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Identification of Chromium Species in Tanning Solutions

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Abstract

This paper presents results of a study on identification of the speciation forms of chromium (III) in the tanning solutions. The cation complexes of Cr(III) were isolated and purified by ion-exchange chromatography. The isolated speciation forms were identified by differential pulse polarography (DPP) and VIS spectrophotometry. The activity of the tanning preparations is determined by the specific speciation forms of Cr(III) present in the solutions and determines their toxicity in the natural environment.

Keywords: Cr(III), tanning solutions, speciation.

Introduction

Chromium belongs to trace elements, but recently its concentrarion in the natural environment has been observed to increase, which has been explained as related to the development of metallurgical, tanning and chemical industries [1]. In natural surface water chromium occurs as two species: Cr(III) an Cr(VI). The species undergo transformations depending on a number of conditions. In well aerated water chromium, mainly Cr (VI), occurs, while in anaerobic conditions Cr(VI) undergoes reduction to Cr(III) [2,3]. In certain conditions chromium precipitates and occures as a suspension. However, its most important property is the possibility of bioaccumulation in living organisms. Recently observed levels of chromium in natural surface water are a result of human activity. Chromium emited from industrial plants is found mainly in surface water and soils. One of the main chromium polluters is the tanning industry. Therefore, a study was undertaken to identify the chromium (III) species occurring in the tanning solutions in order to select the optimum conditions of the natural environment.

Freshly made tanning solutions contain anionic and neutral chromium complexes, which gradually transform into cationic complexes bonding from 80 to 90% of chromium (III) present in such solutions. The problem of identification of the cationic chromium (III) species occurring in the tanning solutions has not yet been fully resolved, despite many attempts. So far an agreement has only been reached as to the presence of aquahydroxo complex and a simple aquasulphate complex $[Cr(H_2O)_5(SO_4)]^+$ [4-12].

Expertimental

Tanning Solutions: Chromal and Chromethane

The isolation and purification of the cationic Cr(III) complexes have been performed using ion-exchange chromatography.

Preparations of Chromatographic Column

Chromatographic separation of different Cr(III) species was performed using a chromatographic column of 10 mm in diameter and 10 cm in length filled with cationic resin Sephadex SP C25 from Merck. Prior to use it was rested in distilled water for 24 hours to swell. Then 0.4 mol/dm^3 HCl was passed through the column till the appearance of H^+ in the effluent. The acid was followed by distilled water passed through the column until pH=7. After this preparation procedure the column was used for separation of cationic complexes of Cr(III) present in tanning solutions.

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The Eluents

The eluents were the solutions of $NaClO_4$ in $HClO_4$ in the following concentrations:

1. 0,5 mol/dm^3 $NaClO_4$ in 0,01 mol/dm^3 $HClO_4$,
2. 1 mol/dm^3 $NaClO_4$ in 0,01 mol/dm^3 $HClO_4$,
3. 2 mol/dm^3 $NaClO_4$ in 0,02 mol/dm^3 $HClO_4$,
4. 4 mol/dm^3 $NaClO_4$ in 0,04 mol/dm^3 $HClO_4$.

Particular chromium (III) species were washed out according to the procedure analogous to that proposed by Stünzi, Marty and Spicci [13-15].

Instruments

Polarographic measurements were performed by a set made by EG&G Princeton Applied Research including: a polarographic analyser 264A, a drop electrode 303A and a recorder RE 0150 X-Y.

Method

The polarographic measurements were performed under the following conditions:

The potential range analyzed: 0.5V to-1.4V, scanning rate 5mV/s, sensitivity 20μA, voltage 100mV, mercury drop size L, electrolyte deoxidisation 8 min.

The polarographic cell with 10 ml of an electrolyte solution contained a mercury electrode, a reference (AgCl/Ag, KCl 3mol/dm^3) electrode, an auxiliary electrode (platinum) and a pipe supplying argon in order to eliminate oxygen from the solution. The cell construction permitted deoxidisation of the electrolyte solution prior to measurements and maintenance of anaerobic atmosphere over the solution during the measurements. Prior to analysis the electrolyte solution was deaerated for 2 min. The measurements of samples studies were performed by the method of differential pulse polarography (DPP).

