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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

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Contents

Foreword **3**
Introduction **3**
1 Scope **3**
2 Normative references **4**
3 Symbols and abbreviations **4**
4 Chromium VI speciation in solid matrices **6**
5 Final conclusions **19**
Bibliography **38**

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 $\left[Cr\left(H_2O\right)_n(OH)_{6-n}\right]^{n-3}$ 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;

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;

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;

— 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 x 10^4 l/mol cm - 8,0 x 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 Method 7196A:	1992	*Chromium, Hexavalent (Colorimetric)*-method using diphenylcarbazide

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

($\varepsilon_{540\ nm}$=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.

4.2.2 Valence-specific-separation methods

A separate category of methods for Cr(VI) speciation is based on selective removing of one species from the subjected sample and subsequent measurement. The separation step comprises primarily:

— chromatography (4.2.2.1);

— extraction (4.2.2.2);

— coprecipitation (4.2.2.3).

The detection usually includes non-specific methods, such as: AES, AAS, MS or spectrophotometric methods.

An interesting overview of the detection techniques for determination of Cr(VI) and/or Cr(III) is presented in Figure 1 [17]. Figure 1 shows all the techniques employed to determine Cr(VI) and/or Cr(III). UV-VIS spectrometry is most often used, (33 %). Other techniques such as Atomic spectrometry techniques either flame or furnace techniques (23 %) or chromatographic techniques (11 %) have also often been used to determine chromium species.

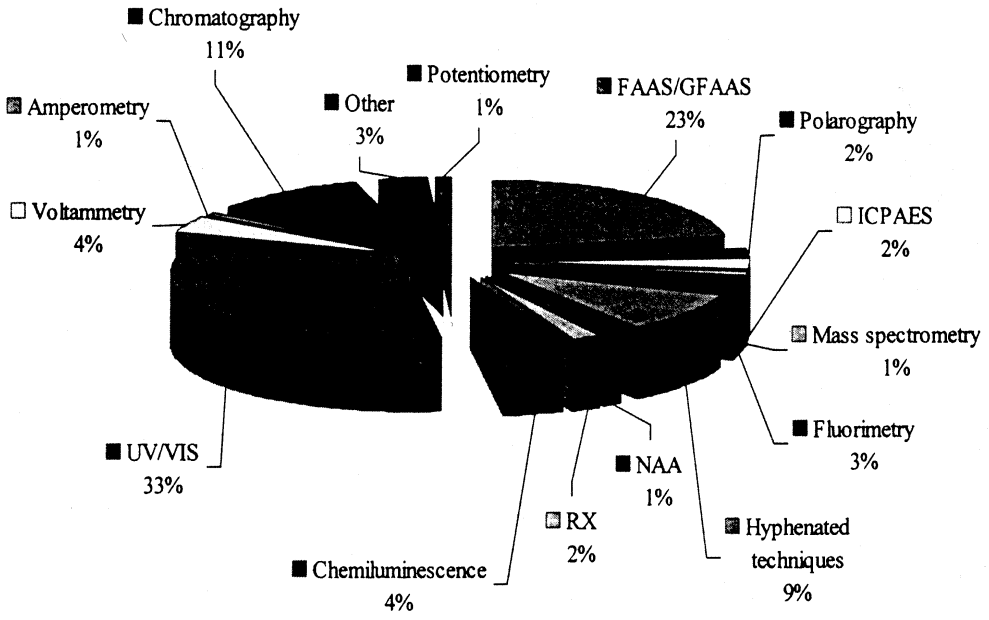


Figure 1 — Detection methods used for the determination of Cr(VI) and/or Cr(III)

4.2.2.1 Chromatographic separation

The application of chromatographic separation techniques is continuously increasing in the field of Cr(VI) speciation.

Preconcentration of Cr(VI) has been carried out using different types of columns, such as columns with melamine-formaldehyde resin, a C18 bonded silica reversed phase sorbent with diethyldithiocarbamate (DDTC) as the complexing agent, a column of Chromabond NH_2, a column containing phosphate treated sawdust as adsorbent, a column containing ZnO and microcolumns such as an alumina micro-column. Different types of resins such as anion-exchange resins, resins with Amberlite diluted in MIBK and liquid anion exchangers such as Amberlite LA-1 or LA-2 have also been used. Different eluents are used to elute Cr(VI), such as HNO_3, NH_4OH or sodium acetate [17].

Preconcentration of both species, Cr(VI) and Cr(III) simultaneously can be carried out in different types of columns packed with materials such as strongly basic anion exchanger with H2SO4, Dionex AG4A, DEAE-Sephadex A-25, polyacrylonitrile sorbent modified with polyethilenepolyamine, anion exchangers Dionex CS5, Dionex IonPack A57,

Excelpak ICS-A23 etc. They can also be retained on a micro-column packed with activated alumina, on methyltrioctylammonium chloride-loaded silica gel or on polymeric Dedata sorbent with aminocarboxylic groups. The most commonly used solvents are HNO_3, $HClO_4$, HCl, H_2SO_4 and methanol for Cr(III) elution and NH_4OH, $HClO_4$, ascorbic acid, Na_2CO_3/$NaHCO_3$ and hydroxylammonium chloride for Cr(VI) elution [17].

Thus, the majority of speciation separations is performed by ion exchange chromatography. The ion-exchange separation of both chromium species in a chromatographic system can be performed based on two different concepts. Sample species can be separated on a column based on affinity differences of the species for the column. Using a complexing reagent in the eluant may also separate the sample species. The complexing reagent changes the form of the sample species allowing the moving down the column to be easier. Thus, the basis of many of the separations has been to convert Cr(III) to an anion by adding a complexing agent. Cr(VI) is already an anion (usually CrO_4^{2}), hence, anion chromatography can be used to separate the chromium species.

The most widely used complexing agents for Cr(III) are: hydroxy-ethylpiperazine-N'-3-propanesulfonic acid buffer/methanolic-8-hydroxi quinoline, hydroxyquinoline, diethyldithiocarbamates (DDTC), SCN-, trifluoroacetylacetone and the pH values for the complexation may vary from pH 2 to pH 8,5 [17].

Interest in element-specific detection for high performance liquid chromatography (HPLC) has increased. A large number of reviews have been published describing the advantages associated with the use of atomic spectrometric techniques as detectors for HPLC. Thus, recently plasma source mass spectrometry is recognized as one of the most powerful analytical technique for trace element analysis of species when coupled to a suitable chromatographic separation system.

With the application of ICP-MS for chromium speciation, major limitations generally arise from the occurrence of non-spectral as well as spectral interferences. The elements that can give rise to interference at the analytical isotope masses of Cr (i.e. 50, 52, 53, 54) are, Ar, C, Ca, Cl, K, O and S, in other words, those normally present in environmental matrices, the plasma gas and as well as in the reagents used for extraction. Thus, a LC technique has the great advantage that, besides the speciation of the chromium species, it gives the opportunity to separate substances, which can otherwise interfere with the isotopes of interest.

A survey of LOD, which were found in literature [4] for different LC techniques coupled with ICP-MS, is given in Table 2.

