Trace Determination of Chromium in Various Water Types by Adsorption Differential Pulse Voltammetry *

J. Golimowski, P. Valenta, and H. W. Nürnberg**

Institute of Applied Physical Chemistry, Nuclear Research Centre (KFA) Juelich, D-5170 Juelich, Federal Republic of Germany

Spurenbestimmung von Chrom in verschiedenen Wassertypen durch Adsorptions-Differentialpuls-Voltammetrie

Zusammenfassung. Eine neue voltammetrische Methode zur Spurenbestimmung von Chrom [als Summe von Cr(III) und Cr(VI)] in natürlichen Gewässern wurde entwickelt. Die Methode beruht auf einer Anreicherung des Cr(III)-DTPA-Komplexes durch Adsorption an der hängenden Quecksilbertropfenelektrode beim Potential −1.0 V. Der adsorbierte Komplex wird anschließend im differentiellen Pulsmodus reduziert und die Peakhöhe beim Peakpotential −1.22 V gemessen. Die katalytische Wirkung von Nitrat- und Bromationen auf die Cr(III)-DTPA-Reduktion wurde mit der cyclischen Voltammetrie geklärt. Die Adsorption der Cr-Komplexe wurde zusätzlich mit der a.c.-Voltammetrie (kapazitive Komponente) untersucht und der Potentialbereich der Adsorption ermittelt. Aufgrund der Untersuchungen wurden die optimalen Bedingungen zur Chrombestimmung im Konzentrationsbereich 20−2000 ng/l festgelegt. Die Bestimmungsgrenze liegt bei 20 ng/l und die relative Standardabweichung beträgt 5% für Konzentrationen ⩾200 ng/l. Die weite Anwendbarkeit der Methode für die zuverlässige und hochempfindliche Analyse von Chromspuren bis zu den natürlichen Ultraspurengehalten in verschiedenen Typen natürlicher Wässer wird an Beispielen der Analyse des gelösten Gesamtgehaltes von Chrom in Flußwasser, Seewasser, Meerwasser und Regenwasser aufgezeigt.

Summary. A new sensitive voltammetric method is presented for the determination of trace amounts of total chromium [Cr(III) and Cr(VI)] in natural waters. The method is based on the preconcentration of the Cr(III)-DTPA complex by adsorption at the HMDE at the potential of −1.0 V. The adsorbed complex is then reduced producing a response with a peak potential of −1.22 V and the peak height of the Cr(III) reduction is measured. The catalytic action of nitrate and bromate ions on the Cr(III)-DTPA reduction has been elucidated using cyclic voltammetry. The adsorption of chromium complexes at the HMDE was investigated using out-of-phase a.c. voltammetry and the potential range of adsorption was determined. Based on these investigations optimal conditions for the determination of the total chromium concentration in the range 20−2,000 ng/l have been established. The determination limit is 20 ng/l and the RSD is 5% for chromium concentrations ⩾200 ng/l.

The usefulness and wide scope of this new voltammetric method for reliable and highly sensitive chromium analysis down to the natural ultra trace levels existing in various types of natural waters is demonstrated by determinations of the total dissolved chromium content in river, lake, sea and rain water.

Introduction

Aquatic chemistry of chromium, which is an important ecotoxic trace metal, has hitherto been handicapped by a lack of sufficiently sensitive analytical methods enabling the reliable determination of pollution and background levels of chromium in natural waters. The relatively inert chromium(III) species and the reactive more toxic chromium(VI) species [1−3] are present in natural waters in various concentrations, from 0.1 to 0.5 µg/l in ocean waters [4] to 200 µg/l in some polluted ground waters [5]. Most of the soluble chromium is present in water as hexavalent chromium but this generally accounts for only a part of the total chromium depending on the oxidation potential of the water system.

Chromium, at concentrations above 50 µg/l, has been determined polarographically in NaOH solution or in the acetate buffer solution of EDTA [6]. The addition of nitrate ions to the latter solution considerably enhances the reduction peak of Cr(III) complexes with EDTA or other ligands [7]. The detection limit at the DME is about 2 µg/l in the differential pulse polarographic (DPP) mode. The increase of the reduction peak of Cr(III) complexes was explained by catalytic action of the nitrate ions. The catalytic enhancement of the Cr(III) reduction was later applied to the determination of chromium in the semiconductor gallium arsenide at the DME using DPP techniques [8, 9]. The use of a solid electrode, i.e. a glassy carbon electrode, in an ammonium buffer [10] or in HCl solution has also been proposed for the chromium determination. However, the latter methods do not give reproducible results. The reason is probably a poor adherence of the $Cr(OH)_3$ deposited at the electrode in alkaline media and a low current efficiency of the deposition of metallic chromium in acid media (pH 2) caused by the simultaneous reduction of hydrogen ions to gaseous hydrogen, which isolates the electrode surface from the solution [11]. The use of a platinum electrode modified

* Dedicated to Prof. Dr. H. Monien on the occasion of his 60th birthday

** Attached from Department of Chemistry of Warsaw University, Poland, within the scope of the joint research project on „Ecotoxic Metals in the Environment"

Offprint requests to: P. Valenta

© Springer-Verlag 1985

by a surface layer of poly(4-vinylpyridine) (PVP) in a voltammetric study of chromates was proposed, but no analytical application of the method was presented [12, 13]. Atomic absorption spectrometry (AAS) is useful for the determination of chromium at concentrations above 2 µg/l. At lower concentrations, however, a preconcentration or a multiple injection into the graphite platform is necessary leading to a rather large error [14]. For a recent review see [15].

In this paper the adsorptive preconcentration of Cr(III)-diethylenetriaminepentaacetic acid (DTPA) complexes at the hanging mercury drop electrode (HMDE) in DTPA-CH_3COONa-$NaNO_3$ solutions of pH 6.2 was studied and applied to the determination of chromium at concentrations down to 20 ng/l in various water types using the method of adsorption differential pulse voltammetry (ADPV) [16] and exploiting in addition the catalytic action of nitrate. Also chromium which is particularly important from ecotoxicological aspects, has now become conveniently determinable by this new method over the whole range of concentration levels occurring in all types of natural waters with voltammetric approach [17], especially suitable and reliable for ecotoxic metals in aqueous media.

