Analytical Method

Determination of water-soluble and water-insoluble inorganic compounds of hexavalent chromium in workplace air

ANALYTICAL METHOD **365**

Applicability
Determination of water-soluble and water-insoluble inorganic compounds of hexavalent chromium in workplace air

Standards [1] (TWAEV [2])
Chromium VI, water-insoluble inorganic compounds (expressed as Cr): 0,01 mg/m³
Chromium VI, water-soluble inorganic compounds (expressed as Cr): 0,05 mg/m³
Calcium chromate (expressed as Cr): 0,001 mg/m³ [CAS 13765-19-0]
Lead chromate (expressed as Cr): 0,012 mg/m³ [CAS 7758-97-6]
Strontium chromate (expressed as Cr): 0,0005 mg/m³ [CAS 7789-06-2]
Zinc chromate (expressed as Cr): 0,01 mg/m³ [CAS 13530-65-9,11103-86-9, 37300-23-5]

Sampling system
Vinyl/acrylic copolymer filter 0,8 µm, 25 mm on plastic support in a 3-piece polypropylene cassette (lower part in the form of a goblet)

Recommended sampling volume and flow rate
Volume: 360 litres (L)
Flow rate: 1,5 to 4 L/min

Analysis
Ion chromatography and spectrophotometric detection at 540 nm

Minimum reported values (MRV)
Chromium VI, water-soluble inorganic compounds (expressed as Cr): 0,04 µg
Chromium VI, water-insoluble inorganic compounds (expressed as Cr): 0,04 µg

Working range
0,04 µg to 5 µg of chromium VI/sample or 0,0001 to 0,014 mg/m³ for a recommended sampling volume of 360 Litres

Reability 3
Impregnated filter, water-soluble compounds: 0,9% and 0,7%
Non-impregnated filter, water-soluble compounds: 0,6% and 1,6%
Non-impregnated filter, water-insoluble compounds: 0,7% and 1,3%

Analytical uncertainty (CVA)
Impregnated filter, water-soluble compounds: 3,6%
Non-impregnated filter, water-soluble compounds: 2,6%
Non-impregnated filter, water-insoluble compounds: 3,8%

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Preamble

The goal of the Act respecting occupational health and safety in Québec is to eliminate, at the source, dangers to the health, safety and physical well-being of workers. Permissible exposure values (PEVs) for chemical substances have been established in Schedule I of the Regulation respecting occupational health and safety (RROHS). Section 44 of this regulation entitled "*Methods*" specifies that:

> *"… These dusts, gases, fumes, vapours and mists found in the workplace environment shall be sampled and analyzed to obtain an accuracy equivalent to that obtained by applying the methods described in the Sampling Guide for Air Contaminants published by the Institut de recherche Robert-Sauvé en santé et en sécurité du travail du Québec…."*.

To achieve these objectives, analytical methods for quantifying the workers' degree of exposure are developed and written to establish appropriate means of control. In order to help health and safety professionals in workplaces, the IRSST publishes, periodically revises, and disseminates the *Sampling Guide for Air Contaminants in the Workplace*, and the Laboratory Services and Expertise Department publishes contaminant analytical methods.

These methods must be used in combination with the following regulatory and normative references:

- ✓ *Act respecting occupational health and safety*. R.S.Q., chapter S-2.1. Éditeur officiel du Québec, (August 1, 2007). http://www2.publicationsduquebec.gouv.qc.ca/dynamicSearch/telecharge.php?type=2&file=%2F%2FS_2_1%2FS2_1_A.htm
- ✓ *Regulation respecting occupational health and safety*. S-2.1, r.19.01, O.C. 885-2001. Éditeur officiel du Québec (July 25, 2007). http://www2.publicationsduquebec.gouv.qc.ca/dynamicSearch/telecharge.php?type=2&file=%2F%2FS_2_1%2FS2_1R19_01_A.htm
- ✓ *Sampling Guide for Air Contaminants in the Workplace*. Operations Division, IRSST, T-15 Guide technique, Montréal, Québec, (March 2005) http://www.irsst.qc.ca/files/documents/PubIRSST/T-15.pdf
- ✓ NIOSH, National Institute for Occupational Safety and Health.
- ✓ ISO Guide 30, Terms and definitions used in connection with reference materials, 2nd edition, 1992.
- ✓ ISO, International vocabulary of basic and general terms in metrology (VIM), 2nd edition, 1993.
- ✓ American Industrial Hygiene Association (AIHA), organization that accredits the IRSST laboratory in the field of workplace chemical contaminant analysis and microbiological environmental analysis.

Furthermore, all the terminology used in this method is described in work instruction "I-G-014" of the document management system associated with the IRSST's quality system.

1. WORKING RANGE

This method applies to the determination of water-soluble and water-insoluble inorganic hexavalent chromium (chromium VI) compounds in workplace air by Ion Chromatography.

