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Determination of metals in workplace air by inductively coupled plasma mass spectrometry (ICP-MS)

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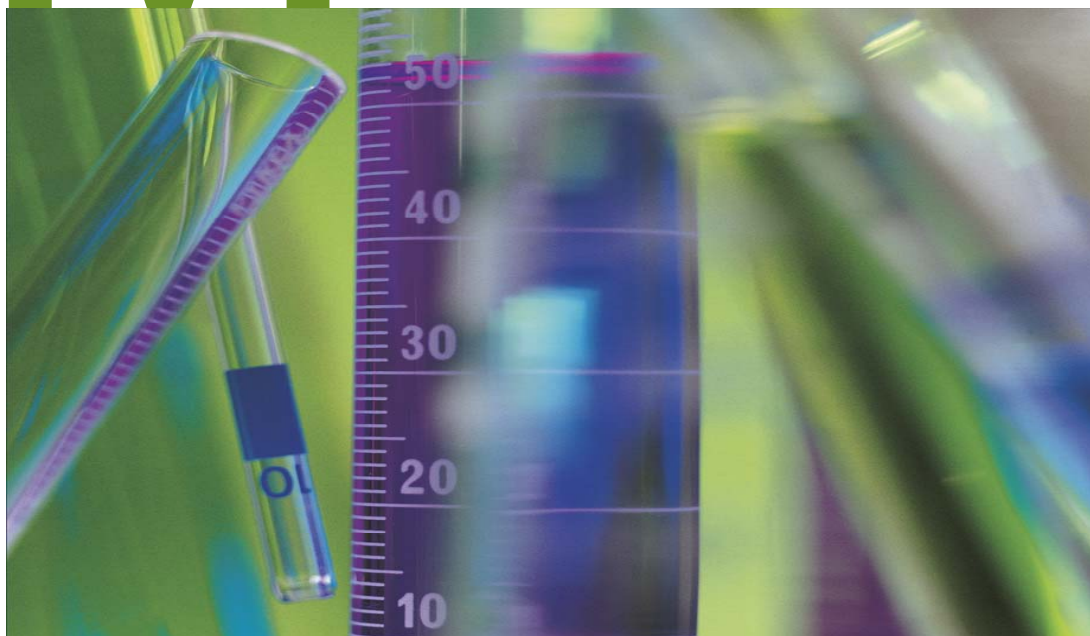
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Analytical Method

**Determination of metals in workplace air
by inductively coupled plasma
mass spectrometry (ICP-MS)**

ANALYTICAL METHOD 362



Applicability

This method applies to the determination of several metals and their compounds in workplace air.

Standard

See Regulation respecting occupational health and safety (ROHS).

Sampling system

MCE FILTER 0,8 μ m, 25 and 37mm.

Recommended sampling flow rate and volume

180L at 1,5 L/min.

Analytical technique

Inductively coupled plasma mass spectrometry (ICP-MS).

Minimum reported value (MRV)

See Appendix 1.

Working range

See Appendix 1.

Reliability

See Appendix 1.

Analytical uncertainty (CV_A et CV_E)

See Appendix 1.



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The results of the research work published
in this document have been peer-reviewed.

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Preamble

The aim of the [Act respecting occupational health and safety](#) in Québec is to eliminate, at source, hazards 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](#) (ROHS). 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 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 analysis 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%2FS2_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%2FS2_2_1%2FS2_1R19_01.htm
- ✓ *Sampling Guide for Air Contaminants in the Workplace*. Operations Division, IRSST, T-015 Technical Guide, Montréal, Québec, (mars 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, 2nd edition, 1993.
- ✓ American Industrial Hygiene Association (AIHA), organization that certifies the IRSST laboratory in the field of workplace chemical and microbiological contaminant analysis.

