SLOVENSKI STANDARD
SIST-TP CEN/TR 14589:2004

01-maj-2004

?UfU_hYf]nUWŒU cXdUX_cj ˙!˙8 c_i a Ybh c ˙g h Ub ˙ˆ ˙hY\ b]_Y ˙!˙8 c`c Yj Ub Y7 f ˙f U ˙j fXbYa

Characterization of waste - State of the art document - Chromium VI specification in solid matrices

Charakterisierung von Abfällen - Bestimmung von Chrom in AbfallStatusbericht

Caractérisation des déchets - Etat de l'art - Spécification du Chrome (VI) dans les matrices solides

Ta slovenski standard je istoveten z: **CEN/TR 14589:2003**

ICS:

13.030.10	Trdni odpadki	Solid wastes

SIST-TP CEN/TR 14589:2004 **en**

iTeh STANDARD PREVIEW
(standards.iteh.ai)

TECHNICAL REPORT

RAPPORT TECHNIQUE

TECHNISCHER BERICHT

CEN/TR 14589

May 2003

ICS 13.030.10

English version

Characterization of waste – State of the art document – Chromium VI specification in solid matrices

Caractérisation des déchets - Etat de l'art - Spécification pour la détermination du Chrome VI dans les matrices solides

Charakterisierung von Abfällen - Bestimmung von Chrom in AbfallStatusbericht

This Technical Report was approved by CEN on 7 April 2003. It has been drawn up by the Technical Committee CEN/TC 292.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36   B-1050 Brussels

Ref. No. CEN/TR 14589:2003 E

CEN/TR 14589:2003 (E)

Contents

iTeh STANDARD PREVIEW
(standards.iteh.ai)

Foreword

This document (CEN/TR 14589) has been prepared by Technical Committee CEN/TC 292 "Characterization of waste", the secretariat of which is held by NEN.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to announce this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and the United Kingdom.

Introduction

Speciation is one of the growing features of analytical chemistry of the last years. It is now recognized that the determination of total trace element contents is no longer sufficient, because the biological and environmental impact of an element is dictated by the physico-chemical form in which it is present in the sample.

Chromium belongs to the category of problematic elements in analytical chemistry, because it behaves as a valence chameleon. The chemistry of chromium compounds is rather complicated, inorganic chromium compounds may occur in oxidation states ranging from -II to +VI [1,2]. However, in natural systems, Cr(III) and Cr(VI) are the most stable forms. Besides Cr(III) which is an essential trace element for mammals, including man, Cr(VI) compounds are genotoxic and potentially carcinogenic in humans. Evidence exists for the carcinogenity of calcium, strontium and zinc chromate [2,3]. The inoffensive nature of Cr(III) ions results from the fact that in biotic environment, it usually appears in aqua-hydroxo complexes of the form $\left[Cr\left(H_2O\right)_n\left(OH\right)_{6-n}\right]^{n-3}$ and their size excludes them almost entirely from penetrating cell membranes [4].

From chemical point of view, Cr(III) shows similarities with that of Al_2O_3: Cr_2O_3 is amfoteric, albeit more basic than acidic. In contrast, Cr(VI) is strongly acidic; all Cr(VI) compounds, except for CrF_6 are oxocompounds: $HCrO_4^-$ (hydrochromate), CrO_4^{2-} (chromate) and $Cr_2O_7^{2-}$ (dichromate) species which are powerful oxidants.