The linearity of the analytical method was verified for quantities from 0,04 to 5 µg of chromium VI, which corresponds to concentrations from 0,0001 to 0,014 mg/m³ in the air for a recommended sampling volume of 360 litres, and from 0,004 to 0,5 µg/mL for a final volume of 10 mL. The coefficient of determination (r^2) obtained during validation of the method was greater than 0,999 for this working range. Higher concentrations can be reported by applying appropriate dilutions to the samples.

This document also presents the method's procedure, performance controls, and proposes a routine analytical sequence.

2. PRINCIPLE OF THE METHOD

In accordance with the parameters described in the IRSST's Sampling Guide, a specific volume of air is collected through a vinyl/acrylic copolymer filter in order to collect the inorganic chromium VI compounds suspended in workplace air.

The inorganic chromium VI compounds coming from processes that generate liquid acid aerosols are collected on a vinyl/acrylic copolymer filter impregnated with a solution of 0,5N NaOH. The other airborne particles containing inorganic chromium VI compounds are collected on a non-impregnated vinyl/acrylic copolymer filter.

The filter and cassette then undergo treatment to dissolve the inorganic chromium VI compounds. Two sample preparation methods are described for the extraction of water-soluble and water-insoluble chromium VI compounds and, depending on the case, one of these two methods or both methods are used to prepare the sample for analysis. Water-soluble inorganic chromium VI compounds are extracted at ambient temperature with an ammonium sulphate/ammonium hydroxide solution. Water-insoluble chromium VI compounds are extracted with a solution containing sodium hydroxide/sodium carbonate in an ultrasonic bath.

Aliquots of the solutions from the samples are then analyzed by ion chromatography in order to separate chromium VI from the other cations. Chromium VI is measured by spectrophotometry at 540 nm, after post-column derivatization with 1,5-diphenyl carbohydrazide (DPC) in an acid medium. Post-column derivatization consists of reacting the chromium VI with the DPC to obtain trivalent chromium and diphenylcarbazone. These two compounds then combine to form a chromogenic complex of trivalent chromium/diphenylcarbazone that has a maximum absorbance at 540 nm. However, the exact reaction process is not fully explained.

The concentration of the sample is determined by comparing the area obtained for the sample with a range of standard solutions.

3. INTERFERENCES

Any substance that produces a response on the detector at 540 nm and that has a retention time similar to chromium VI is potential interference.

4. MATERIAL

This section presents a list of the common and necessary material for both extraction methods for inorganic chromium VI compounds. The specific material is identified in each of the extraction procedures.
NOTE – All reusable ware must be carefully washed before use and decontaminated by soaking it in dilute nitric acid, for example 10% HNO_3, for at least 12 hours, and then rinsed several times with high purity water. All disposable ware must be subjected beforehand to a control to detect the presence of chromium VI.

- Single-use gloves, impermeable, intended to prevent any contamination by hands and to protect the operator from any contact with toxic and corrosive substances, for example nitrile gloves;
- Containers of appropriate volume for storing solutions, for example made of fluorinated ethylene propylene (FEP) or other inert material;
- Volumetric flasks of appropriate volume with leak proof caps for the preparation of solutions, for example made of high density polyethylene (HDPE) or other inert material;
- Volumetric pipettes with disposable tips;
- Vacuum generator, for example the vacuum from a laboratory hood;
- Vacuum filtration assembly for the simultaneous filtration of several samples, for example the modified Visiprep system from Supelco;
- Dionex ICS-3000 ion chromatograph, with the following components:

  NOTE – All the components that come in contact with the sample or the eluent must be made of inert materials, for example polyetheretherketone (PEEK), as well as all the connector tubes.

  - Isocratic pump;
  - Sample injection system, consisting of an injection valve and a sampling loop with a 250 µL capacity;
  - IonPAc AS7 separation column and IonPAc AG7 pre-column from Dionex;
  - Eluent bottles;
  - Pressurized module for introducing the derivatization reagent;
  - Three-way colorimetric reaction chamber and reaction loop;
  - UV-visible spectrophotometric detector;
  - Autosampler and vials;
  - Data acquisition system;
- pH paper, for measuring different levels (pH 8 and pH 2 and below);
- Mechanical stirrer with support for cassette, for example an Eberbach shaker;
- Analytical balance of appropriate precision.

5. REAGENTS

This section presents a list of common and necessary reagents for both extraction methods for inorganic chromium VI compounds. The specific reagents are identified in each of the extraction procedures.
NOTE – The reagents used in the preparation of solutions must be at least of analytical quality. The chromium VI concentration in the reagents and mineral acids must be negligible compared to the lowest concentration to be determined.

