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Water quality — Determination of chromium(VI) and chromium(III) in water — Method using liquid chromatography with inductively coupled plasma mass spectrometry (LC-ICP-MS) after chelating pretreatment

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Foreword

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Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

Chromium (Cr) exists in natural resources and is also widely used in industries as plating agents, paints, dyes, catalysts, and dietary supplements. The Cr(VI) compounds are highly harmful and recognized to be a human carcinogen. The Cr(III) compounds are recently used as a substitute for Cr(VI) compounds in industries, e.g. plating. In wastewater, surface water, or drinking water, chromium mainly exists in two oxidation states: +3 [Cr(III)] and +6 [Cr(VI)]. However, the proportion between Cr(VI) and Cr(III) is quite variable. Therefore, the determination of the individual oxidation states of chromium is crucial to evaluate and control the risk of chromium to human and environmental health. This document will be beneficial to perform a robust, simple, and rapid determination of chromium of the individual oxidation states.

Water quality — Determination of chromium(VI) and chromium(III) in water — Method using liquid chromatography with inductively coupled plasma mass spectrometry (LC-ICP-MS) after chelating pretreatment

WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices.

IMPORTANT — It is absolutely essential that tests conducted according to this document be carried out by suitably qualified staff.

1 Scope

This document specifies a method for the determination of hexavalent chromium [Cr(VI)] and trivalent chromium [Cr(III)] in water by liquid chromatography with inductively coupled plasma mass spectrometry (LC-ICP-MS) after chelating pretreatment.

This method is applicable to the determination of Cr(VI) and Cr(III) dissolved in wastewater, surface water, groundwater, or drinking water from 0,20 µg/l to 500 µg/l of each compound as chromium (Cr) mass. Samples containing Cr at concentrations higher than the working range can be analysed following appropriate dilution of the sample.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods — Part 1: Linear calibration function*

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at https://www.electropedia.org/

4 Principle

The chemical forms of various Cr(III) species in water samples are unified to a stable Cr(III) complex by a chelating pretreatment with 2,6-pyridinedicarboxylic acid (PDCA) or ethylenediaminetetraacetic acid (EDTA) after adjusting the sample solution pH to 6,9 ± 0,1.[1][2] Liquid chromatography combined with inductively coupled plasma mass spectrometry (LC-ICP-MS) determines the chromatographically separated Cr(VI) and the Cr(III)-PDCA complex or Cr(III)-EDTA complex in the pretreated sample solutions.

5 Interferences

5.1 General

If any of the interferences described in 5.2 to 5.5 are recognized or can be expected due to additional information about the sample, the sum of Cr(VI) and Cr(III) concentrations determined by the proposed method should be compared with the total Cr concentration which can be determined by ICP-MS.

If the Cr(III) and Cr(VI) species are properly determined by the proposed method, the sum of Cr(III) and Cr(VI) should agree with the total Cr with a difference of ≤ 30 %. An exceedance of this limit (30 %) indicates the occurrence of interferences.

NOTE The water sample can contain Cr^0 or Cr(III) species that cannot be complexed via EDTA or PDCA (e.g. nanoparticles, colloids). These stable species can be so small that they are not retained even by filtration through a 0,2 µm filter membrane. However, as they are uncomplexed, they will not be detected by the LC-ICP-MS analysis and can thus result in a greater difference between the sum of Cr species determined by LC-ICP-MS and the total Cr determination.

5.2 Samples

Reductants or oxidants in the sample may lead to false results for the Cr(VI) and/or Cr(III) concentration through the reduction of Cr(VI) to Cr(III) or oxidation of Cr(III) to Cr(VI), respectively. For example, divalent iron ions or ascorbic acid at 1 mg/l or 10 mg C/l, respectively, cause the reduction within 10 min.[1] Organic matter at high concentrations may slowly reduce Cr(VI) to Cr(III). For example, tartaric acid at 100 mg C/l reduces Cr(VI) to Cr(III) in one night at room temperature, however, the same compound at 10 mg C/l does not cause the reduction. The sample pH also changes the redox equilibrium between Cr(VI) and Cr(III) and the complexation equilibrium between Cr species with coexisting inorganic and organic substances.[3]

5.3 Sample storage and sample preparation

Potential sources of Cr contamination during sampling, sample storage, and sample preparation include: labware, containers, sampling equipment, reagents, water and human contact. Potential unexpected redox reaction between Cr(III) and Cr(VI) may occur during these operations. All apparatus and labware shall be cleaned using the cleaning procedure (see Clause 7).