Experimental

The differential pulse voltammograms were recorded with the polarograph Metrohm, Polarecord E 506, and the polarographic analyzer EG & G, PAR 174 A, in conjunction with the Metrohm EA 290 hanging mercury drop electrode. The surface area of the mercury drop was 1.38 mm^2. The measurements were carried out with the three-electrode system under the following experimental conditions: clock time 0.4 s, pulse height 50 mV, scan rate 10 mV/s.

For the a.c. voltammetric measurements the dropping mercury electrode with regulated drop time was used. The following parameters were chosen: AC_1 rapid technique, phase angle 90°, frequency 75 Hz, scan rate 5 mV/s, a.c. amplitude 10 mV, drop time 1 s.

The saturated Ag/AgCl electrode was used as a reference electrode. The solution was stirred with a Teflon coated magnetic stirring bar or by the nitrogen stream. The pH was measured with an Orion 701 digital pH-meter applying a combined glass/calomel reference electrode.

Stock solutions of chromium(III) and (VI) were prepared by dilution of "Titrisol" standard solutions. Aqueous 0.1 M EDTA and DTPA stock solutions were prepared by dilution of Merck chemicals in equivalent amounts of NaOH. 1 M CH_3COONa, 1 M KCl and a saturated $NaNO_3$ solution were prepared from Merck "Suprapur" chemicals. The base solution, used for the analytical determination, containing 0.05 M DTPA, 0.2 M CH_3COONa and 2.5 M $NaNO_3$, was prepared by dissolving: 1.96 g DTPA, 1.35 g 30% NaOH sol., 1.64 g CH_3COONa and 21.3 g $NaNO_3$ in water and dilution to 100 ml. This solution should be stored in a quartz flask.

The solutions were purged before the voltammetric determination with 99.999% nitrogen to remove oxygen.

Results and Discussion

In aqueous solutions chromium exists mainly as chromium(III) compounds, i.e. $Cr(H_2O)_6^{3+}$, $Cr(OH)^{2+}$, $Cr(OH)_2^+$, and Cr(VI) compounds, i.e. CrO_4^{2-} and $Cr_2O_7^{2-}$. The polarographic reduction of aquocomplexes of chromium(III) proceeds irreversibly and is not suitable for the polarographic determination of chromium. However, the reduction of Cr(III) chelates can be analytically used, although their reduction potential is more negative than that of the Cr(III)-aquocomplexes and therefore the interference of the reduction of hydrogen ions can be expected. Thus, in acetate buffer solution of EDTA chromate ions are reduced in two steps [6]. The first response at the half-wave potential ($E_{1/2}$) of −0.05 V assigned to the three electron reduction Cr(VI) → Cr(III) is not well developed and cannot be used for the determination. The second one-electron reduction response Cr(III) → Cr(II) at $E_{1/2}$ of −1.22 V is well developed and only slightly disturbed by the reduction of hydrogen ions. The latter response is used for the chromium determination, especially in the a.c. mode as in this case the hydrogen ion reduction is irreversible and thus shifted to more negative potentials.

In acetate solutions of DTPA a similar voltammetric response has been observed. The differential pulse polarogram of Cr(VI) and Cr(III) in an acetate buffer solution of DTPA at the DME is shown in Fig. 1. The Cr(III) complexes are reduced in a one-electron step yielding a response beginning from about −0.95 V ($E_{1/2}$ −1.22 V) (see curve 2). In the presence of Cr(VI) a much steeper decay of the current at the beginning of the voltammogram is caused by the reduction of Cr(VI) to Cr(III) (curve 3). The second reduction response occurs at the same potential as that in the solution of Cr(III) ions and its height changes with the concentration of Cr(VI) ions in the same way as with the concentration of Cr(III) ions. Thus, at potentials more negative than −0.05 V, Cr(III)-DTPA complexes are formed after prior reduction of Cr(VI).

The formation of DTPA-complexes from Cr(III) aquocomplexes and DTPA proceeds rather slowly as the photometric study of this reaction reveals, i.e. within about 20 min [18]. It is possible to accelerate this reaction by heating the solution up to 70° C. On the other hand, the formation of the Cr(III)-DTPA complexes from free Cr^{3+} ions formed by reduction of Cr(VI) and DTPA proceeds instantaneously under polarographic conditions [18, 19]. As the reduction of Cr(III) aquocomplexes at the mercury electrode is irreversible, it seems that the dehydratation of Cr(III) aquocomplexes is a slow rate determining step in both cases.

The one-electron reduction response of chromium(III) at −1.22 V can be enhanced in the presence of nitrate ions. It has been assumed that the nitrate ion chemically oxidizes the Cr(II)-DTPA complexes formed by the reduction of Cr(III) so that a catalytic reduction current results [7]. This effect leads to a large increase of the sensitivity of the voltammetric determination of chromium. In our previous work on Ni, Co [16, 20, 21] and SiO_2-traces [22] an enhancement of the reduction of some complexed metal ions has been achieved, due to interfacial preconcentration by the adsorption of the metal complex species at a suitable adsorption potential at the hanging mercury drop electrode and the subsequent reduction of the adsorbed complex after scanning the potential to the appropriate range. Therefore, the possibility of the accumulation of the Cr(III)-DTPA complex at a HMDE by adsorption has been investigated. Moreover, the reduction process in the presence of the nitrate ions has been elucidated and the dependence of the