Under environmental conditions, dichromates are not formed at a total chromium concentration less than 0,01 mol/l. Certain forms of Cr(III) may oxidize to Cr(VI) in soils and that Cr(VI) may be reduced to Cr(III) in the same soil. Since under alkaline to slightly acidic conditions, Cr(VI) compounds are not strongly absorbed by many soils, they can be very mobile in surface environments. On the other hand, under these conditions, Cr(III) readily precipitates as Cr(OH)₃. Cr(VI) can be reduced to Cr(III) in soils by redox reactions with aqueous inorganic species, electron transfer at mineral surfaces, reactions with non-humic organic substances such as carbohydrates and proteins or reduction by soil humic substances [5]. The latter, which constitutes the majority of the organic fraction in most soils, represents a significant reservoir of electron donors for Cr(VI) reduction. As a result, the opposing solubility and toxicity characteristic of Cr(III) and Cr(VI) and the potential for Cr(III) oxidation in soil represent a unique regulatory challenge for the establishment of protective, health-based clean-up standards for Cr-contaminated soils [6]. Remediation of Cr(VI) containing soils through reduction to Cr(III) will lower the health and ecological hazard of such soils.

As a consequence of previous considerations, most attention is paid to Cr(VI) determination in environmental matter. Unfortunately, just this task is difficult to handle. Intricacies are primarily because of instability of the oxidation states of chromium and the complex character of environmental samples.

1 Scope

This European document describes the state-of-the-art extraction and determination methods for the total content of hexavalent chromium in raw waste and other solid materials.

2   Normative references

This document incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this document only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).;

AS 2882 : (Australia):	1986	*Waters-Determination of chromium (VI)(diphenylcarbazide spectrophotometric method);*
ASTM D 5257	1997	*Test Method for Dissolved Hexavalent Chromium in Water by Ion Chromatography;*
ASTM D 5281:	1998	*Standard Test Method for Collection and Analysis of Hexavalent Chromium in Ambient Atmospheres;*
DSF 38929:	1999	*Packaging-Requirement for measuring and verifying four heavy metals and other dangerous substances present in packaging and their release into the environment- Part 1: Requirements for measuring and verifying four metals present in packaging (lead, cadmium, chromium VI and mercury);*
IRSA (Italy):	1986	*Analytical Methods for Waste-Physico-Chemical Parameters, Method No. 16, Hexavalent Chromium (colorimetric reaction with diphenylcarbazide);*
ISO 11083:	1994	*Water quality-Photometric determination of Chromium VI with 1.5 diphenylcarbazide;*
ISO 3856-5:	1984	*Determination of hexavalent chromium content of pigment portion of liquid paint or paint in powder form-spectrophotometric method with diphenylcarbazide;*
DIN 19734:	1999	*Soil quality-Determination of Chromium (VI) in phosphate extract;*
DIN 38405-24:	1987	*German standard methods for the examination of water, waste water and sludge; photometric determination of Chromium (VI) using 1.5 DPC;*
DIN 53780:	1999	*Pigments and extenders-Determination of matter soluble in water-hexavalent chromium content*

3   Symbols and abbreviations

For the purposes of this document**Error! No text of specified style in document.**, the following symbols and abbreviations apply:

$R^{III}_{50/52}$ is the mass bias corrected measured isotope ratio of ^{50}Cr to ^{52}Cr of Cr(III) in the spiked sample;

$^{50}A_x$ is the atomic fraction of ^{50}Cr in the sample;

C^{III}_x is the concentration of Cr(III) in the sample (µmol/g, unknown);

$^{50}A^{III}_s$ is the atomic fraction of ^{50}Cr in the $^{50}Cr(III)$ spike;

C^{III}_s is the concentration of Cr(III) in the $^{50}Cr(III)$ spike (µmol/g);

C^{VI}_s is the concentration of Cr(VI) in the $^{53}Cr(VI)$ spike (µmol/g);

W^{III}_s is the weight of the $^{50}Cr(III)$ spike (g);