1. WORKING RANGE

This method applies to the determination of different metals present in particles suspended in the air, by means of inductively coupled plasma mass spectrometry (ICP-MS). The tests for method development were performed on a PerkinElmer Elan DRC II ICP-MS. The calibration range for each of the metals is within the limits presented in the table below.

| Elements | Isotope used | Lower limit (µg/L) | (mg/m ³) ¹ | Upper limit (µg/L) | (mg/m ³) ¹ |
|-------------------|--|-----------------------|-----------------------------------|-----------------------|-----------------------------------|
| Aluminium | ²⁷ Al | 100 | 0.006 | 2000 | 0.11 |
| Cadmium | ¹¹⁴ Cd | 0.5 | 0.00003 | 10 | 0.00060 |
| Chromium | ⁵² Cr | 10 | 0.0006 | 200 | 0.011 |
| Cobalt | ⁵⁹ Co | 0.4 | 0.00002 | 8 | 0.00044 |
| Copper | ⁶³ Cu | 4 | 0.0002 | 80 | 0.0044 |
| Iron | ⁵⁷ Fe | 100 | 0.006 | 2000 | 0.11 |
| Magnesium | ²⁶ Mg | 20 | 0.001 | 400 | 0.022 |
| Manganese | ⁵⁵ Mn | 10 | 0.0006 | 200 | 0.011 |
| Nickel | ⁶⁰ Ni | 20 | 0.001 | 400 | 0.022 |
| Lead ² | ²⁰⁶ Pb, ²⁰⁷ Pb & Pb ²⁰⁸ | 1 | 0.0001 | 20 | 0.0011 |
| Vanadium | ⁵¹ V | 1 | 0.0001 | 20 | 0.0011 |
| Zinc | ⁶⁶ Zn | 10 | 0.0006 | 200 | 0.011 |

¹ Concentration for a final volume of 10 mL and a sampling volume of 180 L

² The signals of the three isotopes are added, due to the natural variation in individual abundances

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

2. PRINCIPLE OF THE METHOD

In accordance with the parameters described in the [Sampling Guide for Air Contaminants in the Workplace](#), particles suspended in the air containing different metals and their compounds are collected by passing a volume of air through a mixed cellulose ester (MCE) filter. The collected filter and sample are then treated in such a manner as to dissolve the different metals and their compounds. The sample solution is then analyzed by ICP-MS. Since ICP-MS is a relative analysis technique, the proportionality factor between the response and the concentration of the element is determined by analyzing standard solutions.

3. INTERFERENCES

There are two types of interferences, spectral and non-spectral. The most common spectral interferences are polyatomic (or molecular) interferences produced by the combination of two or more atomic ions having the same nominal mass/charge ratio as the isotope of interest.

These ions are generally formed in the plasma or the interface system from vector gases or constituents of the sample.

Isobaric interferences are caused by isotopes of different elements that form singly or doubly charged ions with the same nominal mass/charge ratio.

Non-spectral interferences, generally called matrix effects, can originate from three different processes or locations: the nebulization process, the plasma, or the zone of the interface and the lens. This type of interference also includes plugging of the nebulizer, the injector tube of the torch and the cones (sampler and skimmer) due to high concentrations of dissolved salts.

The different strategies used in this analytical method to reduce or eliminate interferences are:

- Application of mathematical correction equations;
- Use of a reaction cell;
- Reduction of the water content of the plasma in order to reduce the level of all types of interferences due to oxides. This reduction is achieved by lowering the temperature of the spray chamber by 2°C to 5°C by Peltier effect;
- Addition of an internal standard to the calibration solutions and to the samples as well as matrix matching of the calibration and samples solutions; and
- Optimization of the analytical conditions, in order to maximize the ratio of the analytical signal to the interference signal (plasma power, flow rate of sampling vector gas, sample collection rate, distance between the torch and the top of the sampling cone, rinsing time between two solutions, etc.)

4. **MATERIAL**

NOTE 1 - It is recommended that PP (polypropylene) or PE (polyethylene) plasticware be used.

NOTE 2 – All reusable plasticware must be carefully washed before use and decontaminated by soaking in dilute nitric acid (for example: 10% HNO₃) for at least 12 hours and then rinsed several times with demineralized water.

NOTE 3 – All disposable plasticware must previously be subjected to a control to determine the presence of the different elements to be determined.