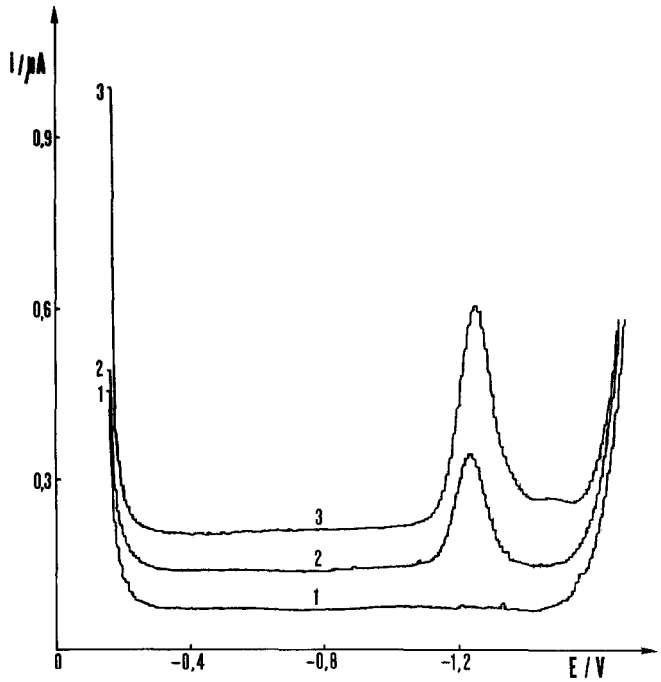

Fig. 1. DP-voltammogram of Cr(III) and Cr(VI) at the DME. *1*: 0.1 M CH_3COONa, 0.01 M DTPA, pH 6.2; *2*: *1* + 5×10^{-5} M Cr(III); *3*: *2* + 5×10^{-6} M Cr(VI)

reduction response on various parameters as pH, electrolyte composition, presence of surfactants and the adsorption potential has been investigated in order to establish optimal conditions for the trace determination of chromium.

Dependence on pH

The pH dependence of the peak height of the Cr(III)-chelate reduction has been studied by Lanza and Taddia [8] and by Ranly and Neeb [19] using differential pulse polarography. In our case of the reduction of the Cr(III)-DTPA complexes at the HMDE a similar pH dependence as that reported by Lanza and Taddia has been obtained (Fig. 2). Maximum peak height is attained at pH 6.0 – 6.2, whereas below pH 4.5 and above pH 7.5 the reduction peak practically disappears. It follows from the equilibrium constants of DTPA, given by Martell and Smith [23], that only one protonation equilibrium according to Eq. (1) has to be taken into account

$$H_3Y^{2-} \rightleftharpoons H^+ + H_2Y^{3-} \quad (pK_3\ 4.3). \qquad (1)$$

It can be shown that using the equilibrium constant pK_3 4.3 and the analytical DTPA concentration of 0.01 M the concentrations of H_2Y^{3-} and H_3Y^{2-} are 9.8×10^{-3} M and 1.8×10^{-4} M, respectively. The concentrations of other DTPA forms are by several orders of magnitude lower at this pH. Thus, it can be assumed that at pH about 6 the Cr(III)-DTPA complexes are formed according to Eqn. (2) and (3)

$$H_2Y^{3-} + Cr^{3+} \rightleftarrows CrY^{2-} + 2H^+ \qquad (2)$$

$$H_3Y^{2-} + Cr^{3+} \rightleftarrows CrY^{2-} + 3H^+ \qquad (3)$$

where CrY^{2-} represents the most stable Cr(III)-DTPA complex with the stability constant of pK 15.34 [24]. The

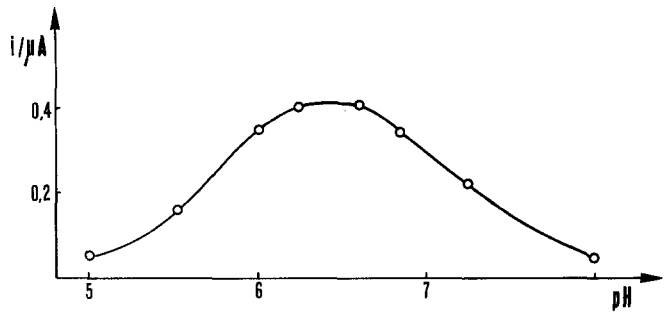

Fig. 2. DP-peak height vs. pH. 200 ng Cr/l, 0.01 M DTPA, 0.04 M CH_3COONa, 0.5 $NaNO_3$

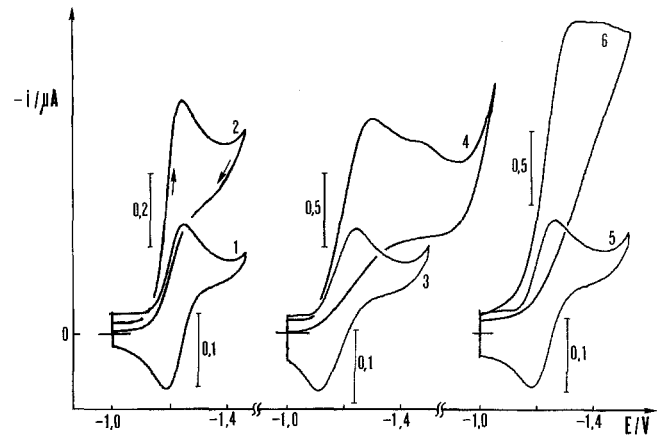

Fig. 3. Cyclic voltammetric curves for Cr(III)-EDTA complexes *1*, *2* and Cr(III)-DTPA complexes *3*, *4* in the absence *1*, *3* and in the presence *2*, *4* of NO_3^-; pH 6.2, scan rate 20 mV/s. *1*: 0.2 M CH_3COONa, 10^{-4} M Cr(III)-EDTA; *2*: *1* + 0.05 M $NaNO_3$; *3* and *5*: 0.1 M CH_3COONa, 10^{-4} M Cr(III)-DTPA; *4*: *3* + 0.05 M $NaNO_3$; *6*: *5* + 10^{-3} M $KBrO_3$

pH dependence of the Cr(III)-DTPA reduction peak corresponds obviously to the stability region of this complex.