- Water, with resistivity greater than 18 MΩ-cm (at 25°C) for all the sample preparations and dilutions (CAS 7732-18-5);
- 1,5-diphenyl carbohydrazide $(C_6H_5\text{-}NH\text{-}NH)_2CO$, mass fraction of DPC> 98% (CAS No. 140-22-7);
- Methanol (CH_3OH), HPLC quality (CAS No. 67-56-1);
- Sulphuric acid (H_2SO_4), concentrated, mass fraction ~ 98% (CAS No. 7664-93-9);
  WARNING - Concentrated sulphuric acid is corrosive and causes burns. Avoid all exposure by contact with the skin or eyes. Use personal protective equipment (including appropriate gloves, face mask or safety glasses, etc.) for all work with concentrated or dilute sulphuric acid. Take precautions when diluting sulphuric acid with water because this process is extremely exothermic. Do not add water to sulphuric acid because this operation produces violent reactions. All work with reagents must be carried out in a hood.
- Ammonium sulphate $(NH_4)_2SO_4$, mass fraction of ammonium sulphate > 99,5% (CAS No. 7783-20-2);
- Ammonium hydroxide solution (NH_4OH), concentrated, mass fraction of ammonia ~ 29% (NH_3) (CAS No. 1336-21-6);
  WARNING – Concentrated ammonium hydroxide is irritating to the respiratory system and causes burns. Avoid all exposure by contact with the skin or eyes, or by inhalation of vapours. Use appropriate personal protective equipment (including appropriate gloves, face mask, or safety glasses, etc.) for all work with a concentrated ammonium hydroxide solution. All work with reagents must be carried out in a hood.
- Nitric acid (HNO_3), concentrated, mass fraction ~ 70% (CAS No. 7697-37-2);
  WARNING - Concentrated nitric acid is corrosive and an oxidizing agent and nitric acid fumes are irritating. Avoid all exposure by contact with the skin or eyes, or by inhalation of fumes. Use personal protective equipment (including appropriate gloves, face mask or safety glasses, etc.) for all work with concentrated or dilute nitric acid. All work with reagents must be carried out in a hood.
- Potassium chromate (K_2CrO_4), mass fraction of potassium chromate > 99,9% (CAS No. 7789-00-6), for the preparation of standard solutions for the calibration curve;
  NOTE – Ideally, 2 sources of chromium VI are necessary; the first can be used in the preparation of standards to establish the calibration curve, and the second, in the preparation of control solutions (calibration, minimum reported value, and quality control on filter). The 2 sources of chromium VI should come from different manufacturers, otherwise from different lots, and as a last resort, from different intermediate solutions. Also, the source used for the preparation of control solutions should have a certified concentration and be traceable to national standards.
- Commercial chromium VI solution, for example certified at 1000 µg/mL, for preparing the control solutions (calibration, minimum reported value and the quality controls on filter).
  NOTE – The concentration of some commercial solutions is expressed in µg/mL of chromates $(CrO_4)^{-2}$ rather than in µg/mL of chromium VI. The analyst must take this into account during the calculations as well as the certified concentration of the solution used for preparing the intermediate solutions.

6. SAMPLING

Airborne inorganic chromium VI compounds are sampled using a 25mm cassette containing a vinyl/acrylic copolymer membrane with a porosity of 0,8µm on a plastic support and a sampling pump whose flow rate has been previously adjusted. For each series of samples, a blank cassette containing a membrane from the same lot must be provided. This blank must be treated in the same way as the cassettes used for sampling for everything relating to storage and transportation towards the sampling point, but no air is passed through this cassette. The samples can be stored at ambient temperature. The sampling parameters recommended for chromium VI are described in the following table; however, the sampling volume can be changed if low or high concentrations of airborne particles are expected. For example, the sampling period should be shorter to avoid overloading the filter.

Flow rate	1,5 to 4 litres/minute
Volume	360 litres

The sampling time must also be long enough to allow chromium VI to be determined at significant levels for industrial hygiene. The minimum sampling time necessary for the quantity of chromium VI sampled to be greater than the analytical method's minimum reported value for an estimated average time-weighted exposure value is calculated using the following equation:

$$T_{min} = MRV / X * TWAEV * Q$$

where

T_{min}	=	Minimum sampling time in minutes
MRV	=	Minimum reported value of the analytical method, in micrograms
X	=	Estimated time-weighted average exposure value, as a decimal fraction
TWAEV	=	Time-weighted average exposure value, in mg/m³
Q	=	Recommended flow rate for sampling, in litres per minute

7. ANALYTICAL PROTOCOL

7.1 General solutions

This section presents a list of solutions to be prepared that are common and necessary for both extraction methods for inorganic chromium VI compounds. The more specific solutions are identified in each of the extraction procedures.

NOTE – The volumes prepared for the solutions are for information purposes only.

- Eluent solutions

  - Stock eluent solution $(NH_4)_2SO_4$ 2,0 mol/L / NH_4OH 1,0 mol/L

    Weigh approximately 264 g of ammonium sulphate and dissolve it in approximately 500 mL of water. Transfer the solution quantitatively to a 1 litre volumetric flask, add 65 mL of concentrated ammonium hydroxide and then mix. Fill to the mark with water, mix, and then pour into a storage container. The shelf life for this solution is 12 months at ambient temperature.

- Working eluent solution $(NH_4)_2SO_4$ 0,2 mol/L / NH_4OH 0,1 mol/L

  Pour 200 mL of the concentrated eluent solution into a 2-L volumetric flask. Fill to the mark with water, mix, and then pour into a storage container. The shelf life for this solution is 1 month at ambient temperature.