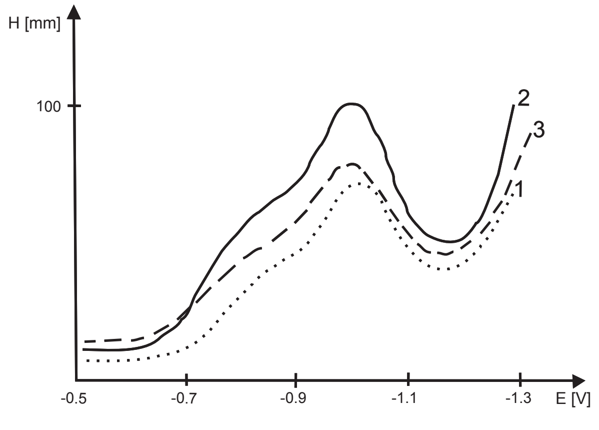

Fig. 1. Polarogram of the tanning solutions. a) Polarogram of the Chromal sample aged for 48 h (curve 1), b) Polarogram of the Chromethane sample aged for 48 h (curve 2), c) Polarogram of the Chromethane after 10 minutes of preparation (curve 3).

Table 1. Results of the chromatographic and polarographic analyses, chromium (III) complexes.

Speciation Forms Cr(III)	Eluent $NaClO_4$ in $HClO_4$	Value potential for max. peak DPP [V]
$[Cr(H_2O)_6]^{3+}$	0.5mol/dm^3	- 0.770
$[Cr(SO_4)]^+$	0.5 mol/dm^3	- 0.940
$[Cr(OH)_2Cr]^{4+}$	2.0 mol/dm^3	- 0.855
$[Cr(SO_4)(OH)Cr]^{3+}$	2.0 mol/dm^3	- 0.995
$[Cr(SO_4)(OH)Cr(SO_4)]^+$	2.0 mol/dm^3	- 1.075

The electrolyte used was a 0.2 mol/dm^3 solution of potassium thiocyanate in 10^{-3} mol/dm^3 sulphuric acid. The electrolyte solution was prepared by dissolving a weighted portion of 1.9434g KSCN in a flask of 100 cm^3 capacity in a 10^{-3} mol/dm^3 sulphuric acid. The sulphuric acid solution was obtained by placing 53.5 ml 95-97% of H_2SO_4 (Merck) in flask of 1000 cm^3 supplementing the flask with deionized water up to the mark.

Results and Discussion

Standard measurments were performed for pure Cr(III) salts and for simulated conditions of solution aging. [16-17]

Identyfication of the Cr(III) Species in Chromal

The material studied was chromal made in Poland of the chemical formula of $2Cr_2(OH)(SO_4) \cdot Na_2SO_4$. It was used to prepare a solution of a typical concentration of chromium used in tanning – of 7.5% Cr(III). The solution was obtained by dissolving the preparation in distilled water. Its polarogram revealed no presence of electroactive forms. The polarographic curve coincided with that obtained for the fundamental electrolyte. As tanning is performed with aged solution, the solution studied was also aged for 48 hours. The polarogram recorded after this time is shown in Fig. 1.

As suggested by the course of polarographic curve (Fig. 1), the solution includes two or more species of Cr(III), which indicated the need for chromatographic separation. The sample was injected onto the column and particular complexes were eluted by $NaClO_4$ solutions of increasing concentrations. The separation led to obtaining four fractions whose VIS spectra and polarograms were taken. On the basis of the earlier studies [18-21] it was possible to assign the species to the potentials at which the maxima of the peaks of their signals appeared, see Table 1. The results of the spectrophotometric and polarographic analysis are presented in Table 2.

Identyfication of the Speciation Forms of Cr(III) in Chromethane

Another solution studied was that of Chromethane made in the UK, of chemical formula $Cr_2(OH)_2(SO_4)_2 \cdot Na_2SO_4 \cdot 10H_2O$. The chromethane was dissolved in

Table 2. Results of the spectrophotometric and polarographic analyses of the Chromal sample aged for 48 h.

Fracions	Speciation forms Cr(III)	λ_{max} [nm]	λ_{max} [nm]	Value potential for max. peak DPP [V]
I	$[Cr(OH)_2Cr]^{4+}$ $[Cr(S0_4)]^+$	416-418 414-418	580-582 583-587	- 0.850 - 0.940
II	$[Cr(S0_4)(OH)_2Cr]^{2+}$	418-419	582-584	- 1.075
III	$[Cr(S0_4)(OH)_2Cr]^{2+}$ $[Cr(H_2O)_6]^{3+}$	417 406	582 573	- 0.770 - 1.075

Concentration sample Chromal 0.2mol/dm^3, pH=3.0

Table 3. Results of the spectrophotometric and polarographic analyses of the Chromethane sample aged for 48 h.