Dependence on the Nitrate Ion Concentration

It is well known that in the presence of nitrate ions the reduction response of Cr(III)-chelates is noticeably enhanced in classical polarography and in differential pulse polarography as well [7, 8]. It has been assumed that at sufficiently positive potentials, i.e. at the foot of the polarographic wave or of the pulse polarographic peak the Cr(II)-chelates formed by the reduction are chemically oxidized by the nitrate and that a catalytic reduction current results.

To examine this supposition, cyclic voltammograms of the reduction of Cr(III)-EDTA and of Cr(III)-DTPA complexes have been investigated in the absence and in the presence of the nitrate ions (Fig. 3). In the absence of the nitrate ions both Cr(III) chelates undergo a reversible one-electron reduction. This is indicated by the difference between the anodic E_a and the cathodic E_c peak, $E_a - E_c$, which is equal to about 60 mV and by the ratio of the anodic to the cathodic peak height which is approximately equal to 1 (see curves 1, 3 and 5 in Fig. 3). In the presence of the nitrate ions, however, the anodic peak disappears whereas the

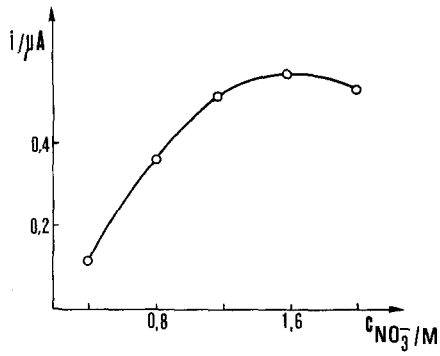

Fig. 4. DP-peak height vs. nitrate concentration at pH 6.2 in: 0.01 M DTPA, 0.04 M CH_3COONa, 200 ng Cr(VI)/l

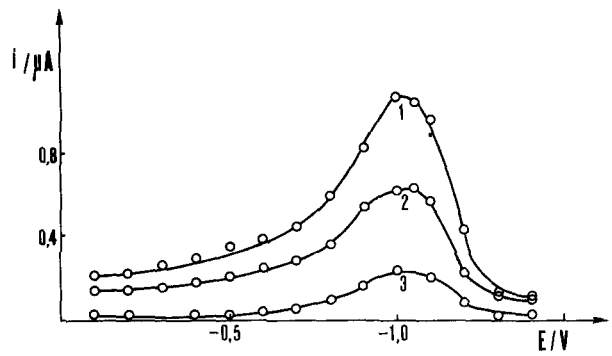

Fig. 5. DP-peak height vs. adsorption potential at HMDE (*1*) in the absence (*2*) and (*3*) in the presence of Triton X-100. *1*: 0.01 M DTPA, 0.04 M CH_3COONa, 0.5 M $NaNO_3$, pH 6.2 Cr(VI) 400 ng/l; *2*: *1* $+4\times10^{-5}$% Triton X-100; *3*: *1* $+1.2\times10^{-4}$% Triton X-100, adsorption time 30 s

cathodic peak is enhanced (curves 2 and 4 in Fig. 3). Obviously, the regeneration of the Cr(III) complexes by the oxidation with the nitrate ions causes an increase of the cathodic peak whereas the depletion of Cr(II)-DTPA complexes at the electrode is the cause for the absence of the anodic peak. Thus, the following mechanism is proposed for the catalytic current

$$Cr(III) \xrightarrow{e^-} Cr(II) \xrightarrow{NO_3^-} Cr(III). \quad (4)$$

The validity of the proposed mechanism is supported by an analogous action of bromate ions (Fig. 3). Comparing curve 6 taken in the presence of the bromate ions with curve 5 taken without the bromate ions the enhancement of the cathodic peak and at the same time a complete missing of the anodic peak can be seen. Thus, the catalytic action of the nitrate ions is a general effect which is not due to some specific property of these ions but is due to their oxidative action on the Cr(II) complexes and the same is the case for the action of the bromate ions.

The dependence of the reduction peak of the Cr(III)-DTPA on the nitrate ion concentration is shown in Fig. 4. A similar dependence of the height of the differential pulse polarographic peak of Cr(III)-DTPA complexes was obtained by Zarebski [7]. Based on these results the determination of chromium can also be performed in the presence of bromate ions. This would be of little interest, however, as the determination limit is worse in the latter case caused by the lack of commercially available pure chemicals.

Dependence on the Adsorption Potential and the Adsorption Time

The peak of the Cr(III)-DTPA reduction at the HMDE in the presence of the nitrate ions exhibits a remarkable dependence on the adsorption potential shown in Fig. 5. The peak height increases with the negativation of the adsorption potential up to -1.0 V, reaches a maximum at this potential and then decreases again until the potential of the onset of the reduction peak at -1.2 V is reached. The peak heights shown in Fig. 5 were obtained by waiting for 30 s at the respective adsorption potential, adjusting then the starting potential to -1.0 V, and recording the voltammogram during the scan into the negative direction. If an increasing concentration of a surfactant is added to the Cr(III)-DTPA solution the peak height is depressed and the whole dependence on the adsorption potential is lowered (see curves 2 and 3 in Fig. 5). If a sufficient concentration of a surfactant is added, the chromium reduction peak is completely suppressed. The peak height dependence on the concentration of the strong surfactant Triton X-100 is shown in Fig. 6. It can be seen that above a Triton X-100 concentra-

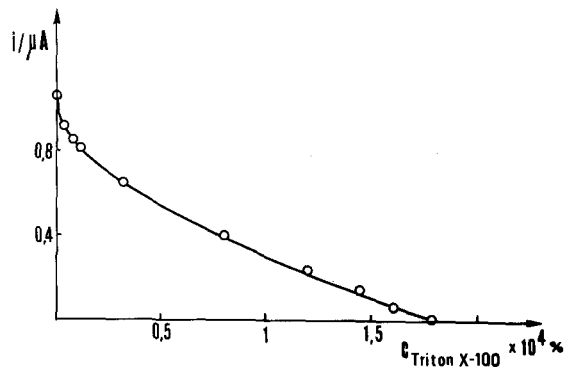

Fig. 6. DP-peak height vs. Triton X-100 concentration E_{ads} -1.0 V, other parameters see Fig. 5