Table 2 — Detection limits (µg/l) for Cr(III) and Cr(VI) with different ICP-MS techniques

LC technique	Detection limits for Cr(III) µg/l	Detection limits for Cr(VI) µg/l
IC-ICP-MS	0,3	0,5
HPLC-ICP-MS	0,4	1,0
HPLC-DIN-ICP-MS	0,18	0,18
HPLC-HHPN-ICP-MS	0,6	1,8
HPLC-TSN-ICP-MS	2,5	2,3

Abbreviations:

LC: liquid-chromatography;

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

HPLC: high pressure liquid-chromatography; **DIN**: direct injection nebulization;

TSN: thermospray nebulization ; **HHPN**: hydraulic high-pressure nebulization.

A largely used method of Cr(VI) determinations by means of HPLC is the standardized USEPA SW-846 Method 7199 (see Table 3). This method [18] provides procedures for the determination of hexavalent chromium using a separation on a column packed with a high capacity anion exchange resin capable of resolving CrO_4^{2} from other sample constituents (Dionex IonPack AS7 or equivalent) and a post-column derivatization of Cr(VI) with DPC in view of detecting of the colored complex at 540 nm. Also, a guard column (Dionex IonPack NG1) is used in order to remove organic constituents from the sample before Cr(VI) as CrO_4^{2} is separated on an anion exchange column. The analyzed sample is adjusted initially at pH=9 to pH=9,5 with a buffer solution and the eluent used is a mixture of $(NH_4)_2SO_4$ (250 mM) and NH_4OH (49 mM).

An alternative approach by means of IC was developed by Barnovski et al [4]. In this study, an IonPack AG5 (Dionex) column for anion exchange chromatography was used. The column is designed for anion exchange with a special selectivity for anions of higher valences like oxoanions. The column material is stable over a pH range from pH 0 to pH 4. Even if as eluent a mixture of $NaHCO_3$-Na_2CO_3 was recommended for the specified column, in order to realize the desired exclusion of carbon compounds, this recommendation was not followed; thus, nitric acid was chosen for conditioning of the column as well as for elution. This eliminated the crucial spectral interference by $^{40}Ar^{12}C$ at mass 52. The choice of nitric acid is possible as a result of the robustness of the column material, which allows a wide range of pH values for the sample and eluent. It should be emphasized that both species are retained on the column and separation during elution by one eluent under compromise conditions, on the basis of the following considerations. The substrate material for ion exchange resins is basically the same for anion exchange as for cation exchange. If adequately conditioned, a certain exchange capacity will be preserved in anion exchange operation for cations, also, so that a mixed bed property of the column is realized in favor of the analytical performance. A similar approach was used by Kingston et al [20], and both Cr(VI) and Cr(III) were separated on a anion-exchange column (CETAC ANX 4605), using HNO_3 as eluent.

An alternative HPLC speciation of Cr(VI) is Ion Chromatography with chemiluminiscence detection [21]. The species are separated by ion chromatography followed by post column reduction of Cr(VI) to Cr(III) before detection. The detection is based on the measurement of the intensity of light emitted when luminol (5-amino-2,3 dihydro-1.4 -phtalazinedione) is oxidized by hydrogen peroxide in the presence of Cr(III). Potential interference effects caused by other metal ions that similarly catalyze the same reaction have been masked by adding EDTA to the sample stream. The developed method is very sensitive and selective. Free Cr(III) ions were found to be only chromium species that catalyze the reaction and in contrast to the other metals ions, the rate of formation of the Cr(III)-EDTA complex is slow such that Cr(III) is still in the free state when the luminol reaction occurs. In a further development, it was shown that the chemiluminescence signal, generated by the Cr(III)-luminol reaction, is enhanced 6-fold in the presence of bromide ions. Recently, the addition of bromide ions has been used with flow injection analysis [21]. Ion chromatography with chemiluminescence detection is a sensitive technique (0,025 µg/l, Detection Limit), a much less costly alternative to most currently available instrumental methods for the study of the distribution of Cr(VI) and Cr(III) in environmental samples.

Another proposed method for speciation of Cr(VI) is reversed-phase ionic-pair HPLC after formation of an ionic pair with tetrabuthylammonium. The method does not involve preconcentration and the detection limits are 0,02 mg/l and 0,08 mg/l for Cr(III) and Cr(VI), respectively [4].

In recent publications [4, 22] a method using a strong anionic phase to separate Cr(VI) and Cr(III) as Cr-EDTA was proposed. For the separation of the chromium species on an anion exchange column (Excelpak ICS-A23), EDTA-$2NH_4$ and oxalic acid were used as the mobile phase (pH=7). Oxalic acid functions as an eluent of the Cr species, while EDTA functions as an eluent of the Cr species and as a stabilizer of Cr(III) complex. For this method, the detection limits were 0,4 µg/l for Cr(III) and 1,1 µg/l for Cr(VI).

Table 3 — The chromatographic separation methods used for Cr(VI) speciation [2].

Chromatographic method	Detection method	Detection Limit µg/l
Separation on highly anion exchange capacity column; elution with $(NH_4)_2SO_4$+NH_4OH; post-column derivatization with DPC (USEPA method);	photometric	0,3
Collection of Cr(VI) on polydithiocarbamate resin; digestion of the resin with HNO_3;	ICP-AES	36
Extraction with ethylenediamine in water; treatment with Dowex anion-exchange resin after acidification; calculation by difference with untreated portion;	ICP-AES	7
Collection of Cr(VI) on Sephadex A-25; desorption by hydroxylammonium chloride solution;	GF-AAS	0,01
Preconcentration of Cr(VI) on C-18 column after complexation with sodium di(trifluorethyl)dithiocarbamate; elution with toluene;	GC	0,05
Ion Chromatography with chemiluminiscence detection;	photometric	0,025
Separation on highly anion exchange capacity column; elution by nitric acid;	MS	
Separation of Cr(VI) and Cr(III) (as CrY^-); elution with EDTA (ammonium salt)+oxalic acid.	MS	1,4

4.2.2.2 Extraction

4.2.2.2.1 Liquid-liquid extraction (LL)

Separation of Cr(III) and Cr(VI) species may be achieved by selective extraction and mostly used is the selective separation of Cr(VI) species. The efficiency of the liquid-liquid (LL) extraction methods depends on the sample composition, since interferences may be expected from other metal ions and should be checked beforehand.

Cr(VI) can be complexed with different dithiocarbamates, such as ammonium pyrolidine- dithiocarbamate, dibenzyldithiocarbamate, Na-diethyldithiocarbamate, ammonium trifluoracetylacetonate, diphenylcarbazide, tetrabuthylammonium. In the extraction these complexes, isobuthylmethylketone is most commonly used, followed by $CHCl_3$, hexane and trybuthylphosphate [17].

An interesting approach for Cr(VI) separation by means of LL uses liquid ion exchangers. Thus, the Cr(VI) and Cr(III) species separation was investigated with different types of liquid ion exchangers (cation and anion exchanger resins as well as complexing resins). A good separation efficiency of Cr(VI)-Cr(III) separation, in a HCO_3^-/CO_2 buffer solution was found by an extraction of Cr(VI) with a liquid anion exchanger [19]. A liquid exchanger, Amberlite LA-2, which was stored in contact with a HCl solution, and MIBK was used. Under these conditions, Cr(VI) was completely extracted into the organic phase, whereas Cr(III) remained in the aqueous phase (99 %-100 % yield determined by labeled ^{51}Cr compounds). However, a critical point using this extraction system is the separation of the two phases. A total phase separation is only possible by using sufficiently high salt concentration in the aqueous solution. After separation, Cr(VI) must be re-extracted from the organic phase into the aqueous phase for isolation of chromium to be measured in the mass spectrometer. The re-extraction by a 6 % (w/w) NH_3 solution has been found to be the most efficient system (98 % isolation yield), with very fast kinetics. Furthermore, for isolation of chromium from both solutions, an electrolytic deposition at Pt electrodes was performed. The electro-deposition was carried out in an ammoniacal solution, which also generated the most

effective pH value for this type of isolation. The electrolytic deposits were dissolved in HNO_3-H_2O_2 (4:1) and then these solutions were evaporated to dryness. After dissolution in diluted HNO_3, the samples were subjected to MS measurements.