5.4 Chelating pretreatment

Transition metal cations at high concentrations in the sample solution may lead to a negative biased value for the Cr(III) concentration because these metals decrease the concentration of free chelating agents due to complex formation with chelating agents. For example, neither cobalt(II) nor nickel(II) up to 10 mg/l interfere, however, these metal ions[1] and also calcium ion interfere above 100 mg/l.

Large amounts of organic matter which strongly binds to Cr(III) species in the sample solution may lead to a negatively biased value for the Cr(III) concentration. For example, Cr(III)-PDCA complex formation in the PDCA chelating pretreatment is depressed by the presence of EDTA as an interfering substance at 100 mg/l level, although not depressed at 10 mg/l.[1] The opposite is also true and Cr(III)-EDTA complex formation in the pretreatment of Cr(III) with EDTA is inhibited by the presence of large amounts of PDCA as an interfering substance. The depression at the chelating procedure can be evaluated by recovery experiments (10.3).

5.5 LC-ICP-MS measurements

Polyatomic ions are formed in the argon plasma of the ICP-MS by the reaction among argon, water, reagents and sample matrix, etc. The formation of $^{40}Ar^{12}C^+$ and $^{37}Cl^{16}O^+$ may interfere with the ICP-MS detection of Cr at mass-to-charge ratio (m/z) 52 and at m/z 53, respectively. Some of the interferences such as $^{40}Ar^{12}C^+$ can be reduced by using a collision-reaction cell of the ICP-MS. On the other hand, some of the interferences such as $^{37}Cl^{16}O^+$ can be reduced by chromatographic separation of chloride (Cl) ions from the Cr species.[1] High-resolution or tandem mass spectrometers, e.g. sector-field or MS/MS-type mass spectrometers, can also reduce the polyatomic interferences very effectively.

LC retention time of Cr species may shift for water samples containing salts or organic matter at high concentrations. If this causes the peak of Cr(III)-PDCA complex [or Cr(III)-EDTA complex] to overlap with Cr(VI), it may cause positive and negative interferences to Cr(VI) and Cr(III), respectively. In such cases, adjust elution conditions such as composition of eluent to ensure adequate separation.

The metallic parts of LC-ICP-MS instruments, e.g. LC columns, tubes, and connectors, potentially contaminate the eluent if in contact. Therefore, metallic parts or pathways should be avoided or reduced to a minimum.

6 Reagents and standards

Unless otherwise indicated, reagents of purity grade “for analysis” or “for trace analysis” are used as reagents. If available, use only reagents of pro analysis grade (or purer) free of compounds containing Cr. Weigh the reagents with an accuracy of ± 1 % of the nominal mass, unless stated otherwise.

Prepare alternative concentrations and volumes of solutions as described hereafter, if necessary. Alternatively, use commercially available stock solutions of the required concentration.

6.1 **Water,** with an electrical resistivity of ≥ 18,2 MΩ cm (25 °C).

The water shall not contain any measurable quantity of Cr(III) and Cr(VI) or interfering compounds at or above one-third the method quantification limit.

6.2 **Nitric acid,** $w(\mathrm{HNO_3}) = 650$ g/kg, $\rho(\mathrm{HNO_3}) = 1{,}4$ g/ml.

NOTE Nitric acid is available as $\rho(\mathrm{HNO_3}) = 1{,}38$ g/ml [$w(\mathrm{HNO_3}) = 610$ g/kg] and $\rho(\mathrm{HNO_3}) = 1{,}42$ g/ml [$w(\mathrm{HNO_3}) = 690$ g/kg] as well as $\rho(\mathrm{HNO_3}) = 1{,}40$ g/ml [$w(\mathrm{HNO_3}) = 650$ g/kg].

6.3 **Nitric acid stock solution,** $c(\mathrm{HNO_3}) = 6$ mol/l.

Transfer 25 ml of water (6.1) to 100 ml volumetric flask (7.14), and add 27 ml of nitric acid (6.2) and then fill up to mark with water (6.1).

6.4 **Nitric acid solution for pH adjustment,** $c(\mathrm{HNO_3}) = 2$ mol/l.

Transfer 33 ml of nitric acid stock solution (6.3) to a 100 ml volumetric flask (7.14) and fill up to mark with water (6.1).

6.5 **Sodium hydroxide,** NaOH.

6.6 **Sodium hydroxide solution for pH adjustment,** $c(\mathrm{NaOH}) = 2$ mol/l.