- Solution of 1,5-diphenyl carbohydrazide (DPC) reagent

Pour approximately 500 mL of water into a 1-litre volumetric flask. Slowly and carefully add 25 mL of concentrated sulphuric acid, mix, and allow cooling. Weigh approximately 0,5 g of 1,5-diphenyl carbohydrazide and dissolve in 100 mL of methanol, transfer the obtained solution quantitatively to the volumetric flask containing the sulphuric acid and then fill to the mark with water. Mix, and then pour into a storage container. The shelf life for this reagent is 7 days at ambient temperature.

- Solutions of chromium VI

  - Chromium VI stock solution at 1000 mg/L

    Weigh precisely approximately 375 mg of potassium chromate (K_2CrO_4) and dissolve in a minimum amount of water. Transfer the solution quantitatively to a 100-mL volumetric flask and then fill to the mark with water. Mix, and then pour into a storage container. The shelf life for this solution is 6 months at ambient temperature.

  - Intermediate chromium VI solution at 100 mg/L

    Pipette 1 mL of the chromium VI stock solution of 1000 mg/L (prepared previously) into a 10-mL volumetric flask containing approximately 5 mL of water, and then fill to the mark with water. Mix, and then pour into a storage container. The shelf life for this solution is 3 months at ambient temperature.

  - Intermediate chromium VI solution at 10 mg/L

    Pipette 100 µL of the chromium VI stock solution of 1000 mg/L (prepared previously) into a 10-mL volumetric flask containing approximately 5 mL of water, and then fill to the mark with water. Mix, and then pour into a storage container. The shelf life for this solution is 3 months at ambient temperature.

  - Intermediate chromium VI solution at 90 mg/L

    Pipette 900 µL of a commercial chromium VI solution at 1000 mg/L into a 10-mL volumetric flask containing approximately 5 mL of water, and then fill to the mark with water. Mix, and then pour into a storage container. The shelf life for this solution is 3 months at ambient temperature.

  - Intermediate chromium VI solution at 9 mg/L

    Pipette 1 mL of the intermediate chromium VI solution at 90 mg/L into a 10-mL volumetric flask containing approximately 5 mL of water, and then fill to the mark with water. Mix, and then pour into a storage container. The shelf life for this solution is 3 months at ambient temperature.

7.2 Determination of water-soluble inorganic chromium VI compounds

7.2.1 Specific materials

- 25mm polypropylene (PP) sampling cassettes, 3 pieces, goblet style (SKC #225-8585) with a vinyl/acrylic copolymer filter 25mm 0,8µm (Pall DM Metricel #64501) impregnated with 0,5N NaOH held by a plastic support pad (SKC #225-2901);
- 25mm polypropylene (PP) sampling cassettes, 3 pieces, goblet style (SKC #225-8585) with a vinyl/acrylic copolymer filter 25mm 0,8µm (Pall DM Metricel #64501) held by a plastic support pad (SKC #225-2901).

7.2.2 Specific solutions

- Extraction solutions
  - Stock extraction solution $(NH_4)_2SO_4$ 0,5 mol/L / NH_4OH 0,5 mol/L

    Weigh approximately 66 g of ammonium sulphate and dissolve in approximately 500 mL of water. Transfer the solution quantitatively into a 1-litre volumetric flask, add 34 mL of concentrated ammonium hydroxide and then mix. Fill to the mark with water, mix, and then pour into a storage container. The shelf life for this solution is 12 months at ambient temperature.

  - Working extraction solution $(NH_4)_2SO_4$ 0,05 mol/L / NH_4OH 0,05 mol/L at pH 8

    Pour 100 mL of concentrated extraction solution into a 1-litre volumetric flask, and then fill to the mark with water. Mix, and then pour into a storage container. The shelf life for this solution is 3 months at ambient temperature.
    NOTE – Check and adjust the pH, if necessary, with a few drops of concentrated NH_4OH or H_2SO_4.

- Standard chromium VI solutions for the calibration curve

  Pipette, according to the following table, the appropriate volumes of the intermediate chromium VI solutions (section 7.1) into 100-mL volumetric flasks containing approximately 25 mL of the working extraction solution, fill to the mark with this same solution and mix. The shelf life for these solutions is 3 months at ambient temperature.

	Final volume (mL)	Solution at 10 mg/L (µL)	Solution at 100 mg/L (µL)	Final concentration (µg/mL)	Final concentration (µg/10 mL)
S0	100	-	-	0	0
S1	100	100	-	0,01	0,1
S2	100	-	50	0,05	0,5
S3	100	-	100	0,10	1,0
S4	100	-	300	0,30	3,0
S5	100	-	500	0,50	5,0

- Chromium VI solutions for the calibration check (ICV) and the minimum reported value (MRV)

  Pipette, according to the following table, the appropriate volumes of the intermediate chromium VI solutions (section 7.1) into 100-mL volumetric flasks containing approximately 25 mL of the working extraction solution, fill to the mark with this same solution and mix. The shelf life for these solutions is 3 months at ambient temperature.