However, LL extraction is a multi-step procedure that often result in loss of analytes during the process, frequently making sample preparation the major source of errors in analysis and making it impeditive for integration with the rest of the analytical process.

4.2.2.2.2 Solid phase extraction (SPE)

Solid-phase extraction is a simple and effective adsorption and desorption technique which eliminates the need for solvents or complicated apparatus, for concentrating compounds in liquid samples or headspace. Essentially, the extraction procedure consists of exposing the SPE fibre to a small amount of aqueous sample for a certain time.

The use of a solid phase extraction permits simultaneous preconcentration and separation of Cr(III) and Cr(VI). Several studies have used a solid phase for retention of Cr(III) or Cr(VI) and determination of total chromium by a previous oxidation or reduction. Other authors have proposed the use of two different solid phases [23], but this method is still in the development stage.

4.2.2.2.3 Supercritical fluid extraction (SFE)

SFE has been used successfully in metal extraction by a number of research groups [24], but attempts at metal valence speciation have not been reported. However, the potential for speciation is theoretically possible since different oxidation states of the same metal often possesses vastly different formation and extraction constants with the same reagent. In addition, when using SFE, the differences in solubility in supercritical carbon dioxide for the chelated metal species would also contribute to the potential speciation. Optimising the parameters by addition of various modifiers, different chelating agents or changes in the supercritical fluid conditions of pressure and temperature would produce differences in chelation/extraction equilibrium constants in order to separate the different oxidation states o the same metal. Good results were obtained using two different chelating agents, namely dibuthyl-dithiocarbamate (TBDTC) and lithium bis(trifluoroethyl) dithiocarbamate (LiFDDC). In conjunction with traditional determination of total chromium, an efficient speciation of Cr(VI) could be achieved.

The mostly used extraction methods for Chromium speciation are summarized in Table 4, including the standardized method USEPA SW-846 Method 7197 based on the chelation of hexavalent chromium with APDC and extraction with MIBK [25].

Table 4 — The extraction and separation methods for Cr(VI) speciation

Extraction method	Detection method	Detection Limit µg/l
Complexation with Aliquat-336; extraction in toluene; direct analysis of organic phase;	GF-AAS	0,01
Extraction of APDC-complex in MIBK; direct analysis of organic phase;	FAAS	-
Extraction of DDTC complex in MIBK; direct analysis of organic phase;	FAAS	-
Complexation with Aliquat-336; extraction in MIBK or toluene; direct analysis of organic phase;	GF-AAS	1,2
Extraction of Cr(VI)-thiosemicarbazide complex in MIBK; direct analysis of organic phase;	FAAS	30
Precipitation of Cr(III) with hydrated iron(II) oxide; extraction of Cr(VI)-APDC-complex in MIBK; direct analysis of organic phase;	FAAS	0,06

Extraction method	Detection method	Detection Limit µg/l
Complexation with DDTC and extraction of the complex in chloroform; back extraction into a Hg(II) solution for analysis;	GF-AAS	0,01
Extraction of APDC-complex in MIBK from phthalate buffer; direct analysis of organic phase.	GF-AAS	0,02

Abbreviations:

APDC: ammonium pyrolidine dithiocarbamate; **DDTC:** diethyldithiocarbamate;

Aliquat-336: methyltricaprylammonium; **MIBK:** methyl isobuthyl ketone.

4.2.2.3 Coprecipitation

Even coprecipitation represents an interesting approach of Cr(VI) speciation nowadays this separation method is used in a reduced manner. However, the most reliable is the standardized USEPA SW-846 Method 7195 [26]. This is based on the separation of Cr(VI) from solution by coprecipitation of lead chromate with lead sulfate in a solution of acetic acid. After separation, the supernatant (containing Cr(III)) is drawn off and the precipitate is washed to remove occluded Cr(III). The Cr(VI) is then reduced and resolubilized in nitric acid and quantified as Cr(III) by either flame or furnace atomic spectrometry. Other coprecipitation techniques for Cr(VI) speciation are summarized in Table 5.

Table 5 — The mostly used coprecipitation separation methods for Cr(VI) speciation

Coprecipitation	Detection method	Detection Limit µg/l
Coprecipitation of Cr(III) and Cr(VI) with hydrated iron(III) oxide(Cr(III)) or bismuth oxide(Cr(III)+Cr(VI)); dissolution of precipitate in hydrochloric acid; Cr(VI) calculated by difference;	GF-AAS	0,001
Coprecipitation of Cr(VI) with lead sulfate; dissolution in nitric acid	GF-AAS	0,05
Coprecipitation of Cr(VI) with barium sulfate; fusion of the precipitate potassium sodium carbonate; dissolution of the melt in hot water;	Photometric with DPC	0,02
Coprecipitation of Cr(III) with iron(III) hydroxide and Cr(III)+Cr(VI) with iron(III)+iron(II) hydroxide; calculation by difference;	XRF	-
Precipitation of Cr(VI) with DBDTC; coprecipitation of Cr(III) with hydrated iron(III) oxide.	XRF	-

4.3 Speciation Isotope Dilution Mass Spectrometry (SIDMS)

4.3.1 General

Traditional speciation methods, including spectrophotometric, electrochemical and chromatography methods are prone to error and cannot correct for speciation degradation. Accurate measurement of species requires a diagnostic tool that is not subjected to those limitations. Primarily, the specific problems causing errors in speciation analysis are [20]:

— many species are reactive and may be transformed or converted to other species during the sampling, storage and measurements steps;

— because the species are reactive they continue to react during these processes and are altered many times prior to the numerical measurements;

— the methods do not allow for the species possible reaction, with separating agents.

As a result, although analysis through these methods may be both precise and replicable, they are not defensible in court. The traditional analytical method required a complete separation prior to analytical detection. A technique that is not subject to these quantitative limitations is needed to address this balance between separation efficiency and species degradation. The decomposition of the matrix to free the species while preserving the species itself is not a simple task and requires extensive preparation.

Chromatography separation has been used to distinguish between the two different forms of chromium in a mixture before presentation to a species non-specific detector, such as: AAS, AES or MS. However, because each species can react with its surroundings and even with the separating agents, detection after a chromatographic separation is only a snapshot of the species distribution at that time. Each species may react with other sample components or reagents or be transformed during the storage and analysis step. Thus, with time resolution, there is no way to determine how much chromium was actually present in each speciated form when the sample was originally taken. Fundamentally, traditional speciation analytical methods attempts to keep the species from being either degraded or transformed during the measurement processes. Essentially, traditional methods fight the element's natural properties. These problems lead to bias and inaccuracies limiting the use of these measurements in environmental decision -making and severely reduce or eliminate their legal defensibility.