C_x^{VI}	is the concentration of Cr(VI) in the sample (µmol/g, unknown);
B	is the bias per mass unit;
c_x, c_s	is the concentration of analysed sample and spike, respectively (µg/g);
I	is the true number of counts, that means the number of counts that would have been detected if there had been not dead time;
I_m	is the number of counts measured on a channel;
K	is the mass discrimination factor;
M_1, M_2	is the atomic mass of isotope "1" and "2", respectively;
M_x, M_s	is the atomic mass of analysed sample and spike, respectively (µg/mol);
N_i	is the number of atoms;
N_x, N_s	is the total number of atoms in unknown sample and spike, respectively;
R	is the real isotope ratio;
R'	is the measured isotope ratio;
R_c, R_m	is the corrected-isotope ratio and the measured dead-time-corrected isotope ratios of the sample, respectively;
R_t, R_m	is the certified isotope ratio and the measured isotope ratios of the standard material (dead time corrected);
W_x, W_s	is the weigh of unknown sample and spike, respectively (g);
α	is the percentage of Cr(III) oxidized to Cr(VI) after spiking (unknown);
β	is the percentage of Cr(VI) reduced to Cr(III) after spiking (unknown);
τ	is the dead time;
Aliquat-336:	methyltricaprylammonium;
APDC:	ammonium pyrolidine dithiocarbamate;
DDTC:	diethyldithiocarbamate;
DIN:	direct injection nebulization;
DPC:	Diphenylcarbazide;
DPP:	differential pulse polarography;
DPTA:	Diethylenetriaminepentaacetic;
HHPN:	hydraulic high-pressure nebulization;

CEN/TR 14589:2003 (E)

HMDE: hanging mercury drop electrode;

HPLC: high pressure liquid-chromatography;

IC: ion-chromatography;

IC-DPC: ion chromatography diphenylcarbazide;

IC-ICP-MS: ion chromatography inductively coupled plasma mass spectrometry;

ICP-MS: inductively coupled plasma-mass spectrometry;

ID: Isotope Dilution method;

LC: liquid-chromatography;

LiFDDC: lithium bis(trifluoroethyl) dithiocarbamate;

LL: Liquid-liquid extraction;

MIBK: methyl isobuthyl ketone;

NPP: normal pulse polarography;

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ORP: Oxidation Reduction Potential;

SFE: Supercritical fluid extraction;

SIDMS: Speciation Isotope Dilution-Mass Spectrometry;

TBDTC: dibuthyl-dithiocarbamate;

TOC: Total Organic Carbon;

TSN: thermospray nebulization;

4   Chromium VI speciation in solid matrices

4.1   Chromium VI extraction from solid matrices

4.1.1   Sample pre-treatment

To quantify total Cr(VI) in solid matrices, three criteria must be satisfied:

a) the extraction solution must solubilize all forms of Cr(VI);

b) the conditions of the extraction must not induce reduction of native Cr(VI) to Cr(III);

c) the method must not cause oxidation of native Cr(III) contained in the sample.

Thus, it has been recognized that Cr(VI) must be leached from samples in an alkaline medium rather than in acidic medium in order to inhibit Cr(VI) to Cr(III) reduction by possible reductants present in sample [2]. An alkaline extraction procedure, USEPA SW-846 Method 3060 for the preparation of soil samples in view of analysis of total Cr(VI) was used for a number of years. But an USEPA funded research study did not achieved consistent results among samples using this method [7]. The researches concluded that the Cr oxidation state is matrix specific and may be unstable and unpredictable (in environmental samples) once it is solubilize in either an acidic or basic aqueous extraction medium [8]. Based on these considerations, in June 1997 the USEPA promulgated SW-846 Method 3060A for inclusion in the Third Update to the Test Method for Evaluating Solid Waste, SW-846, 3rd ed. [5]. Although the basic chemistry has remained the same, the modifications to USEPA SW-846 Method 3060 have enhanced the efficiency of the extraction process, principally by reducing the soil sample weight and decreasing the ratio of sample weight to alkaline digest volume.