Weigh 8 g of sodium hydroxide pellets (6.5) and transfer them to a 100 ml beaker. Then add approximately 50 ml water (6.1) and stir with a stirrer (7.12) until the pellets have dissolved. Transfer to a 100 ml volumetric flask (7.14) and fill up to the mark with water (6.1). Commercially available solution of sodium hydroxide can be used to dilute them to the required concentration.

6.7 **2,6-Pyridinedicarboxylic acid (PDCA),** CAS Registry Number®1) 499-83-2, $C_7H_5NO_4$.

6.8 **Disodium hydrogenphosphate,** Na_2HPO_4.

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1) Chemical Abstracts Service (CAS) Registry Number® is a trademark of the American Chemical Society (ACS). This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

6.9 Ammonium acetate, CH_3COONH_4.

6.10 Ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA) disodium salt dihydrate (CAS 6381-92-6, $C_{10}H_{14}Na_2N_2O_8 \cdot 2H_2O$) **or EDTA dipotassium salt dihydrate** (CAS 25102-12-9, $C_{10}H_{14}K_2N_2O_8 \cdot 2H_2O$).

6.11 Ammonia solution, mass fraction, $w(NH_4OH) = 280$ g/kg.

6.12 Ammonia solution for pH adjustment, $c(NH_3) = 1$ mol/l.

6.13 Potassium dichromate, $K_2Cr_4O_7$.

6.14 Chromium(III) nitrate nonahydrate, $Cr(NO_3)_3 \cdot 9H_2O$.

6.15 Cr(VI) stock solution, ρ[Cr(VI)] = 1 000 mg/l.

WARNING — Potassium chromate can be carcinogenic.

Heat 5 g of potassium dichromate (6.13) at 150 °C for 1 h and then cool at room temperature in a dried desiccator. Dissolve 2,829 g of the dried potassium dichromate (6.13) with water (6.1) in a 1 000 ml volumetric flask (7.14) and fill up to mark with water (6.1). Commercially available Cr(VI) stock solution of the required concentration can be used.

6.16 Cr(VI) standard solution, ρ[Cr(VI)] = 10 mg/l.

Transfer 1,00 ml of the Cr(VI) stock solution (6.15) to a 100 ml volumetric flask (7.14) and fill up to the mark with water (6.1). Prepare this solution on the day of use.

6.17 Cr(III) stock solution, ρ[Cr(III)] = 1 000 mg/l.

Dissolve 7,696 g of chromium(III) nitrate nonahydrate (6.14) in 250 ml water and transfer to a 1 000 ml volumetric flask (7.14). Add 50 ml of nitric acid stock solution (6.3) and fill up to the mark with water (6.1). Commercially available Cr(III) stock solution of the required concentration can be used.

6.18 Cr(III) standard solution, ρ[Cr(III)] = 10 mg/l.

Transfer 1,00 ml of the Cr(III) stock solution (6.17) to a 100 ml volumetric flask (7.14) and fill up to the mark with water (6.1). Prepare this solution on the day of use.

6.19 PDCA solution, c(PDCA) 0,02 mol/l.

Dissolve 3,35 g of 2,6-pyridinedicarboxylic acid (6.7), 2,85 g of disodium hydrogenphosphate (6.8), and 38,5 g of ammonium acetate (6.9) to 900 ml of water (6.1) in a bottle (7.16) of 1 000 ml. Adjust the pH of the solution to pH 6,9 ± 0,1 using a pH meter (7.11) by adding the sodium hydroxide solution (6.6). Transfer the adjusted PDCA solution to a 1 000 ml volumetric flask and fill up to the mark with water (6.1).

The amount of NaOH solution is approximately 16,5 ml. The pH adjustment from pH 6,0 should be carefully performed by adding of NaOH solution by small degrees (e.g. 0,1 ml), because the change of pH is drastic.

6.20 EDTA solution, c(EDTA) 0,025 mol/l.

Dissolve 9,31 g of ethylenediamine-*N,N,N',N'*-tetraacetic acid disodium salt or 10,1 g of the dipotassium salt (6.10) to 900 ml of water (6.1) in a bottle (7.16) of 1 000 ml. Adjust the pH of the solution to pH 6,9 ± 0,1 using a pH meter (7.11) by adding the sodium hydroxide solution (6.6). Transfer the adjusted EDTA solution to a 1 000 ml volumetric flask and fill up to the mark with water (6.1).