SIDMS is the first method to evaluate species conversion and to correct mathematically for them (using additional degrees of freedom). This is a fundamentally different approach and its accuracy, value and reliability was demonstrated [19, 20, 27-33]. It has several advantages over conventional calibration methodologies. Partial loss of the analyte after equilibration of the spike and the sample will not influence the accuracy of the determination. Furthermore, even if the complete separation of the species is desired, SIDMS permits incomplete separation. Thus, the low resolution of the chromatographic separation will not influence the deconvolution of species concentration [20]. Less physical and chemical interference influences the determination as they have similar effects on each isotope of the same element.

A theoretical treatment of Isotope Dilution (ID) is presented in Annex C.

4.3.2 Application of SIDMS for Cr(VI) determination on solid matrices

Theoretically, IDMS method is applicable to elements with more than one stable isotope. USEPA SW-846 Method 6800 lists the elements of interest, namely: Sb, B, Ba, Cd, Ca, Cr, Cu, Fe, Pb, Mg, Hg, Mo, Ni, K, Se, Ag, Sr, Tl, V and Zn. Other elements with multiple isotopes may also be analysed by means this method. For an extensive review on the derivation of the SIDMS calculations we refer to the USEPA SW-846 Method 6800 [31] (see Annex D)

For the determination of Cr(VI) on solid matrices the sample is spiked with known amounts of stable enriched isotopes that have been chemically converted into the same forms of the species to be analysed. The isotopic spike for each species has a unique isotope enrichment. In the case of chromium, two isotopic spikes, ^{53}Cr(VI) enriched in ^{53}Cr and ^{50}Cr(III) enriched in ^{50}Cr, are added. The concept of SIDMS when using an alkaline extraction is however slighlty changed in comparison with USEPA SW-846 Method 6800 due to the precipitation of the enriched Cr(III) under alkaline conditions. This results in the impossibility to correct for interconversion (original amount of Cr(III) in the sample is not determined) but still allows the determination of

— Cr(VI) extracted from the solid material

— the recovery of the enriched spike $^{53}Cr(VI)$

— the amount of converted spike $^{50}Cr(III)$

Unlike spectrophotometric method for Cr(VI) detection, SIDMS monitors the stability of the Cr (VI) during the extraction and the (possible) oxidation of Cr(III) (see Annex F).

5 Final conclusions

Knowledge of the occurrence and behavior of Cr(VI) in environment is still fragmentary, valence-specific analysis appears to be rather difficult and consequently, data on speciation of Cr(VI) are scarce. There exists a lack of standardized analytical methods with respect to the speciation of chromium. Although pollution control measures seem to become effective the last few years, the need for chromium speciation still exists, because of the carcinogenic potential of chromate and the still increasing use of chromium in our society.

With regards to the solid sample pre-treatment, the alkaline digestion, USEPA SW-846 Method 3060A represents a reliable method for the extraction of total Cr(VI) from solid matrices. Satisfactory matrix spike recoveries (75 % - 125 %) have been observed in many of non-reducing environmental samples. Evaluation of the proposed method demonstrated that method-induced reduction is not the cause of low or 0 % matrix spike recoveries when they occur in such non-reducing samples. Soils that exhibit highly reducing characteristics (e.g., anoxic sediments) are not capable of maintaining Cr in the +6 valence state in an environmental setting or after adding Cr(VI) matrix spike in the laboratory. Where low or 0 % matrix spike recoveries are observed, the results of redox-indicating ancillary parameters must be evaluated to assess if the sample in question has the capacity to support Cr(VI). Data obtained using the proposed USEPA SW-846 Method 3060A on those samples demonstrating to be highly reducing should be considered acceptable for use as reported.

Evaluation of the proposed USEPA SW-846 Method 3060A has shown that partial method-induced oxidation of Cr(III) to Cr(VI) occurs when soluble Cr(III) or freshly precipitated $Cr(OH)_3$ is present, which is not likely in environmental samples except those associated with a fresh spill. In the event soluble Cr(III) is suspected or observed, the method specifies the addition of Mg(II), which has been shown to suppress potential oxidation of Cr(III).

USEPA SW-846 Method 7196A, a spectrophotometric determination method of Cr(VI) is proposed, by detecting the red-violet colored complex at the specific pH=2. However, several problems arise when this method is applied to real samples with complex matrices. The coexisting matrix components such as Fe(II) and some organic matter can interfere with Cr(VI) by reducing it during measurements.

The effects of species on chemical reaction points out the need to sample, separate and measure different species and determine whether any interchange occurs during each of the various processes. Tracking species in reactive systems and monitoring their distribution in various forms requires specific measurement methods. With conventional measurement techniques, the origin of one species, as well as its possible transformation or distribution between several species, is impossible to determine.

Currently, the reliability of speciated data measurements is discredited in the courts. There has not been a diagnostic method previously to provide quality assurance for speciated measurements of such elements as Cr(VI) and other transformable and highly reactive species. The proposed method of speciation isotope dilution, SIDMS, permits the monitoring of species shifts that have occurred during analysis and also during other portions of sample handling if they are included in the method protocol. This could provide both a measurement technique and a diagnostic tool to validate or calibrate other speciation measurements methods for a variety of different species.

The development of methods to determine very low levels of Cr(VI) at unfavorable Cr(VI)/Cr(III) ratio and further elucidation of the Cr(VI)/Cr(III) transformations in environment remain challenges to environmental studies.

An overview of several regulatory values for Cr(VI) concentration in different types of environmental samples is presented in Annex E.

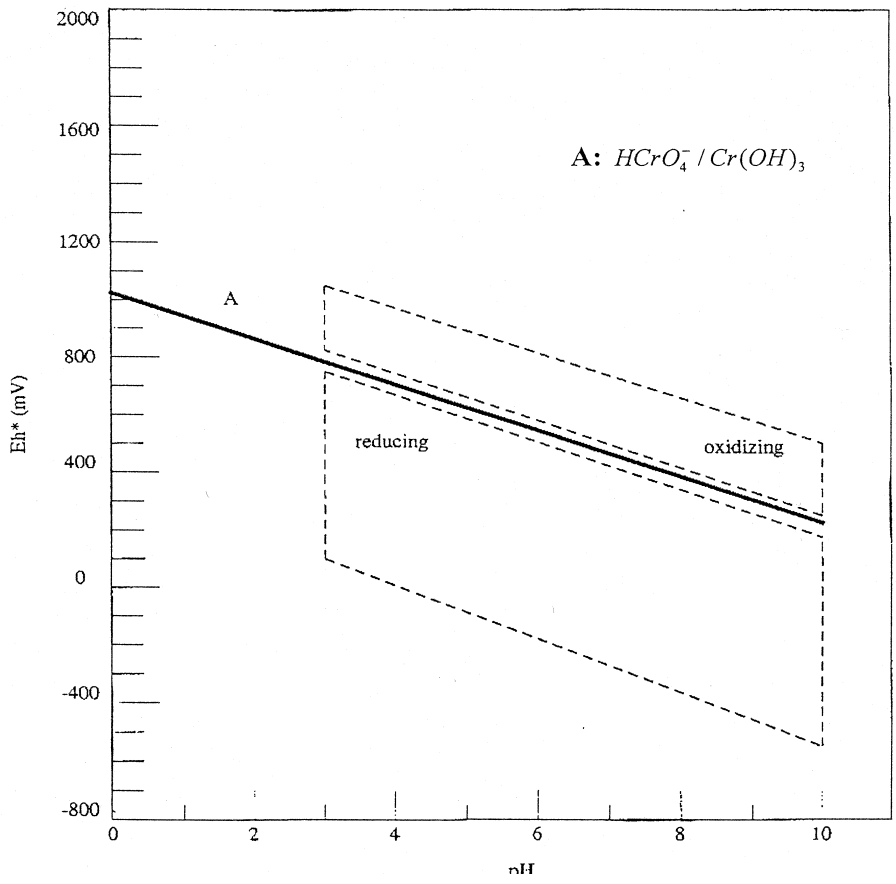
Annex A
(informative)

Eh/pH phase diagram for $HCrO_4^-$ /$Cr(OH)_3$

Annex 1.