4.1.2 USEPA SW-846 Method 3060A [9]

4.1.2.1 Summary of USEPA SW-846 Method 3060A

The solid sample is digested using a mixed solution (pH>11,5) consisting of Na_2CO_3 (0,28 M) and NaOH (0,5 M) and heating at 90 °C – 95 °C for 60 minutes, in order to dissolve the Cr(VI) and stabilize it against reduction to Cr(III)

For waste materials or soils containing soluble Cr(III) greater than four times the laboratory Cr(VI) detection limit, Cr(VI) results obtained using this method may be high biased because of method-induced oxidation. Thus the method recommends the addition of Mg(II) in a phosphate buffer to the alkaline extraction solution to suppress this oxidation. When analysing a sample digest for total Cr(VI) it is appropriate to determine the reducing/oxidizing tendency of each sample matrix. This can be accomplished by characterization of each sample by means of four major redox-indicating ancillary parameters:

— pH (USEPA SW-846 Method 160);

— Oxidation Reduction Potential (ORP) (ASTM D1498-76);

— sulfides (USEPA SW-846, Method 9030);

— Total Organic Carbon (TOC) (USEPA SW-846 Method 9060, ASTM-1976).

Based on the research performed on a wide variety of samples using USEPA SW-846 Method 3060A and departing from the conventional interpretative approach for QC data for total metals, data associated with low or 0 % Cr(VI) matrix spike recoveries must be evaluated in accordance with established redox chemistry of Cr in soils or sediments. With pH and ORP having such significance with regards to the redox status of a soil or sediment sample the method refers to an E-pH diagram for $HCrO_4^-$/Cr(OH)$_3$ (see Annex A), which can be used to asses the redox characteristics of a sample.

4.1.2.2 Advantages of Method 3060A

The proposed method meets the three previous criteria for a wide spectrum of solid matrices. Under the alkaline conditions of the extraction, minimal reduction of Cr(VI) or oxidation of Cr(III) occurs.

A quite comprehensive study concerning the efficiency of different methods of Cr(VI) extraction from soils was carried out [6]. For this task, the USEPA SW-846 Method 3060A (Na_2CO_3, 0,28 M and NaOH, 0,5 M and heating) was compared with four other digestion methods, using different extractants, namely:

— Distilled water (pH=5,7);

— Phosphate buffer (pH=7,0);

— NaOH 0,1 M (pH=13,0) with sonication;

CEN/TR 14589:2003 (E)

— Mixture Na_2CO_3 (0,28 M) + NaOH (0,5 M), without heating.

Distilled water and phosphate buffer extractions can be used just to quantify soluble and exchangeable forms of Cr(VI). The fraction of Cr(VI) which can not be solubilized in water or phosphate buffer solution is the non-exchangeable form. The soluble and exchangeable fractions of Cr(VI) are useful parameters for estimating soils levels of Cr(VI) that may leach to groundwater, form a soluble "blush" on soil surface or be absorbed by plants and micro organisms. However, the quantification of total Cr(VI) in soil samples is necessary to assess the Cr hazard in the environment. The study demonstrated that the heated carbonate-hydroxide solution (USEPA SW-846 3060A) was the most effective extractant for total Cr(VI) in soils that contain native Cr(VI) or in soils that had a sufficiently high redox status to maintain chromium as Cr(VI). To asses the redox status of solid matrix, ancillary chemical parameters, including ORP, pH, S^{2-} and TOC should be quantified and interpreted to explain poor Cr(VI) recoveries. It was demonstrated [6] that the strongly reducing samples cannot maintain Cr(VI) laboratory matrix spikes. Thus, if reducing conditions are shown for Cr(VI), poor spike recovery is probably due to soil reduction and not attributable to method-induced reduction. But if oxic conditions are indicated by the ancillary parameters (above the $HCrO_4^- / Cr(OH)_3$ line, see Annex A), poor spike recovery is probably the result of technical error, since method-induced reduction is improbable.