	Final volume (mL)	Solution at 9 mg/L (µL)	Solution at 90 mg/L (µL)	Final concentration (µg/mL)	Final concentration (µg/10mL)
ICVH[1]	100	-	500	0,45	4,5
ICVL[2]	100	-	50	0,045	0,45
MRV	100	45	-	0,004	0,04

[1] High level; [2] Low level

7.2.3 Preparation of quality control samples on filter

NOTE – The preparation of control samples is identical for the 2 types of cassettes (impregnated filter or not impregnated filter).

- Remove the caps on the air inlet side of the cassettes;
- Add 50 µL of the intermediate chromium VI solution at 90 mg/L to each of the cassettes and then replace the caps.
  NOTE – The quantity of water-soluble chromium VI on the filter (4,5 µg/filter) represents 25% of the TWA for a sampling volume of 360 litres and a final extraction volume of 10 mL.

7.2.4 Preparation of samples

NOTE – The same procedure must be followed in the preparation of the samples, the quality controls on filter, and the reagent blanks. Note in the laboratory records all pertinent remarks about the condition of the sample and/or observations during the extraction procedure. Rinse each used connector of the vacuum filtration assembly three (3) times with water between samples.

- Remove the caps on the air inlet side of the cassettes;
  IMPORTANT – Make sure that the cap on the air outlet side is in place and inserted tightly.
- Using a pipette, add 5 mL of working extraction solution to each cassette, and then firmly replace the cap;
- Shake the cassettes mechanically (approximately 225 oscillations/min) for one hour so that the extraction solution comes in contact with all inside walls of the cassette;
- Remove the caps on the air outlet side of each cassette and connect the cassette to the support connectors of the Visiprep support, taking care to place a test tube underneath, identified with the corresponding sample number;
- Again remove the caps on the air inlet side, and then very gently turn on the vacuum to recover the solution in the corresponding test tube;
  NOTE – Too strong a vacuum may cause the sample to splash.

- Shut off the vacuum, add 3 mL of dilute extraction solution to each cassette, and then let them sit for a few minutes;
- Turn on the vacuum again and then recover the solution in the same test tube;
- Shut off the vacuum and remove the test tubes from the system;
- Fill to the 10 mL mark with the working extraction solution, and then cap each test tube until analysis.

  NOTE – For the determination of only water-soluble inorganic chromium VI compounds, go to section 7.4. After the final extraction, it is important to rinse each connector of the Visiprep system three (3) times with the extraction solution and then with water. Dry the system, making sure that no water remains in the connector tubes.
  IMPORTANT – If water-insoluble inorganic chromium VI compounds on non-impregnated filter also have to be determined, keep all the cassettes for later treatment.

7.3 Determination of water-insoluble inorganic chromium VI compounds

7.3.1 Specific materials

- 250mL beakers, for example made of polytetrafluoroethylene (PTFE) or other inert material, for sample preparation;
- Tweezers with non-metallic tips, to remove the filter from the cassette;
- Ultrasonic bath;
- Waxed paper.

7.3.2 Specific reagents

- Sodium carbonate (Na_2CO_3), anhydrous, mass fraction of sodium carbonate >99,9% (CAS No. 471-34-1);
- Sodium hydroxide (NaOH), 10N, mass fraction > 99,5% (CAS No. 1310-73-2);
  WARNING — Sodium hydroxide is irritating to the respiratory system and causes burns. Avoid all exposure by contact with the skin or eyes, or by inhalation of dust. Use appropriate personal protective equipment (including appropriate gloves, face mask or safety glasses, etc.) for all work with sodium hydroxide pellets or with a concentrated sodium hydroxide solution. All work with reagents must be carried out in a hood.
- Lead chromate ($PbCrO_4$), mass fraction of lead chromate > 99,5% (CAS No. 7758-97-6), for the preparation of quality control samples on filter.

7.3.3 Specific solutions

- Extraction solutions
  - Stock extraction solution (2% NaOH / 3% Na_2CO_3)

    Pour 50 mL of 10N sodium hydroxide into a 1-litre volumetric flask containing approximately 250 mL of water, and then add 30 g of sodium carbonate mix to ensure that the sodium carbonate is dissolved and allow cooling. Fill to the mark with water, mix, and then pour into a storage container. The shelf life for this solution is 12 months at ambient temperature.

- Working extraction solution (0,2% NaOH/ 0,3% Na_2CO_3)

  Pour 100 mL of concentrated extraction solution into a 1-litre volumetric flask containing approximately 500 mL of water, and then fill to the mark with water. Mix, and then pour into a storage container. The shelf life for this solution is 6 months at ambient temperature.

- Standard chromium VI solutions for the calibration curve

  Pipette, according to the following table, the appropriate volumes of the intermediate chromium VI solutions (section 7.1) into 100-mL volumetric flasks containing approximately 25 mL of the working extraction solution, fill to the mark with this same solution and mix. The shelf life for these solutions is 3 months at ambient temperature.