Fracions	Speciation forms Cr(III)	λ_{max} [nm]	λ_{max} [nm]	Value potential for max. peak DPP [V]
I	$[Cr(H_2O)_6]^{3+}$ $Cr(SO_4)]^+$	406 414-418	573 583-587	-0.770 -0.940
II	$[Cr(OH)_2Cr]^{4+}$ $[Cr(SO_4)(OH)Cr]^{3+}$	416-418 420-422	580-582 585-586	-0.850 -1.010

Concentration sample Chromal 0.2mol/dm^3, pH=3.0

distilled water to obtain a solution concentration of 7.5%. Fresh chromethane solution did not contain electroactive Cr(III) species. Prior to the study the solution was aged for 48 hours, and then its polarogram was taken (Fig. 2).

The course of the polarographic curve suggests the presence of two or more Cr(III) species. in order to separate them the solution was subjected to HPL procedure. The particular complexes were eluted with solutions of different concentrations of $NaClO_4$. The three fractions obtained were characterized by VIS spectroscopy and polarogram. The results of the spectrophotometric analysis are shown in Table 3. The solution of chromal was found to contain four Cr(III) species appearing in specific conditions. The course and character of tanning process is determined by the quantitive composition of this solution. Determination of the optimum conditions of getting a desired mixture of complexes helps to establish the optimum conditions of tanning, which is of economical importance (Fig.3).

Also in the solution of chromethane four Cr(III) species were identified as: $[Cr(H_2O)_6]^{3+}$, $[Cr(SO_4)]^+$, $[Cr(OH)_2Cr]^{4+}$ and $[Cr(SO_4)(OH)Cr]^{3+}$. The compositions of chromal and chromethane differ by the presence of one species: chromal contained $[Cr(OH)_2SO_4Cr]^{2+}$ and chrom ethane$[Cr(SO_4)(OH)Cr]^{3+}$. The complexes $[Cr(H_2O)_6]^{3+}$ and $[Cr(SO_4)]^+$ are water soluble so they will be easily transformed into hydroxy species $[Cr(OH)_2Cr]^{4+}$ and $[Cr(SO_4)(OH)_2Cr]^{2+}$. Moreover, their significant charge and molecular weight indicate in particular soil water, which leads to sedimentation.

Therefore, in the natural surface water chromium is found in highest concentrations in bottom sediments, where it is sequentially bonded and its mobility is closely dependent on climatic and chemical conditions [18-21].

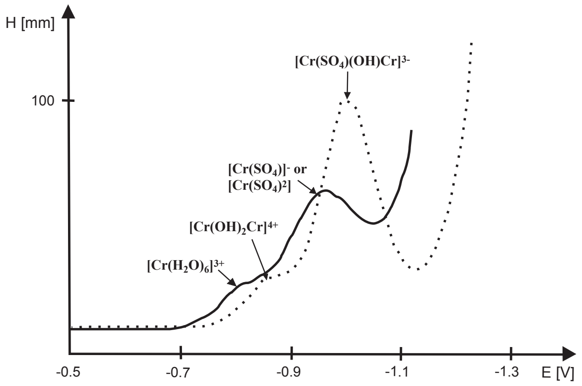

Fig. 2. Polarogram two chromatographic fraction of chromethane sample aged for 48 h with identyfication species of Cr (III) complexes.

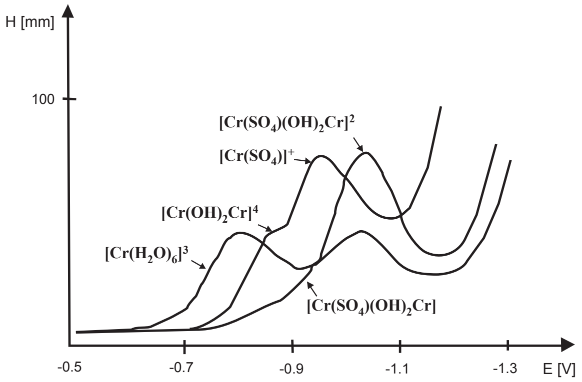

Fig. 3. Polarogram three chromatographic fractions of Chromal sample aged for 48 h with identification species of Cr (III) complexes.

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