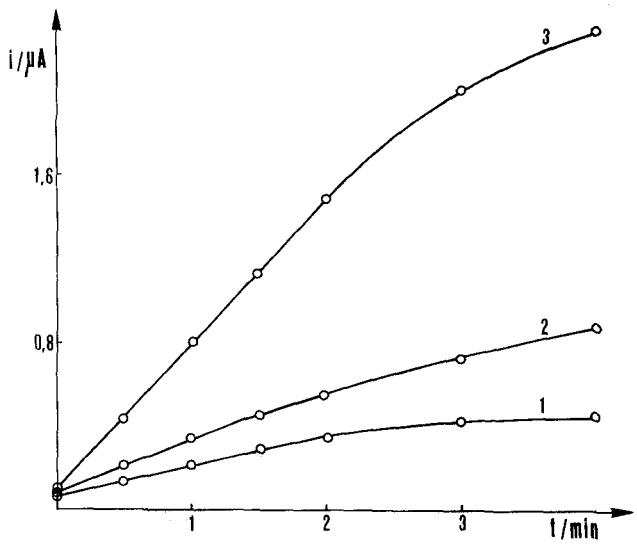

Fig. 7. DP-peak height vs. adsorption time at the HMDE at pH 6.2 in: 0.01 M DTPA, 0.04 M CH_3COONa, 0.5 M $NaNO_3$ *1*: 90; *2*: 180; *3*: 450 ng Cr(VI)/l

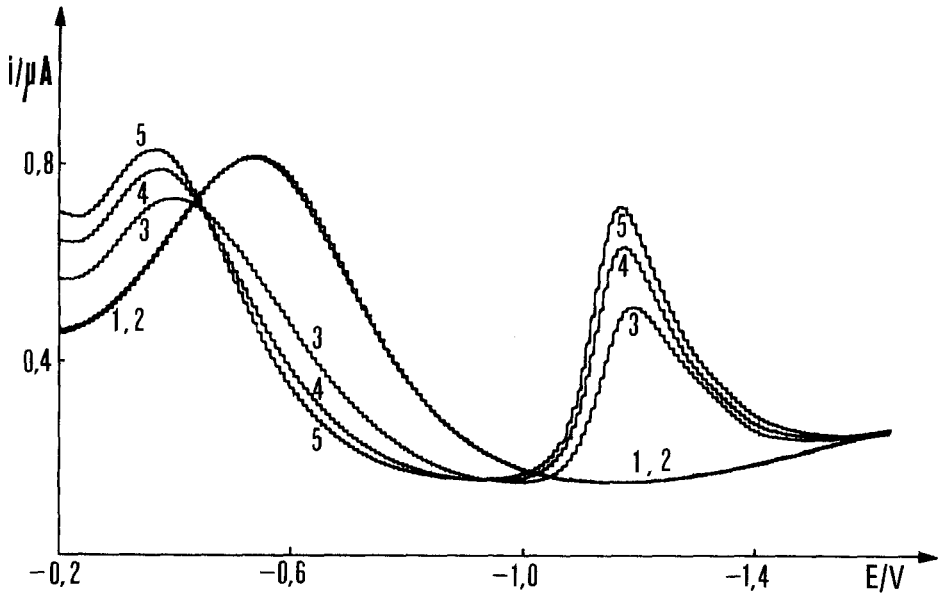

Fig. 8
Out-of-phase a.c.-polarograms of DTPA and Cr(III)-DTPA complexes, recorded at the DME in $NaNO_3 + CH_3COONa$ solution at pH 6.2. *1*: 0.5 M $NaNO_3$, 0.05 M CH_3COONa; *2*: *1* $+10^{-3}$ M DTPA; *3*: *2* $+5\times10^{-4}$ M Cr(III)-DTPA; *4*: *2* $+10^{-3}$ M Cr(III)-DTPA; *5*: *2* $+2\times10^{-3}$ M Cr(III)-DTPA