Eh/pH PHASE DIAGRAM

The dashed lines define Eh-pH boundaries commonly encountered in soils and sediments.



[a] The dashed line define Eh-pH boundaries commonly encountered in soils and sediments.

Figure A.2 — Eh/pH phase diagram for $HCrO_4^-$ /$Cr(OH)_3$ [a]

Annex B
(informative)

Standardized methods for Cr(VI) speciation (including solid, water and air analysis)

B.1 Spectrophotometric methods

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

USEPA SW-846 Method 7199:1996 *Determination of Hexavalent Chromium in Drinking Water, Groundwater and Industrial Waste Water Effluents by Ion Chromatography*;

USEPA SW-846 Method 0061:1996 *Determination of Hexavalent Chromium Emissions from Stationary Sources*;

B.2 Electrochemical methods

USEPA SW-846 Method 7198:1986 *Chromium, Hexavalent (Differential Pulse Polarography)*;

B.3 Atomic absorption spectrometry methods

USEPA SW-846 Method 7195:1986 *Chromium, Hexavalent (Coprecipitation)*;

B.4 Mass spectrometry methods

USEPA SW 846 Method 6800:1998 *Elemental and Speciated Isotope Dilution Mass Spectrometry*;

Annex C
(informative)

Theoretical consideration on Isotope Dilution (ID) method

C.1 General

ID is a technique for the quantitative determination of elemental concentrations in a sample, on the basis of measured isotope ratios of elements only. It is based on the addition of a known amount of enriched isotope to the subjected sample. Equilibration of the spike isotope with the natural element/species in the sample alters the isotope ratio that is measured. With the known isotopic abundance of both spike and sample and the altered isotope ratio, the concentration of the element/species in the sample can be calculated.

For a bi and poli-isotopic element, the basic principle for ID is presented. The isotope ratio (*R*) is defined as the ratio of the number of atoms of the two isotopes (1 and 2, respectively) of an element. As experimentally, a mass discrimination exists against one of the two isotopes, it is normally not the true isotope ratio that is measured. This mass discrimination is assumed to be linear, thus:

$$R' = K \quad R = \frac{N_2}{N_1}$$

where

R is the real isotope ratio;

R' is the measured isotope ratio;

K is the mass discrimination factor;

Ni is the number of atoms.

Using the subscripts, x-for sample (unknown), s-for spike and m-for mixed (measured) sample, the following isotope ratios can be written:

$$R_x^{'} = \frac{N_{x,2}}{N_{x,1}} \qquad R_s^{'} = \frac{N_{s,2}}{N_{s,1}} \qquad R_m^{'} = \frac{N_{x,2} + N_{s,2}}{N_{x,1} + N_{s,1}}$$

But the number of isotopes "1" and "2", respectively is correlated with the total number of isotopes, through relative abundance:

$$N_{x,1} = A_{x,1} \quad N_x \qquad N_{x,2} = A_{x,2} \quad N_x$$

$$N_{s,1} = A_{s,1} \quad N_s \qquad N_{s,2} = A_{s,2} \quad N_s$$

where

N_x, N_s is the total number of atoms in unknown sample and spike, respectively.

In this case, the measured isotopic ratio is:

$$R_m^{'} = \frac{A_{x,2} \quad N_x + A_{s,2} \quad N_s}{A_{x,1} \quad N_x + A_{s,1} \quad N_s}$$

Furthermore, the total number of atoms can be correlated with the concentration of the sample by means the following equations:

$$N_x = \frac{c_x \quad W_x}{M_x} \qquad N_s = \frac{c_s \quad W_s}{M_s}$$

where

c_x, c_s is the concentration of analysed sample and spike, respectively (µg/g);

W_x, W_s is the weigh of unknown sample and spike, respectively (g);

M_x, M_s is the atomic mass of analysed sample and spike, respectively (µg/mol).

In this specific case, M_x and M_s have different values, because of different abundance of composed isotopes. Thus:

$$M_x = \frac{1}{100}(A_{x,1} \quad M_1 + A_{x,2} \quad M_2 + ... + A_{x,n} \quad M_n)$$

$$M_s = \frac{1}{100}(A_{s,1} \quad M_1 + A_{s,2} \quad M_2 + ... + A_{s,n} \quad M_n)$$

Taking into account the previous equations, the measured isotope ratio and the concentration of unknown sample are:

$$R'_m = \frac{A_{x,2} \quad \frac{c_x \times W_x}{M_x} + A_{s,2} \quad \frac{c_s \times W_s}{M_s}}{A_{x,1} \quad \frac{c_x \times W_x}{M_x} + A_{s,1} \quad \frac{c_s \times W_s}{M_s}}$$

$$c_x = \frac{M_x}{W_x} \quad \frac{c_s \quad W_s}{M_s} \quad \frac{A_{s,2} \quad R'_m \quad A_{s,1}}{R'_m \quad A_{x,1} \quad A_{x,2}}$$

or by means of individual isotope ratios:

$$c_x = \frac{M_x}{W_x} \quad \frac{c_s \quad W_s}{M_s} \quad \frac{A_{s,1}}{A_{x,1}} \quad \frac{R_s \quad R'_m}{R'_m \quad R_x}$$

C.2 Precision and accuracy [28]

In order to achieve the best possible precision and accuracy, the parameters on which they depend must be scrutinized. These parameters can be divided into those, which are experimentally adjustable, and those, which are not.

a) The parameters, which can be adjusted are:

- the amount of spike added to the sample; generally, R'_m is chosen such that it does not deviate much from 1 (i.e. $0.1<R'_m<1$);
- the enrichment of the spike.

b) Parameters which can not be adjusted, are:

- the isotope ratio in sample;
- the precision and accuracy with which the(certified) isotope ratio or isotope abundance for the studied element is known;
- the precision of the measurements(e.g., ICP-MS measurements);
- the concentration level of the element to be determined in sample; if this level is low, the precision will decrease for the same parameters(due to counting statistic); improvement in the relation between concentration and precision can be made by preconcentration procedures or by utilization of alternative introduction techniques, such as electrothermal vaporization or ultrasonic nebulization.

C.3 ID with ICP-MS detection

Apart from considerations, on the statistics, of ID, experimental aspects of ICP-MS must be taken into account. Two of these require special attention [27, 28]:

- the dead time of the detection system (C.3.1);
- the mass discrimination factor of the instrument for the isotopes subjected (C.3.2).

C.3.1 The dead time of the detection system

The number of counts measured on a channel (I_m) can be corrected for the dead time (τ), by the following equation:

$$I = I_m \frac{1}{1 \quad I_m}$$

where

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.