Concluding, the high frequency of acceptable matrix spike recoveries attained using even the sparingly soluble chromate compounds, $BaCrO_4$ and $PbCrO_4$ has demonstrated the reliability and robustness of USEPA SW-846 Method 3060A [5]. The collective research that established the basis for SW-846 Method 3060A demonstrated that method-induced reduction of Cr(VI) to Cr(III) did not contribute to low or 0 % matrix spike recoveries. The method contains detailed decision to assist the user in the interpretation of quality control (QC) data that are needed to substantiate the quantification of the Cr(VI) results. In situation where low or zero percent matrix spike recoveries were observed and a reducing sample is suspected, USEPA SW-846 Method 3060A stipulates the measurement of a number of previous ancillary redox-indicating parameters.

4.1.2.3 Limitations of USEPA SW-846 Method 3060A

With respect to a limitation of USEPA SW-846 Method 3060A, method induced oxidation of Cr(III) to Cr(VI) has been observed in samples demonstrated to contain soluble forms of Cr(III) and high levels of MnO_2. However, in most cases, the percentage of Cr(VI) formed will not exceed 15 % [2]. When subjected to aerated alkaline

conditions, soluble forms of Cr(III) can form a fresh $Cr(OH)_3$ precipitate and $Cr(OH)_4^-$ at pH=12-13. This fresh precipitate is available to be partially oxidized to Cr(VI) under the aerated conditions. However, with the exception of a fresh spill of soluble Cr(III), the soil-born forms of Cr(III) found in environmental samples are aged, crystalline, $Cr(OH)_3$ and Cr_2O_3, both of which have not been observed to oxidize under the aerated alkaline conditions of the method. Performing a water extraction and analysing the resultant leached for both Cr(VI) and total Cr ; the presence of soluble Cr(III) in samples can be approximated. If soluble Cr(III) or freshly precipitated $Cr(OH)_3$ is suspected of being present in a sample, the method specifies the addition of Mg(II), which is capable to reduce or eliminate the occurrence of oxidation of Cr(III) to Cr(VI). Moreover, for the fixation of Cr(III), a solution of EDTA is recommended to use. In this way, losses of Cr(VI) over 7 days have been reported to be reduced from 80 % to less than 20 % [2].

4.2 Chromium (VI) speciation methods

With regards to chromium speciation in solids, the accuracy of the methods remains a field of additional effort and improvement. A review on analytical methodologies for chromium speciation in solid matrices by Marques et al [10] emphasis the lack of reported recovery by most authors. However, the variety of methods for Cr(VI) speciation may be classified into two fundamental categories:

a) valence-specific-direct measurements (4.2.1)- which include:

  — spectrophotometric methods (4.2.1.1);

  — electrochemical methods (4.2.1.2).

b) valence-specific-separation measurements (4.2.2)- based on selectively removing of one chromium species from the sample and subsequent unspecific measurement, by means of straightforward methods, such as: AES, AAS and MS.

4.2.1 Valence-specific-direct measurements

4.2.1.1 Spectrophotometric methods

Spectrophotometric methods are often used for the determination of the speciation forms of some elements without preliminary separation. The existing spectrophotometric methods for chromium speciation have a series of limitations and they are not always suitable for the analytical practice [11]. Thus, the disadvantages of these methods are the following:

— the molar absorptivities of the ions associated used in these methods are rather low ($0{,}14 \times 10^4$ l/mol cm - $8{,}0 \times 10^4$ l/mol cm);

— the color of the used dyes is not stable and the value of blank tests is high.

Therefore, the development of the new analytical procedures with improved sensitivity and selectivity is a very important question. However, it should be emphasized that nowadays in a quite large number of laboratories the spectrophotometric methods for Cr(VI) speciation are still used (see Annex B). The most widely used is the method with diphenylcarbazide (DPC) and this due to the fact it doesn't require organic extractants and more, it is easily associated with USEPA SW-846 Method 3060A for chromium extraction. The reaction of Cr(VI) with DPC is the most common and reliable spectrophotometric method for Cr(VI) solubilized in alkaline digestate. The use of DPC has been well established in a large number of standardized methods, such as:

DIN 19734:   1999   *Soil quality-Determination of Chromium(VI) in phosphate extract*;