	Final volume (mL)	Solution at 10 mg/L (µL)	Solution at 100 mg/L (µL)	Final concentration (µg/mL)	Final concentration (µg/10 mL)
S0	100	-	-	0	0
S1	100	100	-	0,01	0,1
S2	100	-	50	0,05	0,5
S3	100	-	100	0,10	1,0
S4	100	-	300	0,30	3,0
S5	100	-	500	0,50	5,0

- Chromium VI solutions for the calibration check (ICV) and the minimum reported value (MRV)

  Pipette, according to the following table, the appropriate volumes of the intermediate chromium VI solutions (section 7.1) into 100-mL volumetric flasks containing approximately 25 mL of the working extraction solution, fill to the mark with this same solution and mix. The shelf life for these solutions is 3 months at ambient temperature.

	Final volume (mL)	Solution at 9 mg/L (µL)	Solution at 90 mg/L (µL)	Final concentration (µg/mL)	Final concentration (µg/10mL)
ICVH[1]	100	-	500	0,45	4,5
ICVL[2]	100	-	50	0,045	0,45
MRV	100	45	-	0,004	0,04

[1] High level; [2] Low level

7.3.4 Preparation of quality control samples on filter

- Weigh precisely approximately 100 µg of crushed PbCrO4 on a filter, and then place the filter in a beaker. Note the weight of the PbCrO4 and calculate the mass equivalent of chromium VI.
- Place a watch glass on the beaker and put aside until analysis.
  NOTE – The quantity of water-insoluble chromium VI on the filter (16 µg/filter) represents approximately 400% of the TWA for a sampling volume of 360 litres and a final extraction volume of 10 mL. The gravimetric factor is 0,1609.

7.3.5 Preparation of samples

NOTE – The same procedure must be followed in the preparation of the samples, the quality controls on filter, and the reagent blanks. Note in the laboratory records all pertinent remarks about the condition of the samples and/or observations during the extraction procedure.

- First extract the water-soluble inorganic chromium VI compounds according to step 7.2.5 and, if necessary, keep all the collected solutions for later treatment;
- Open the cassette, recover and put the upper part (air inlet) of the cassette aside;
- Carefully recover the filter from each cassette using plastic tweezers and then transfer it, sample face down, into the beaker identified with the corresponding sample number;
  NOTE – If there is loss of dust during transfer to the extraction beaker, an appropriate note is added to the laboratory records in order to document this observation in writing in the analytical report.
- Rinse the upper part of the cassette with 5 mL of dilute extraction solution above the corresponding beaker in order to recover any remaining particles;
- Place a watch glass on each beaker and then seal with waxed paper;
- Place the beakers in the ultrasonic bath for 1 hour;
- Recover the solution from each beaker in a test tube identified with the corresponding sample number by rinsing three (3) times the beaker quantitatively with the dilute extraction solution;
- Fill to the 10-mL mark with the working extraction solution and then cap the test tube until analysis.
  NOTE – After the final extraction, it is important to rinse each connector of the vacuum filtration assembly three (3) times with the extraction solution and then with water. Dry the system, making sure that no water remains in the connector tubes.

7.4 Calibration

- Calibrate the ion chromatograph according to the manufacturer's recommendations and the analytical method. The most important parameters are identified in the following table:

Eluent flow rate	1,5 mL/min
Reagent (DPC) flow rate	~ 0,5 mL/min
Pressure in the DPC regulator	~ 40 psi
UV-Visible detector	AU*min units
Wavelength	540 nm
Pump pressure	~ 2400 psi
Injection loop	250 µL
Retention time	~ 4,3 min
Analysis time	7 min
Calibration method	Linear regression (with 1/y weighting)
Ordinate at the origin	Ignore
Integration method	Peak area
Integration threshold (AU*min)	0,0005

- Start the chromatographic system and allow the baseline to stabilize for a minimum of one hour;
  NOTE – To ensure a quantitative reaction of the 1,5-diphenylcarbazide with the chromium VI, the pH of the mixture must be very acidic. If necessary, adjust the pH of the eluent to a value less than or equal to pH 2, by reducing the ratio between the eluent flow rate and the reagent flow rate or by increasing the concentration of sulphuric acid in the diphenylcarbazide reagent. Allow the system to stabilize for a period of at least 15 minutes if an adjustment of the pH was necessary. It is important that the ratio between the eluent flow rate and the reagent flow rate remain constant, that the total flow rate not exceed the detector's maximum flow rate, and that excess reagent be present. The ratio between the eluent flow rate and the reagent flow rate is generally in the order of 3/1.
- Inject a standard of identical concentration three (3) times to check the stability of the signal;
  NOTE – The relative standard deviation (RSD) of the results obtained must not vary by more than 5%; otherwise, allow the system to stabilize for a longer time.
- Mix, and then carefully transfer an aliquot of each standard solution into 5-mL vials identified with the corresponding sample number, and then close with the appropriate cap;
- Inject the different calibration solutions in increasing order of concentration in order to construct a calibration curve of at least five concentrations (the blank solution and four calibration solutions) and measure the absorbance of chromium VI, in "peak area" mode, for each calibration solution.