The dead time can be determined by measuring the isotope ratio for the element in a number of solutions with different concentration. Using different values for the dead time in the calculations for the isotope ratio, from the raw scanning data, different values for the isotope ratio for every measured concentration are obtained.

The best approximation gives equal ratios (i.e., the standard deviation is minimal) for the different elemental concentrations. Of course, the concentration range has to be selected carefully. High concentrations must be avoided because of saturation and at very low concentration the decreased precision of the ratio determined has to be taken into account.

C.3.2 The mass discrimination factor of the instrument for the isotopes subjected

Instrumental discrimination effects are changes induced in the "true" isotope ratio from the ionization process or from differential transmission/detection by mass spectrometer; this effect can bias the ratio either positively or negatively.

Normally, to correct the mass bias, the mass bias factor should be determined with isotopically certified materials.

$$K = \frac{R_t}{R_m}$$

where

R_t, R_m is the certified isotope ratio and the measured isotope ratios of the standard material (dead time corrected).

The dead-time-corrected isotope ratios of the sample can be corrected using the following equation:

$$R_c = K \quad R_m$$

where

R_c, R_m is the corrected-isotope ratio and the measured dead-time-corrected isotope ratios of the sample, respectively.

There are, however a number of elements where there is no reliable information about natural abundances of their isotopes, e.g., they may change with time, such as those for lead, or no isotopic reference material exists. For these elements, the ID results, in term of precision will be worse than those for elements with well defined isotope ratios, because the determination of the mass bias factor is subjected to a poorer analysis. In some instances, a different approach may be followed to prevent such poor precision of K, by means of following equation:

$$R_m^{'} = R\frac{1}{1 + B(M_2 \quad M_1)}$$

where

B is the bias per mass unit;

M_1, M_2 is the atomic mass of isotope "1" and "2", respectively.

This enables the calculation of the mass bias factor of other isotope pairs based on the measurement of one pair of isotopes but this must be verified experimentally.

However, mass discrimination is a time-dependent instrumental effect, so the mass bias factor must be determined periodically during the measurements of the sample. Samples are run with the assumption that mass bias factors remain constant. Generally, this is stable over several hours for ICP-MS measurements.

Annex D
(informative)

Application of Speciation Isotope Dilution-Mass Spectrometry (SIDMS) for Cr(VI) determination

Theoretically, IDMS method is applicable to elements with more than one stable isotope.
EPA Method 6800 lists the elements of interest, namely: Sb, B, Ba, Cd, Ca, Cr, Cu, Fe, Pb, Mg, Hg, Mo, Ni, K, Se, Ag, Sr, Tl, V and Zn. Other elements with multiple isotopes may also be analysed by means of this method.

For an extensive review of the SIDMS calculations we refer to the USEPA SW-846 Method 6800 [31]. Herein is demonstrated that the concentration of the different species as well as the interconversion can be deconvoluted from the following equations:

$$R^{III}_{50/52} = \frac{\left({}^{50}A_x C^{III}_x W_x + {}^{50}A^{III}_s C^{III}_s W^{III}_s\right)(1\quad) + \left({}^{50}A_x C^{VI}_x W_x + {}^{50}A^{VI}_s C^{VI}_s W^{VI}_s\right)}{\left({}^{52}A_x C^{III}_x W_x + {}^{52}A^{III}_s C^{III}_s W^{III}_s\right)(1\quad) + \left({}^{52}A_x C^{VI}_x W_x + {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s\right)}$$

$$R^{III}_{53/52} = \frac{\left({}^{53}A_x C^{III}_x W_x + {}^{53}A^{III}_s C^{III}_s W^{III}_s\right)(1\quad) + \left({}^{53}A_x C^{VI}_x W_x + {}^{53}A^{VI}_s C^{VI}_s W^{VI}_s\right)}{\left({}^{52}A_x C^{III}_x W_x + {}^{52}A^{III}_s C^{III}_s W^{III}_s\right)(1\quad) + \left({}^{52}A_x C^{VI}_x W_x + {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s\right)}$$

$$R^{VI}_{50/52} = \frac{\left({}^{50}A_x C^{III}_x W_x + {}^{50}A^{III}_s C^{III}_s W^{III}_s\right) + \left({}^{50}A_x C^{VI}_x W_x + {}^{50}A^{VI}_s C^{VI}_s W^{VI}_s\right)(1\quad)}{\left({}^{52}A_x C^{III}_x W_x + {}^{52}A^{III}_s C^{III}_s W^{III}_s\right) + \left({}^{52}A_x C^{VI}_x W_x + {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s\right)(1\quad)}$$

$$R^{VI}_{53/52} = \frac{\left({}^{53}A_x C^{III}_x W_x + {}^{53}A^{III}_s C^{III}_s W^{III}_s\right) + \left({}^{53}A_x C^{VI}_x W_x + {}^{53}A^{VI}_s C^{VI}_s W^{VI}_s\right)(1\quad)}{\left({}^{52}A_x C^{III}_x W_x + {}^{52}A^{III}_s C^{III}_s W^{III}_s\right) + \left({}^{52}A_x C^{VI}_x W_x + {}^{52}A^{VI}_s C^{VI}_s W^{VI}_s\right)(1\quad)}$$

where

$R^{III}_{50/52}$ 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^{VI}_x is the concentration of Cr(VI) in the sample (µmol/g, unknown);

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).

These formulas are based on a chemical pure isotope enriched spike of both components. In other words the chromium isotope enriched material contains only one redox species of chromium. To confirm this assumption both solutions of isotope enriched material should be analysed in order to control their chemical purity.

In case of alkaline extraction USEPA Method 3060A the Cr(III) is precipitated and only Cr(VI) is measured with ICP-MS, however based on the following ratios of the integrated peak areas of the measured Cr(VI)

— the ratio of mass 53/52;

— the ratio of mass 50/52.

The different fractions of the chromium (VI) present in the leachate can be calculated:

— fraction (natural) Cr(VI);

— fraction enriched spike ^{53}Cr(VI);

— fraction converted spike ^{50}Cr(III).

The total amount of Cr(VI) is calculated by means of an external calibration line based on the sum of the integrated peak areas of Cr(VI) on mass 50, 52, 53 and 54.

The concentration of each of the three different chromium species is then calculated as the product of each fraction with the total amount of chromium (VI) resulting in:

— concentration (natural) Cr(VI);

— concentration enriched spike ^{53}Cr(VI);

— concentration converted spike ^{50}Cr(III).

Annex E
(informative)

Regulatory values for Cr(VI) concentration in different types of samples

Table E.1 — Regulatory values for Cr(VI) concentration in different types of samples

No	Country	Type waste/sample	Cr(VI)[a*]	Reference[b]
1	Austria	Waste for excavated-soil landfill	0,05 mg/l	1
		Waste for demolition-waste landfill	0,05 mg/l	
		Waste for residual-materials landfill	0,1 mg/l	
		Waste for mass-waste landfill	2,0 mg/l	
2	Belgium[c]	Industrial waste water effluents	0,2 mg/l	2
		Acceptance criteria waste deposits Cat I and II (soluble fraction after leaching tests)	0,5 mg/l	
		Acceptance criteria for dredging sludge	0,5 mg/l	
		Background concentration for soil quality	37 mg/kg **Cr(III)**	
		Soil remediation legislation	130 mg/kg **Cr(III)**	3
		Indoor work(8 h) atmosphere	0,01 mg/m^3	4
3	European Community	Drinking water	0,05 mg/l	5
		Poluted soil	5 mg/kg	
4	France[c]	Industrial waste (soluble fraction after leaching test)	5 mg/kg	5
		Leachate of landfill (class 1)	0,1 mg/l	
		Incineration of domestic waste (category V) soluble fraction after leaching test	1,5 mg/kg	
5	Germany	Inert waste	0,05 mg/l	6
		Ordinary waste	0,1 mg/l	
		Hazardous waste	0,5 mg/l	

No	Country	Type waste/sample	Cr(VI)[a*]	Reference[b]
6	Italy[c]	Existing and new legislation (not specified)		
7	World (WFO)	Alimentation	0,1 mg/kg	5

[a] Maximum acceptable concentration in eluate/solid material/water/air.