DIN 38405-24:   1987 *German standard methods for the examination of water, waste water and sludge; photometric determination of Chromium(VI) using 1.5 DPC*;

ISO 11083:   1994 *Water quality-Photometric determination of Chromium VI with 1.5 diphenylcarbazide*;

ISO 3856-5:   1984 *Determination of hexavalent chromium content of pigment portion of liquid paint or paint in powder form-spectrophotometric method with diphenylcarbazide*;

DIN 53780:   1999 *Pigments and extenders-Determination of matter soluble in water-hexavalent chromium content*;

AS 2882 (Australia):   1986 *Waters-Determination of chromium (VI) (diphenylcarbazide spectrophotometric method)*;

ASTM D 5257:   1997 *Test Method for Dissolved Hexavalent Chromium in Water by Ion Chromatography;*

ASTM D 5281   1998 *Standard Test Method for Collection and Analysis of Hexavalent Chromium in Ambient Atmospheres*

DSF 38929:   1999 *Packaging-Requirement for measuring and verifying four heavy metals and other dangerous substances present in packaging and their release into the environment-Part 1: Requirements for measuring and verifying four metals present in packaging (lead, cadmium, chromium VI and mercury)*;

IRSA (Italy):   1986 *Analytical Methods for Waste-Physico-Chemical Parameters, Method No. 16, Hexavalent Chromium* (colorimetric reaction with diphenylcarbazide);

USEPA SW-846   1992 *Chromium, Hexavalent (Colorimetric)-method using diphenylcarbazide*
Method 7196A:

4.2.1.1.1 Summary of DPC method [12]

Dissolved hexavalent chromium, in the absence of interfering amounts of substances such as Mo, V and Hg is determined colorimetrically by reaction with DPC, in acidic solution (pH=2). The reaction is sensitive

CEN/TR 14589:2003 (E)

($\varepsilon_{540\ nm}$=4,17 x 10^4 l/mol cm); addition of an excess of DPC yields the red-violet product and its absorbance is measured photometrically at 540 nm. The Cr(VI) reaction with DPC is usually free from interferences; however, certain substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react with DPC forming color with the reagent; however, the red violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/l of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble. Iron in concentration greater than 1 mg/l may produce a yellow color, but it is not strong and difficulty is not normally encountered if the absorbance is measured at the appropriate wavelength.

Even the well-established DPC reaction with Cr(VI) is in fact valence-specific, however it is subject to be interfered by metal ions and by Cr(VI) reduction in acidic solution. Thus, to avoid the limitations, an extensive sample pre-treatment is required comprising the following steps [1]:

a) precipitation of polyvalent cations including Cr(III) by phosphate buffer/aluminum sulfate(floculant agent);

b) oxidation of strong reductants by hypochlorite addition;

c) destruction of hypochlorite excess;

d) finally, color development with DPC.

However, DPC method is still one of the most used spectrophotometric method, but with inherent limitations.

A recent paper was published with regards to spectrophotometric determination of Cr(VI) by means of formation and extraction(in toluene) of Cr(VI) ion associates with symmetric cyanine dyes. The study was carried out with a number a five cyanine dyes and the molar absorptivity of ion associates is ranging from 2,501 05 l/mol cm - 3,621 05 l/mol cm, depending on the dye used. This method is suitable for speciation measurements without separation of Cr(VI) and by comparison with known spectrophotometric methods is more sensitive and avoids the use of hazardous chemicals [11].

4.2.1.1.2 Limitations of the spectrophotometric methods [13]

The distribution of Cr(VI) and Cr(III) species strongly depends on pH and potential. According to the E-pH diagram of Cr species as given in Annex A, Cr(VI) is thermodynamically stable at relatively high pH and E values, while Cr(III) at relatively lower pH and E. Corresponding to the change of pH, the formal reduction potential of Cr(VI)/Cr(III) changes from –0,04 (pH=13) to 0,52 (pH=7,4) then to 1,07 (pH=2). Based on these thermodynamic data, the reduction of Cr(VI) may occur during neutralization step, because Cr(VI) may react with coexisting reducing matrix rather than DPC and consequently cause negative errors. In addition, some chromate compounds have a much lower solubility in the neutral solution than in the strong basic solution.