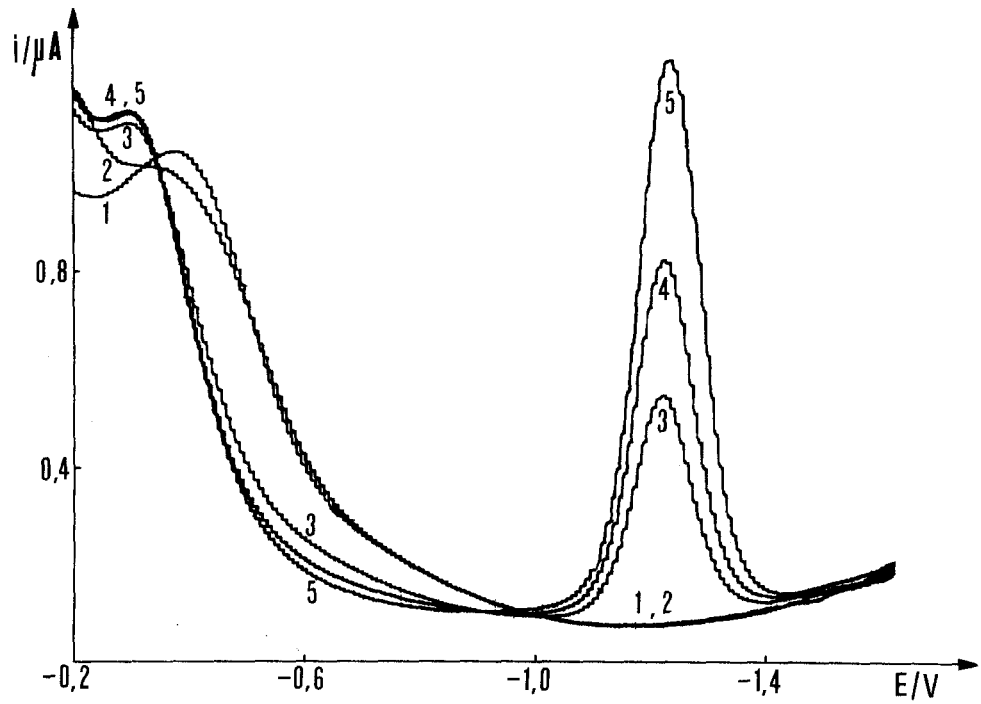

Fig. 9
Out-of-phase a.c.-polarograms of DTPA and Cr(III)-DTPA complexes, recorded at the DME in $KCl + CH_3COONa$ solution at pH 6.2. *1*: 0.1 M KCl, 0.05 M CH_3COONa; *2*: *1* $+10^{-3}$ M DTPA; *3*: *2* $+5\times10^{-4}$ M Cr(III)-DTPA; *4*: *2* $+10^{-3}$ M Cr(III)-DTPA; *5*: *2* $+2\times10^{-3}$ M Cr(III)-DTPA

tion of 2×10^{-4}% the chromium peak is completely suppressed.

The peak height dependence on the adsorption time at the adjusted adsorption potential for various bulk concentrations of chromium is depicted in Fig. 7. It can be seen that the peak height increases linearly with time up to about 2 min and then levels off attaining a maximum value which is different for different bulk concentrations of chromium.

All the experimental facts summarized in Figs. 5 to 7 indicate that adsorption plays a decisive role in the reduction of Cr(III)-DTPA complexes. The proof of the adsorption of the Cr(III)-DTPA complexes at the HMDE will be given in the next section by out-of-phase a.c. voltammetric measurements. Here, the remarkable peak height dependence on the adsorption potential (Fig. 5) will be discussed. It was stated above that at potentials more negative than −0.05 V the Cr(VI) present in the solution will be reduced to Cr(III) at the electrode. In the absence of chelates the Cr(III) formed at the electrode would diffuse towards the bulk of the solution and form aquocomplexes. In the presence of DTPA, however, the Cr(III) formed by the reduction of Cr(VI) will be immediately complexed by DTPA. As the DTPA complexes are adsorbed at the electrode already at rather positive potentials (see Figs. 8 and 9), the chromium complexes will not diffuse towards the bulk of the solution but will be accumulated at the electrode at the adjusted

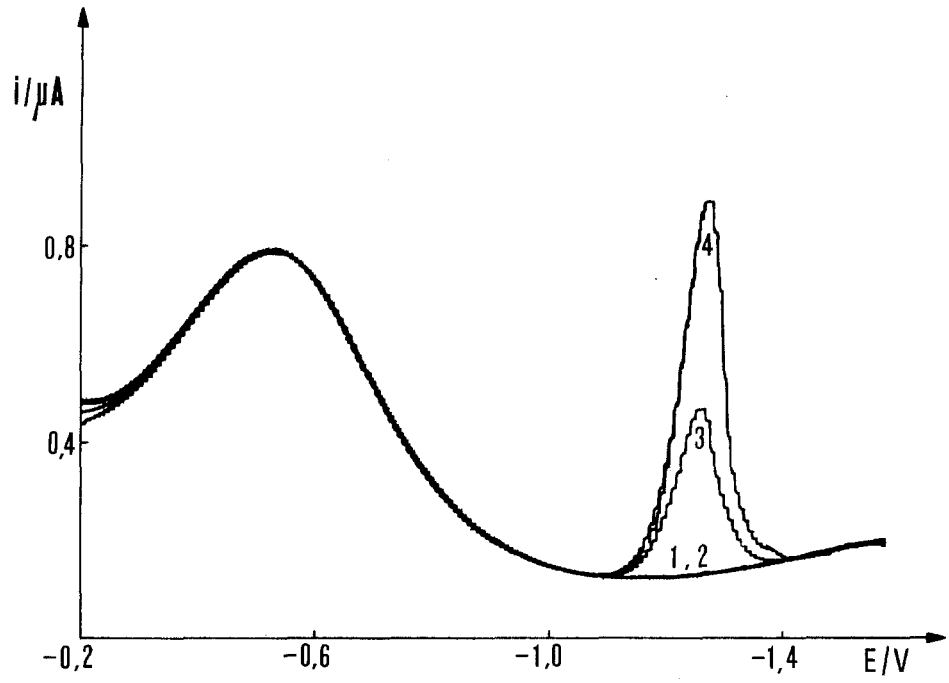

Fig. 10
Out-of-phase a.c.-polarograms of EDTA and Cr(III)-EDTA complexes, recorded at the DME in $NaNO_3 + CH_3COONa$ solution *1*: 0.5 M $NaNO_3$, 0.05 M CH_3COONa; *2*: *1* $+10^{-3}$ M EDTA; *3*: *2* $+5\times10^{-4}$ M Cr(III)-EDTA; *4*: *2* $+10^{-3}$ M Cr(III)-EDTA

adsorption potential. At more negative potentials where the reduction of Cr(III) to Cr(II) is possible, i.e. from about −0.8 V onwards, the accumulation of Cr(III)-DTPA complexes is further enhanced, due to the chemical oxidation by the nitrate ions of Cr(II)-DTPA complexes formed by the electrochemical reduction. This process runs more rapidly at more negative potentials up to −1.0 V. At even more negative potentials the catalytic reduction of Cr(III) is followed by the desorption of the formed Cr(II)-DTPA complexes from the electrode interface (see Fig. 8). Thus, at adsorption potentials more negative than −1.0 V the peak height decreases again. It should be noted in this respect that the elevated values of the peak height at the adsorption potentials more positive than −0.8 V are partly caused by the accumulation of Cr(III)-DTPA complexes at the starting potential of the scan from −1.0 V in all experiments, as at the scan rate adjusted 10 to 20 s elapse before the onset of the reduction peak.

The explanation proposed by us is supported by the experimental fact that in the solution of EDTA no elevation of the peak height of the Cr-EDTA complexes with the negativation of the starting potential is observed in the presence of the nitrate ions. On the other hand, it can be seen from Fig. 10 that the Cr(III)-EDTA complex is not adsorbed in the electrode interface in the whole range of potentials more positive than the reduction peak.