The calibration curve is calculated by the acquisition software by linear regression and is expressed in the form of the following equation:

$$S = m[\mathrm{CrVI}] + b$$

where:

S	=	Signal, in AU*min
m	=	Slope of the calibration curve
[Cr VI]	=	Chromium VI concentration, in µg/10 mL
b	=	Ordinate at the origin

NOTE – The coefficient of determination (r^2) must be greater than 0,990. Otherwise, one calibration point can be eliminated and the data reprocessed to obtain a coefficient above 0,990, but a minimum number of 4 calibration points must be respected, including the calibration blank.

7.5 Analysis

After the calibration curve has been produced, the calibration check samples, the minimum reported value, reagent blanks, quality control samples on filters and the samples are successively analyzed according to the proposed analytical sequence (section 7.5.2). The chromium VI concentration in the samples is then determined by comparing the peak area obtained for the sample and for the range of standard solutions.

NOTE – One standard solution is analyzed every 7 samples. If the relative standard deviation between two results for this same standard varies by more than ± 5%, the instrument must be recalibrated and the samples that were being analyzed when the change in sensitivity occurred must be reanalysed.

The chromium VI concentration determined in the sample must be in the analytical method's working range. If the sample's chromium VI concentration is greater than the highest concentration in the working range, the sample is appropriately diluted to match the matrix of the calibration solutions, and the analysis is repeated by taking the dilution factor into account in the calculations.

7.5.1 Quality control

Several types of controls are analyzed during the analytical sequence in order to check the calibration and the variation in sensitivity. Each control must comply with the criteria established for this control and any deviation must be documented and the appropriate action specified in the quality system must be taken.

- Initial Calibration Verification (ICV). These two (2) control samples are solutions analyzed just after the instrument is calibrated. Their concentrations are approximately 10% (ICVL) and 90% (ICVH) of the maximum on the calibration curve.
- Initial Blank Verification (IBV). The IBV control is the same solution as the calibration blank solution. It is analyzed after the 2 ICV controls, and the results must be comparable to the results obtained during the analysis of the calibration blank solution.
- Minimum Reported Value (MRV). This control sample is a solution analyzed after the calibration checks (ICV and IBV). This control verifies the instrument response at the analytical method's minimum reported value.
- Continuous Calibration Verification (CCV). This control sample is one of the standard solutions prepared for the calibration curve and is analyzed every 7 samples. Its concentration represents approximately the concentration at mid-point on the calibration curve.
- Continuing Calibration Blank (CCB). The CCB control is the same solution as the calibration blank solution and is analyzed after every CCV. The results of the CCB must be comparable to the results of the calibration blank solution.
- Laboratory Reagent Blank (LRB). This control sample is a solution that contains only the reagents. It undergoes all of a sample's preparation and analysis steps. It is used to verify whether the preparation steps result in contamination of the samples.
- Quality Control on filters (QC). These control samples are fortified filters with chromium VI (water-soluble or water-insoluble). They undergo all of a sample's preparation and analytical steps. Two (2) control samples at the same concentration are analyzed for each analytical sequence. The results are used to check the accuracy and precision of the analytical method.

7.5.2 Proposed analytical sequence

- Stabilization standard check (3X)
- Calibration Standards
- Controls ICVL, ICVH, IBV and MRV
- CCV and CCB
- Laboratory Reagent blank(s)
- Quality control on filter #1
- Quality control on filter #2
- 4 samples
- CCV and CCB
- 7 samples
- CCV and CCB
- 7 samples
- Etc.
- CCV and CCB
- MRV
- Water

8. CALCULATIONS

The chromium VI concentration of the air sample at ambient conditions is calculated using the following equation:

$$[\text{Cr VI}] = (([\text{Cr VI}]_1 \times V_1 \times F) - ([\text{Cr VI}]_0 \times V_0)) / V$$

where:

[Cr VI]	=	Chromium VI concentration in the sample (expressed as chromium), in mg/m^3
$[\text{Cr VI}]_0$	=	Chromium VI concentration in the solution blanks[1], in µg/10 mL
$[\text{Cr VI}]_1$	=	Chromium VI concentration in the sample, in µg/10 mL
V	=	Sampling volume, in litres (L)
V_0	=	Final volume of solution blanks, in millilitres (mL)
V_1	=	Final volume of the sample, in millilitres (mL)
F	=	Dilution factor (F=1 when there is no dilution)

[1]The chromium VI concentration in the solution blanks comes from the sum of the results obtained during the analysis of the reagent blanks and filter blanks. The concentration of the filter blanks is determined for each lot of impregnated filters and represents the average chromium VI concentration obtained from 10 samples subjected to the entire analytical procedure. The results for the samples are not corrected for the results obtained for the field blank samples. The results for the field blank samples are reported as total mass (µg).

9. VALIDATION PARAMETERS

9.1 Limit of detection, limit of quantification and minimum reported value

The method detection limit (MDL) represents the lowest concentration for a compound analyzed in a real matrix which, when it undergoes all the steps of a complete method including the chemical extractions and pre-treatment, produces a detectable signal with a defined reliability and that is statistically different from that produced by a "blank" under the same conditions. The MDL represents the concentration equivalent to 3 times the standard deviation obtained from 10 samples enriched with hexavalent chromium at very low concentration and subjected to the entire analytical procedure. The method quantification limit (MQL) represents the concentration equivalent to 10 times the standard deviation obtained with these same samples.