[b] References:

1. Technical Instructions on the Recycling, Treatment and Other Management of Wastes from Human Settlements (TA Siedlungsabfall), Dated 14 May, 1993, Federal Gazette No 99 (Germany);
2. VLAREM, Titel II, Besluit van de Vlaamse Regering houdende algemene en sectorale bepaling inzake milieuhygiene, 1995(Belgium);
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4. Legislation concerning work area hygiene, 1995 (Belgium);
5. INERIS, Commision AFNOR, X30J analyse des eluats;
6. Deponieverordnung BGBI Nr. 49/1996 (Austria).

[c] See also CEN/TC292/WG3 N145 and N154 and N156

Annex F
(informative)

Comparison water extraction and alkaline extraction for the determination of Cr(VI) on waste material

F.1 General

In order to study the differences in extraction efficiency between alkaline and water extraction, 3 waste samples were analysed :

— waste 1 : filter cake;

— waste 2 : chomium dust;

— waste 3 : low carbon pitslag.

Each waste sample was extracted in water and alkaline medium. In each medium the samples were extracted as such and spiked with an aliquot of enriched isotope $^{50}Cr(III)$ and enriched isotope $^{53}Cr(VI)$. The samples were analysed with ion chromatography diphenylcarbazide (IC-DPC) and ion chromatography inductively coupled plasma mass spectrometry (IC-ICP-MS).

F.2 Alkaline digestion for hexavalent chromium (EPA method 3060A)

F.2.1 As such (unspiked)

Approximately 2,5 g of a sample is placed into a 250 ml digestion vessel and 50 ml of the digestion solution is added. The digestion solution consists of a 0,5 M NaOH and a 0,28 M Na_2CO_3 solution. Also approximately 61 mg $Mg(NO_3)_2$ is added as well as 0,5 ml of a 0,5 M K_2HPO_4 / KH_2PO_4 buffer (pH 7). The addition of Mg^{2+} in a phosphate buffer to the alkaline extraction solution has been showed to suppress the oxidation of Cr(III). The sample is covered witch watch glass and heated at 363 K –368 K for at least 60 minutes with continuous stirring. Heating in an ultrasonic bath is also possible as alternative.

The contents is quantitatively transferred, after gradually cooling to room temperature, to the filtration apparatus (0,45 µm membrane filter). The filtrate and rinses of the digestion vessel are collected in a 100 ml volumetric flask and diluted with Milli-Q water.

F.2.2 Spiked

Approximately 2,5 g of a sample is placed into a 250 ml digestion vessel and spiked with an aliquot of enriched isotope $^{50}Cr(III)$ and enriched isotope $^{53}Cr(VI)$, finally 50 ml of the digestion solution is added. Follow the same procedure as above.

F.3 Water extraction for hexavalent chromium

F.3.1 As such (unspiked)

Approximately 2,5 g of a sample is placed into a 250 ml digestion vessel and 50 ml water is added. The sample is covered witch watch glass and heated at 363 K – 368 K for at least 60 minutes with continuous stirring. Heating in an ultrasonic bath is also possible as alternative.

The contents is quantitatively transferred, after gradually cooling to room temperature, to the filtration apparatus (0,45 µm membrane filter). The filtrate and rinses of the digestion vessel are collected in a 100 ml volumetric flask and diluted with water.

F.3.2 Spiked

Approximately 2,5 g of a sample is placed into a 250 ml digestion vessel and spiked with an aliquot of enriched isotope ^{50}Cr(III) and enriched isotope ^{53}Cr(VI), finally 50 ml water is added. Follow the same procedure as above.

F.4 Measurement IC-DPC

Aliquots of the sample solutions are subjected to ion chromatography in order to separate the extracted hexavalent chromium from trivalent chromium and other metal cations. Following this separation, hexavalent chromium is measured spectrophotometrically at 540 nm after post-column derivatisation with 1,5-diphenylcarbazide in acid solution. Post-column derivatisation involves reaction of 1,5-diphenylcarbazide with hexavalent chromium to produce trivalent chromium and diphenylcarbazone. These then combine to form a trivalent chromium-diphenylcarbazone complex containing the characteristic magenta chromagen ($_{max}$= 540 nm). However, the exact mechanism of this reaction is not fully understood.

IC-DPC measures the total amount of chromium (VI) present in the solution.

F.5 Measurement Speciated isotope dilution mass spectrometry (SIDMS)

Samples were analysed on an Elan 6000 ICP-MS system (Perkin-Elmer, SCIEX, Thornhill, ON, Canada) equipped with a MCN-100 micro-concentric nebuliser (Cetac technologies, Omaha, NE, USA) fitted to a cyclonic spray chamber (Glass Expansion SARL, Romainmôtier, Switzerland). The speciation of the redox species was carried out by anion exchange chromatography on an IONPAC AS 10 microbore column (Dionex, Sunnyvale, CA, USA). The column was provided with a guard column to remove dissolved and particulate contaminants from the sample and eluent before reaching the column. The eluent was pushed through the column via a HPLC pump model 2250 (BISCHOFF, Leonberg, Germany), all fittings as well as the pump head were made in PEEK . A FIAS 400 (Perkin-Elmer) peristaltic pump provided the filling of a 25 µl PEEK sample loop. The sample loop was connected to an automated 6-port valve (LabPRO 6, Rheodyne, California, USA). The measurement system, including sample uptake, filling of the loop, injection on the column and ICP-MS measurement is computerized. The integration of the chromatograms was performed with Turbochrom (Perkin-Elmer). Before analysis, the instrument was preconditioned by aspirating the eluent for at least 1 hour.

The calculations are performed in Matlab software, based on the following parameters measured with IC-ICP-MS on the extracted samples:

— the ratio of mass 53/52 (integrated peak area);

— the ratio of mass 50/52 (integrated peak area).

On the basis of those ratios the different fractions of the chromium (VI) present in the sample are calculated :

— fraction (natural) Cr(VI) present in the sample;

— fraction enriched spike ^{53}Cr(VI);

— fraction converted spike ^{50}Cr(III).

The total amount of Cr(VI) is calculated based on an external calibration line

— the sum of the integrated peak areas on mass 50, 52, 53 and 54.

The concentration of each of the three different chromium species is then calculated as the product of each fraction with the total amount of chromium (VI):

— concentration (natural) Cr(VI) present in the sample;

— concentration enriched spike $^{53}Cr(VI)$;

— concentration converted spike $^{50}Cr(III)$.