A. C. Voltammetric Measurements

To elucidate the role of adsorption in the reduction of the Cr(III)-DTPA complexes at the HMDE the out-of-phase a.c. voltammograms were recorded in the solution of DTPA containing acetate buffer and $NaNO_3$ (see curve 2 in Fig. 8) or KCl (see curve 2 in Fig. 9). In both media DTPA is not adsorbed. The Cr(III)-DTPA complexes, however, are adsorbed in both supporting electrolytes in the potential range from about −0.3 V to the potential of the onset of the reduction peak as is indicated by the lowering of the corresponding capacity current in this potential range (see curves 3−5 in Figs. 8 and 9). At more negative potentials the reduction product Cr(II)-DTPA is desorbed from the electrode interface as is indicated at potentials more negative than −1.5 V by the coincidence of the capacity current corresponding to the solution of the supporting electrolyte and to the solution containing chromium complexes. For comparison, the out-of-phase a.c.-voltammetric curves of Cr(III)-EDTA complexes in acetate buffer solutions containing EDTA are shown in Fig. 10. No adsorption can be seen either of the chelate or of the Cr(III)-EDTA complex. Only the Cr(III)-EDTA reduction response is displayed. This is a further proof that the different behaviour of EDTA- and DTPA-complexes of Cr(III) is caused by their different adsorption properties at the mercury electrode. The reduction peak of Cr-DTPA is displayed in full height in the out-of-phase a.c. mode, although in this case a Faradaic process and not a non-Faradaic process takes place. This evidences that the reduction of Cr(III)-DTPA-complexes proceeds from the adsorbed state.

Determination of Chromium in Various Natural Water Types

The sampling was carried out according to the method previously described by Mart [25]. Then the water samples were filtered through cellulose nitrate membrane filter of 0.45 μm pore size in the device SM 16511 from Sartorius, Göttingen.

Natural waters are known to contain surface-active organic substances which can disturb the voltammetric determination of chromium as well as other heavy metal traces. For this reason the natural water samples have to be subjected to UV-irradiation, if possible in presence of a small amount of H_2O_2 to decompose the dissolved organic matter by photolysis [17]. This causes, however, especially in acid medium (HCl, pH 2), a large loss of chromium (up to 90%).

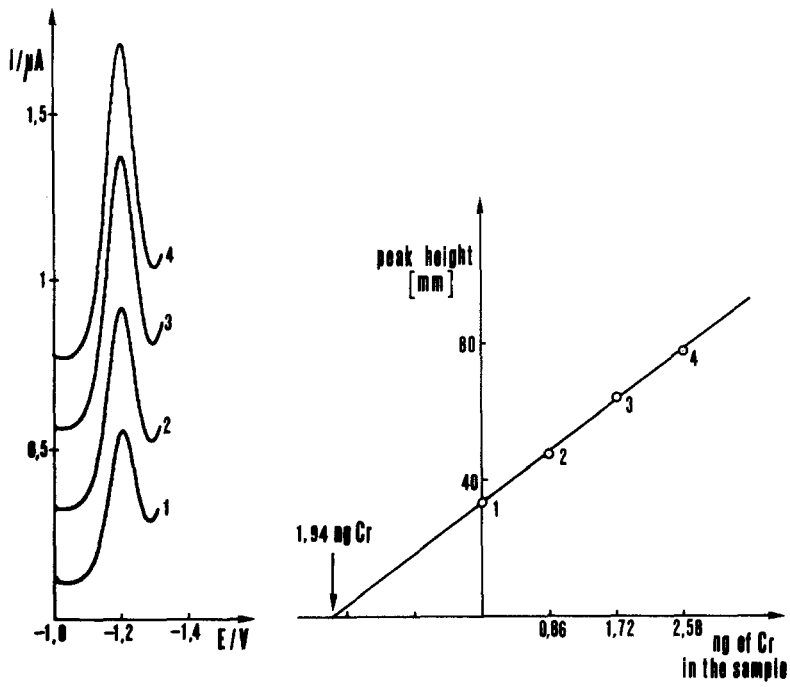

Fig. 11
ADPV determination of chromium in rain water sample (5.6 ml) collected in Essen 30. 3. – 6. 4. 1983. The sample was subjected before to UV irradiation. Supporting electrolyte 0.01 M DTPA, 0.04 M CH_3COONa, 0.5 M $NaNO_3$. Curve *1* – sample; curve *2*, *3* and *4* – standard additions. The determined amount of 1.94 ng Cr in the sample corresponds to a chromium concentration of 348 ng/l

Chromium(VI) compounds can be reduced under these conditions to CrO_2 through volatile CrO_2Cl_2 and partly even to insoluble Cr_2O_3 [26]. However, the application of UV-irradiation for photolysis of dissolved organic matter to samples at natural pH 7 to 8 does not cause any losses of chromium. Thus, it is recommended to determine chromium immediately after sampling and filtering. In case the samples cannot be directly analyzed, an addition of HNO_3 to pH 2 and neutralization with diluted NaOH solution before the determination under pH-meter control is recommended.

A typical chromium determination in rain water is presented in Fig. 11. Examples of chromium determinations in different natural water types are given in Table 1.

No further in principle possible improvement of the detection limit by an increase of nitrate ion concentration has been attempted to maintain low blank values. Under our experimental conditions the blank was below 10 ng/l. Thus, the determination limit L is defined as:

$$L = \bar{x} + 3\delta_b$$

where

$\bar{x}$ = average blank value;
δ_b = standard deviation of blank value.

L is equal to 20 ng/l for an adsorption time of 2 min. The relative standard deviation (RSD) was about 5% for chromium contents $\geqslant 200$ ng/l. The results obtained by this new method are in good agreement with those obtained by AAS, using the flameless technique with platform in the graphite furnace and with multiple injections of sample (see Table 1).

