80.5 and 194ppm. The content of chromium(VI) in leather samples was calculated in accordance with IUC 18 method and found as 19,5 and 23 ppm. In the solution which was extracted according to IUC 18 method, chromium(III) content was found to vary between 4 and 10 fold of chromium(VI) content.

6. Results and Discussions

After masking chromium(III), chromium(VI) analysis was tried to be performed sensitively by CCAdSV in the presence of DTPA with nitrate as catalyst at leather samples which have excessive amounts of chromium(VI) beside chromium(III). Here as

a result of depositing at -900mV, chromium(VI) ions were reduced in the form of $Cr(OH)_3$, and Cr(II)-DTPA complex was formed. This complex is absorbed on the electrode surface. Then by cathodic stripping CrII-DTPA peak was observed. By the catalytic effect of nitrate chromium(II) was oxidized, after the reducing and oxidizing processes an increase was observed in the peak of CrIII-DTPA.

This increase in current can be summarized as;
$Cr(III)\text{-}DTPA + e^- \rightarrow Cr(II)\text{-}DTPA$
$Cr(II)\text{-}DTPA + NO_3^- \rightarrow Cr(III)\text{-}DTPA$

The definition limit of spectrophotometric method is approximately $3 mgkg^{-1}$. This value is equal to the forbidden limit of chromium(IV) in most of the leather products; therefore a more sensitive method is required. The sensitivity of voltammetric method is about 0,1 $mgkg^{-1}$ leather.

However owing to complexation of NTA also with chromium(VI) low values were obtained. By performing additional studies we are planning to separate chromium(III) with other complexing agents and/or separate chromium(III) by suitable columns.

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