The minimum reported value (MRV) is the minimum amount of contaminant that is quantified in the IRSST laboratories. It takes into account one or more of the following aspects: the method's linearity under the experimental conditions used, the recovery efficiency, and the relevance of the determination at very low concentration levels.

INORGANIC CHROMIUM VI COMPOUNDS	TYPE OF FILTER	MDL (µg per filter)	MQL (µg per filter)	MRV (µg per filter)
Water-soluble [1]	impregnated	0,003	0,010	0,04
Water-soluble [2,4]	non-impregnated	0,003	0,009	0,04
Water-insoluble [3,4]	non-impregnated	0,004	0,012	0,04

[1] K_2CrO_4; [2] $CaCrO_4$ and K_2CrO_4; [3] $PbCrO_4$, $SrCrO_4$ and $ZnCrO_4$; [4] quadratic mean of the results

9.2 Reliability

Reliability corresponds to the closeness of agreement between the results obtained by applying the experimental process several times under well-determined conditions. Depending on the test's execution conditions, this characteristic is expressed in the form of replicability or repeatability for an analytical method. Reliability corresponds to the method's precision.

Replicability is determined from the individual results obtained from 24 samples subjected to the same analytical procedure (4 concentration levels, 6 samples per concentration level) in the same laboratory and under the following conditions: same analyst, same instrument, on the same day.

Repeatability is determined from the individual results obtained from 24 samples subjected to the same analytical procedure (4 concentration levels, 6 samples per concentration level) in the same laboratory and where at least one of the following aspects was different: the analyst, the instrument, and/or the day.

INORGANIC CHROMIUM VI COMPOUNDS	TYPE OF FILTER	REPLICABILITY (%)	REPEATABILITY (%)
Water-soluble [1]	impregnated with NaOH	0,9	0,7
Water-soluble [2,4]	non-impregnated	0,6	1,6
Water-insoluble [3, 4]	non-impregnated	0,7	1,3

[1] K_2CrO_4; [2] $CaCrO_4$ and K_2CrO_4; [3] $PbCrO_4$, $SrCrO_4$ and $ZnCrO_4$; [4] quadratic mean of the results

9.3 Accuracy

Accuracy corresponds to the closeness of agreement between the value certified by a recognized organization (or associated with a NIST traceable one) and the result obtained from 10 samples subjected to the entire analytical procedure. Accuracy is measured, at a given concentration level, in the method's working range. It is expressed in relation to the relative error.

INORGANIC CHROMIUM VI COMPOUNDS	TYPE OF FILTER	ACCURACY (%)
Water-soluble [1]	impregnated with NaOH	99,5
Water-soluble [2,4]	non-impregnated	96,5
Water-insoluble [3, 4]	non-impregnated	92,9

[1] K_2CrO_4; [2] $CaCrO_4$ and K_2CrO_4; [3] $PbCrO_4$, $SrCrO_4$ and $ZnCrO_4$; [4] quadratic mean of the results

9.4 Recovery

The recovery rate corresponds to the difference (in percentage) between the measured concentration of a fortified sample and the measured concentration of the same sample but unfortified, divided by the concentration of the added substance. This relationship takes into account the chemical change that occurred, if applicable. The following table contains the recovery percentages obtained for different water-soluble and water-insoluble inorganic chromium VI compounds.

CHROMIUM VI COMPOUNDS	RECOVERY (%)	N	CV (%)
Potassium chromate[1] [CAS #7789-00-6]	98,6	35	1,6
Potassium chromate[2] [CAS #7789-00-6]	95,6	35	2,9
Calcium chromate [CAS #13765-19-0]	101	35	1,4
Lead chromate [CAS #7758-97-6]	99,9	35	1,3
Strontium chromate [CAS #7789-06-2]	101	35	2,6
Zinc chromate [CAS #13530-65-9]	99,9	35	1,1

[1] on impregnated filter [2] on non-impregnated filter

9.5 Measurement uncertainty

The uncertainty of the method's analytical measurement (CV_A) is calculated using the individual results obtained from 35 samples (5 concentration levels, 7 samples per level) subjected to the entire analytical procedure. The uncertainty of the analytical measurement is equal to the square root of the sum of the squares of the CVs divided by the number of concentrations.
The expanded measurement uncertainty (CV_E) for the entire determination and sampling was calculated by taking into account a coefficient of variation estimated at 5% for the sampling, and a 95% probability threshold.

INORGANIC CHROMIUM VI COMPOUNDS	TYPE OF FILTER	CV_A (%)	CV_E (%)
Water-soluble [1]	impregnated	3,6	12,1
Water-soluble [2,4]	non-impregnated	2,6	11,1
Water-insoluble [3, 4]	non-impregnated	3,8	12,3

[1] K_2CrO_4; [2] $CaCrO_4$ and K_2CrO_4; [3] $PbCrO_4$, $SrCrO_4$ and $ZnCrO_4$; [4] quadratic mean of the results

10. REFERENCES

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