The influence of other metals contained in natural waters, especially Pb, Cd, Cu, Fe and Mn, up to a concentration of 1 mg/l, is negligible.

The optimal conditions for the determination of chromium Cr(III) + Cr(VI) in natural waters are as follows:

– supporting electrolyte: 0.5 M $NaNO_3$, 0.1 M DTPA, 0.04 M CH_3COONa. The easiest way of preparing this solution is the addition of the concentrated base solution (see Experimental) to the water sample;
– pH 6.2 ± 0.1;
– adsorption potential -1.0 V;
– adsorption time up to 3 min.

Table 1. Determination of total chromium levels in natural water types by adsorption differential pulse voltammetry (ADPV) and by graphite furnace atomic adsorption spectrometry (GFAAS)

Sample	n	$\bar{x}$	
		ADPV (ng/l)	GFAAS (ng/l)
Lake of Zürich, 15 m depth 12. 5. 1984	6	188	186
Lake of Zürich, 120 m depth 12. 5. 1984	2	102	95
Maas/Lottum, surface water 23. 8. 1984	2	269	–
Rain water, Bückeburg 14. 10. – 27. 10. 1983	2	45	–
Rain water, Essen 30. 3. – 6. 4. 1983	2	350	–
Sea water, South Pacific, 32°07′S, 127°17′W, 4308 m depth 8. 9. 1980	2	120	–

Analytical Overall Procedure for Natural Water Samples

The water sample (ca. 5 g) is put into a quartz crucible and pH is adjusted to 7 – 8 by addition of NaOH or CH_3COOH if necessary. Then 10 μl of 30% H_2O_2 are added. The sample is then irradiated by a 150 W UV lamp for 1 h in a device which isolates the sample from the laboratory atmosphere and thus eliminates contamination risks [27]. Then, 1 ml of

a solution containing 0.05 M DTPA, 0.2 M CH_3COONa and 2.5 M $NaNO_3$ is added. The required pH value 6.2 ± 0.1 is adjusted by addition of 1 M NaOH or 1 M CH_3COOH solution under pH-meter control. The quartz crucible containing the prepared analyte is placed inside the polarographic vessel, Metrohm EA 875-20. After the removal of oxygen by a nitrogen stream, preconcentration by adsorption at the HMDE is carried out during 1 – 3 min at the optimal adsorption potential of −1.0 V under stirring by a magnetic stirrer or by a regulated nitrogen stream. Then, the stirring is stopped and the cathodic scan is started in the differential pulse mode (50 mV pulse height, 0.4 s clock time, 10 mV/s scan rate) at −1.0 V. The peak potential of the Cr(III) reduction response appears at −1.22 V.

The evaluation of the total Cr concentration is achieved by the standard addition method (see Fig. 11).

Acknowledgement. Financial support by the KFA during the stay of one of the authors (J.G.) as guest scientist is gratefully acknowledged.

References

1. Friberg L, Nordberg GF, Vouk B (1979) Handbook on the toxicology of metals. Elsevier/North Holland; Biomedical Press, Amsterdam New York Oxford
2. Merian E, Geldmacher-v. Mallinckrodt M, Machata G, Nürnberg HW, Schlipköter H, Stumm W (1984) Metalle in der Umwelt. Verlag Chemie, Weinheim
3. Vercruysse A (1984) Hazardous metals in human toxicology. Elsevier, Amsterdam Oxford New York Tokyo
4. Bruland KW (1983) In: Riley JP, Chester R (eds) Chemical oceanography, 2nd ed. Academic Press, London, pp 157 – 220
5. Carry EE (1982) In: Langård S (ed) Biological and environmental aspects of chromium, chapt 3. Elsevier Biomedical Press, Amsterdam New York Oxford
6. Rubel S, Golimowski J, Wojciechowski M (1974) Chem Anal (Warsaw) 19:41 – 52
7. Zarebski J (1977) Chem Anal (Warsaw) 22:1037 – 1048
8. Lanza P, Taddia M (1984) Anal Chim Acta 157:37 – 44
9. Ferri D, Zignani F, Buldini PL (1982) Fresenius Z Anal Chem 313:539 – 541
10. Neeb R, Kiehnast J (1974) Fresenius Z Anal Chem 268:193 – 197
11. Golimowski J, unpublished work
12. Cox JA, Kulesza PJ (1983) Anal Chim Acta 154:71 – 78
13. Cox JA, Kulesza PJ (1983) J Electroanal Chem 159:337 – 346
14. Tölg G (1984) In: Welz B, Fortschritte in der atomspektrometrischen Spurenanalytik, Bd 1. Verlag Chemie, Weinheim, S. 6 – 8
15. Griepink B (1984) Pure Appl Chem 56:1477 – 1498
16. Pihlar B, Valenta P, Nürnberg HW (1981) Fresenius Z Anal Chem 307:337 – 346
17. Nürnberg HW (1984) Anal Chim Acta 164:1 – 21
18. Tanaka N, Ebata K (1964) J Electroanal Chem 8:120 – 126
19. Ranly W, Neeb R (1978) Fresenius Z Anal Chem 292:285 – 289
20. Golimowski J, Nürnberg HW, Valenta P (1980) Lebensmittelchem Gerichtl Chem 34:116 – 120
21. Ostapczuk P, Goedde M, Stoeppler M, Nürnberg HW (1984) Fresenius Z Anal Chem 317:252 – 256
22. Iyer CSP, Valenta P, Nürnberg HW (1981) Anal Lett, Ser A 14:921 – 923
23. Martell AE, Smith RM (1974) Critical stability constants, vol 1. Plenum Press, New York, p 281
24. Krumina WG, Astachow KW, Barkow SA (1969) Zh Fiz Khim 43:2792 – 2795
25. Mart L (1979) Fresenius Z Anal Chem 299:97 – 102
26. Gmelins Handbuch der Anorganischen Chemie (1962) Bd 52. Verlag Chemie, Weinheim, S. 263 – 280
27. Mart L (1982) Talanta 29:1035 – 1040

Received March 21, 1985