- Felt marker;
- Single-use impervious gloves (powder-free), for example made of nitrile, to prevent any possibility of hand contamination and contact with corrosive substances;
- Digestion beakers, 50 mL, made of Teflon, for dissolving the samples;
NOTE 4 – Beakers are previously decontaminated by reflux heating with concentrated HNO_3 at 120°C for 2 hours.
- Non-metallic tweezers, for removing the filters from the cassettes;
- Distributors for the acids;
- Stirring hot plate, thermostatically controlled, that can maintain a surface temperature of at least 200°C ;
NOTE 5 – The surface temperature may vary considerably, depending on the position on the hot plate. It may therefore be useful to characterize the hot plate's performances before it is used.
- Wash bottle;
- Piston stroke volumetric pipettes with disposable tips, for preparing calibration solutions, calibration control solutions, and for diluting sample solutions;
- Volumetric flasks of appropriate volumes with corresponding stoppers;
- Volumetric test tubes, single use, compatible with the autosampler;
- Dilution test tubes, single use, compatible with the autosampler;
- Syringes, polypropylene, 10 mL, with filter incorporating a membrane of porosity less than or equal to $0.8\mu\text{m}$, single use);
NOTE 6 – Since the digestion method does not always allow the sample to be completely dissolved, the undissolved material can be eliminated from the sample solution by filtration.
- Storage bottles with corresponding tops;
- Inductively coupled plasma mass spectrometer (PerkinElmer Elan DRC II), quadrupole type equipped with a reaction cell, platinum cones, all interfaced to a computerized system. Data acquisition and processing is done by ELAN software from PerkinElmer;
 - Three-channel peristaltic pump;
 - Black/black PVC tube (2 bridges, calibrated at 0.32 mL/min) for the carrier solution;
 - Orange/green PVC tube (2 bridges, calibrated at 0.1 mL/min) for the internal standard;
 - T mixing connection for the sample and internal standard;
 - Injection valve with 2 mL sampling loop;
 - Cyclonic spray chamber made of quartz cooled by Peltier effect with nebulizer made of Teflon™ PFA;
 - Injection tube, sapphire, 1.8 mm with quartz torch.
- ESI auto sampler with SC-2 Fast rinse station equipped with an 0.8 mm inert sampling probe;
- Argon and ammonium hydroxide of suitable purity;
- MCE membranes, 37 mm, for quality controls on filter.

5. REAGENTS

NOTE 7 – The concentration of the elements to be determined that are present in the reagents, the water and the acids must ideally be negligible compared to the lowest concentration to be determined.

NOTE 8 – Use commercial solutions of certified concentration and guaranteeing traceability to national standards.

NOTE 9 – Commercial solutions used for preparing calibration control solutions and control samples on filter must ideally come from a different manufacturer than the one used for the calibration standards, or from a different lot or, ultimately, from a different intermediate solution.