F.6 Discussion

The columns in the Table F.1 to Table F.4 represent

a) Ion-Chromatography DPC

— Cr(VI) µg/l: the amount of chromium (VI) present in the solution, µg/l;

— recovery: the theoretical recovery assuming that added spike (e.g. 160 µg/l Cr(VI)) is completely recovered. The recovery is calculated as the difference between the total amount of chromium (VI) present in the spiked and unspiked (as such) solution;

— Cr(VI) mg/kg ds: the amount of chromium (VI) extracted from the sample, mg / kg dry matter.

b) SIDMS

— Cr(VI) µg/l: the amount of chromium (VI) present in the solution, µg/l;

— Cr(VI) natural: the amount of extracted natural chromium (VI) present in the solution, µg/l;

— Cr(VI) spike: the amount of enriched chromium (VI) spike present in the solution, µg/l;

— recovery: The recovery is calculated as the difference between the amount of chromium (VI) spike present in the solution (Cr (VI) spike) and the theoretical added amount of spike (e.g. 160 µg/l);

— Cr(III) oxidised: the amount of enriched chromium (III) spike converted to Cr(VI), µg/l;

— Oxidation: The oxidation is calculated as the difference between the amount of converted chromium (III) spike (Cr(III) oxidised) and the theoretical added amount of spike (in this case 160 µg/l);

— Cr(VI) mg/kg ds: the amount of chromium (VI) extracted from the sample, mg/kg dry matter;

The following conclusions can be deduced from the experimental results:

— The alkaline extraction is more reproducable then the water extraction (the differences in the duplo analysis are smaller);

— The extraction efficiency for Cr(VI) is higher for the alkaline extraction in comparison with the water extraction;

— The added Cr(VI) spike is stable during the alkaline extraction (recovery > 90 %). The recovery of the spike in the water extraction amounts 46 % to 90 %;

— The oxidation of the added Cr(III) spike is negligible during the alkaline extraction.

Table F.1 — Results water extaction[a]

			Ion-chromatography DPC			SIDMS						
	Mass G	**Dry mass** g	**Cr VI** µg/l	**Recovery** %	**Cr VI** mg kg ds	**Cr VI** µg/l	**Cr VI natural** µg/l	**Cr VI spike** µg/l	**Recovery** %	**Cr III oxidised** µg/l	**Oxidation** %	**Cr VI** mg kg ds
blank			0			0						
blank + spike Cr(III)			14,5			14,2						
blank + spike Cr(VI)			169			169						
waste 1	0,252	0,175	259		74	260						74
waste 1+Cr(III)+Cr(VI)	0,249	0,173	541	176%	110	561	416	138	86%	6,1	3,8%	120
waste 2	0,250	0,249	2155		433	1838						369
waste 2+Cr(III)+Cr(VI)	0,254	0,252	3856	532%	701	3238	2985	246	77%	7	2,2%	592
waste 3	0,250	0,250	240		48	230						46
waste 3+Cr(III)+Cr(VI)	0,257	0,256	379	87%	43	365	266	74	46%	25,2	15,8%	52

[a] spike waste 1 and 3 : 160 µg/l ^{50}Cr(III)+ 160 µg/l ^{53}Cr(VI);

spike waste 2 : 320 µg/l ^{50}Cr(III)+320 µg/l ^{53}Cr(VI).

Table F.2 — Results water extaction[a]

			Ion-chromatography DPC			SIDMS						
	Mass G	**Dry mass** g	**Cr VI** µg/l	**Recovery** %	**Cr VI** mg kg ds	**Cr VI** µg/l	**Cr VI natural** µg/l	**Cr VI spike** µg/l	**Recovery** %	**Cr III oxidised** µg/l	**Oxidation** %	**Cr VI** mg kg ds
blank			3,76			0						
blank + spike Cr(III)			12,1			14,2						
blank + spike Cr(VI)			170			174						
waste 1	0,255	0,178	281		79	269						76
waste 1+Cr(III)+Cr(VI)	0,255	0,178	372	57%	60	378	246	127	79%	4,6	2,9%	69
waste 2	0,256	0,254	1984		390	2218						436
waste 2+Cr(III)+Cr(VI)	0,256	0,255	3915	603%	706	3560	3290	266	83%	4	1,3%	646
waste 3	0,254	0,253	240		47	212						42
waste 3+Cr(III)+Cr(VI)	0,258	0,257	391	94%	45	384	237	144	90%	2,6	1,6%	46

[a] spike waste 1 and 3 : 160 µg/l $^{50}Cr(III)$+ 160 µg/l $^{53}Cr(VI)$;

spike waste 2 : 320 µg/l $^{50}Cr(III)$+320 µg/l $^{53}Cr(VI)$.

Table F.3 — Results alkaline extaction[a]

			Ion-chromatography DPC			SIDMS						
	Mass G	**Dry mass** g	**Cr VI** µg/l	**Recovery** %	**Cr VI** mg kg ds	**Cr VI** µg/l	**Cr VI natural** µg/l	**Cr VI spike** µg/l	**Recovery** %	**Cr III oxidised** µg/l	**Oxidation** %	**Cr VI** mg kg ds
blank			3,5			2						
blank + spike Cr(III)			6,2			3,3						
blank + spike Cr(VI)			169			162						
waste 1	0,254	0,177	2334		659	1964						554
waste 1+Cr(III)+Cr(VI)	0,255	0,178	2469	84%	649	2241	2078	157	98%	3	1,9%	584
waste 2	0,248	0,247	5056		1024	4459						903
waste 2+Cr(III)+Cr(VI)	0,257	0,256	5530	148%	1019	loss of HPLC pump pressure						
waste 3	0,258	0,257	421		82	394						77
waste 3+Cr(III)+Cr(VI)	0,260	0,260	603	114%	85	621	450	168	105%	3	1,9%	87

[a] spike waste 1 and 3 : 160 µg/l ^{50}Cr(III)+ 160 µg/l ^{53}Cr(VI);

spike waste 2 : 320 µg/l ^{50}Cr(III)+320 µg/l ^{53}Cr(VI).

Table F.4 — Results alkaline extaction[a]

			Ion-chromatography DPC			SIDMS						
	Mass G	**Dry mass** G	**Cr VI** µg/l	**Recovery** %	**Cr VI** mg kg ds	**Cr VI** µg/l	**Cr VI natural** µg/l	**Cr VI spike** µg/l	**Recovery** %	**Cr III oxidised** µg/l	**Oxidation** %	**Cr VI** mg kg ds
blank			4,7			6,7						
blank + spike Cr(III)			6,6			4						
blank + spike Cr(VI)			194			156						
waste 1	0,257	0,179	2242		626	2023						565
waste 1+Cr(III)+Cr(VI)	0,257	0,179	2100	-89%	542	2070	1919	151	94%	2,5	1,6%	536
waste 2	0,254	0,252	5007		993	4745						941
waste 2+Cr(III)+Cr(VI)	0,257	0,255	5288	88%	973	4876	4570	298	93%	8	2,5%	895
waste 3	0,256	0,255	411		81	370						72
waste 3+Cr(III)+Cr(VI)	0,258	0,257	586	109%	83	543	384	157	98%	2,5	1,6%	75

[a] spike waste 1 and 3 : 160 µg/l ^{50}Cr(III)+ 160 µg/l ^{53}Cr(VI);

spike waste 2 : 320 µg/l ^{50}Cr(III)+320 µg/l ^{53}Cr(VI).

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Note: All specified USEPA methods are available on the following Web site:
http://www.epa.gov/epaoswer/hazwaste/test/main.htm

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