4.2.1.2 Electrochemical methods

4.2.1.2.1 Summary of electrochemical methods

Up to now there are not many standardized electrochemical methods for Cr(VI) speciation. In literature several publications using this techniques have been described [1,14,15].

Among the electrochemical methods, mainly the polarographic methods have been used for Cr(VI) speciation. The classic polarography is a voltammetric method (measuring the electrolysis cell current as a function of electrode potential) at controlled potential in which the working electrode consists of a dropping mercury electrode and the potential is changed in a linear mode.

But the most widely electrochemical methods used are normal (NPP) and differential pulse polarography (DPP). In NPP, the potential is kept at a suitable constant base potential throughout the drop lifetime but in DPP the potential does not return to a constant value.

An overview of mostly used electrochemical analytical methods, including the USEPA SW-846 Method 7198 [16] is shown in Table 1 [2]

Table 1 — Electrochemical methods for Cr(VI) speciation

Electrochemical methods for Cr(VI) speciation	Detection Limit (μg/l)
Ammonia buffer solution as the supporting electrolyte; detection with differential pulse polarography (USEPA method) ;	1,6
Addition of ammonium acetate buffer and ethylenediamine detection with differential pulse polarography (DPP);	10,0
Differential pulse polarography in 0,2 M NaF solution;	0,8
DPP in 0,1 M dibasic ammonium citrate solution;	2
Polarographic determination in 0,1 M NH_4Cl+NH_3/KNO_2; catalytic current; pH=10,0;	2
Separation of interfering cations with aluminum from phosphate-buffered solution; detection with DPP.	30

By A. C. Harzdorf [1], the polarographic method provides the best potential for Cr(VI) speciation. Hexavalent chromium is electrochemically active over the entire pH-range, so that medium pH can be chosen throughout which offers ideal conditions for stabilizing the oxidation states of chromium. Furthermore, a variety of supporting electrolytes is suitable so that the operating conditions can readily be adapted to the composition of the given sample. In order to eliminate the interferents as much as possible, polyatomic inorganic cations are removed by precipitation with phosphate buffer solution. Removal is completed by addition of aluminum sulfate as floculant. During this treatment, coprecipitation of Cr(VI) proved to be negligible. In the residual phosphate buffer solution, Cr(VI) can readily measured.

Although differential pulse polarography is the most sensitivity direct polarographic technique, an even greater sensitivity can be obtained by imploying stripping voltammetry. This technique involves a preconcentration step before the final voltammetric determination. This step consists of the controlled electrodeposition, at a fixed potential, of the species of interest on a stationary electrode. This is followed by the determination step, which consists of electrolytically stripping the deposited species back into solution.

A new sensitive stripping voltammetry method for the determination of trace amounts of total chromium Cr(III) and Cr(VI) was proposed by Golimovski [14]. The method is based on preconcentration of the Cr(III)-DPTA (diethylenetriaminepentaacetic) complex by adsorption at HMDE (hanging mercury drop electrode) at the potential –1,0 V. The adsorbed complex is then reduced producing a response and the peak height of the Cr(III) reduction is measured. The determination limit is 20 ng/l and the RSD is 5 % for chromium concentrations > 200 ng/l.

4.2.1.2.2 Limitations of the electrochemical methods

Despite the promising features of polarography in the given field, it does not cover all requirements in environmental chromium analysis because of the limited sensitivity. Moreover, the detection limit strongly depends on the sample background and the lower limit of the methods is not always suitable for environmental studies. Stripping voltammetry is an important, but limited technique, mainly because of the pre-concentration step, which requires the production of an insoluble product that can be reproducibly stripped from the electrode surface in the determination step.