- **Water** of resistivity equal to or greater than 18 MΩ-cm (at 25°C) and final filtration on 0.1μ for all sample preparations and dilutions (CAS 7732-18-5);
- **Nitric acid** (HNO₃) concentrated, for example from Fisher, TraceMetal grade (CAS No. 7697-37-2);
WARNING – Concentrated nitric acid is corrosive and an oxidant, and nitric acid vapours are irritants. Avoid all exposure by skin or eye contact, or by vapour inhalation. Use personal protective equipment (appropriate gloves, face shield or safety goggles, etc.) for any work with concentrated or dilute nitric acid.
- **Perchloric acid** (HClO₄) concentrated, for example from J.T. Baker, InstraAnalyzed grade (CAS No. 7601-90-3);
WARNING – Perchloric acid is corrosive and an oxidizer and its fumes are irritants. Avoid all exposure by skin and eye contact, or by inhalation of the fumes. Use appropriate personal protective equipment (including appropriate gloves, face shield or safety goggles, etc.) for any work with concentrated or dilute perchloric acid, and any dissolving with perchloric acid must be done under a hood with a purifier specially designed for use with perchloric acid.
- **Hydrochloric acid** (HCl) concentrated, for example from Fisher, Optima grade (CAS No. 7647-01-0);
WARNING – Concentrated hydrochloric acid is corrosive, and hydrochloric acid vapours are irritants. Avoid all exposure by skin or eye contact, or by inhalation of the vapours. Use appropriate personal protective equipment (for example gloves, face shield or safety goggles, etc.) for any work with concentrated or dilute hydrochloric acid. Handle open containers of concentrated hydrochloric acid in a hood. The vapour pressure of hydrochloric acid is high; as a result, pay attention to the pressure created in capped vials when preparing hydrochloric acid/water mixtures.
- **Hydrogen peroxide** (H₂O₂), for example from EMD, Supra quality (CAS No. 7722-84-1);
WARNING – Hydrogen peroxide is corrosive and an oxidant. Avoid all exposure by skin or eye contact. Use personal protective equipment (including appropriate gloves, face shield or safety goggles, etc.) for any work with hydrogen peroxide.
- **Multi-element commercial solution for instrument and mass optimization** (for example: SPEX Tuning Solution, Claritas quality at 10 mg/L). This solution contains Ba, Be, Ce, Co, In, Li, Mg, Pb, Rh, Ti, U and Y.
- **Multi-element commercial solution for the internal standard** (for example: SPEX Internal Standard Solution, Claritas quality at 10 mg/L). This solution contains Li⁶, Sc, Ge, Y, In, Tb and Bi.

- **Multi-element commercial solution "custom made" for the preparation of standard solutions** (for example: SPEX CertiPrep, Claritas quality of corresponding concentrations as needed for each element). This solution contains Al, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn;
- **Multi-element commercial solution "custom made" for the preparation of calibration control solutions and control samples on filter** (for example: SCP Science, PlasmaCal quality of corresponding concentrations as needed for each element). This solution contains Al, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, V and Zn;
- **Triton X-100**, for example from Sigma, Ultra quality (CAS No. 09002-93-1).

6. SAMPLING

The different elements and their compounds suspended in the air are collected using a cassette containing a mixed cellulose ester (MCE) membrane with a porosity of 0.8µm, and a sampling pump with a previously adjusted flow rate. For each series of samples, a control cassette containing a membrane from the same lot must be planned for. This control must be treated in the same way as the cassettes used for sampling for all aspects relating to storage and transport to the sampling point, but must not be used for sampling. The samples are stored at ambient temperature. The recommended sampling parameters are described below:

- Flow rate: 1.5 L/min
- Volume: 180 L

These parameters take into account the exposure standard, the sensitivity of the analytical method, and the capacity of the sampling system; however, the sampling volume can be modified to adapt to environmental constraints. When high concentrations or particles suspended in the air are expected, the sampling period should be shorter in order to avoid overloading the filter.

The sampling period must also be sufficiently long for determining the different elements at significant industrial hygiene levels. To calculate the minimum sampling time necessary for the sampled amount to exceed the minimum reported value for the analytical method for an estimated time weighted average exposure value, the following equation is used:

$$T_{\min} = MRV / VE \times TWA \times Q \quad [1]$$

where

| | |
|------------|--|
| T_{\min} | is the minimum sampling time, in minutes (min) |
| MRV | is the minimum reported value for the analytical method, in µg |
| VE | is the estimated weighted average exposure value, as a decimal fraction (for example, 0.1 for 10% of the standard) |
| TWA | is the time-weighted exposure value, in mg/m ³ |
| Q | is the recommended flow rate for sampling, in L/min |

7. ANALYTICAL PROTOCOL

7.1 Analytical solutions

NOTE 10 – The stability of the solutions depends on several factors, for example the concentration of the element, the test matrix, the type of storage container, and the storage conditions. Prepare fresh solutions every day or keep them for a maximum time determined from the results of stability experiments.

- **1% HNO₃ solution (v/v);**
- **3% HNO₃ solution (v/v);**
- **Mixed solution of concentrated HNO₃ and HClO₄ [4:1];**
- **Solution for optimizing the instrument at 1 µg/L in 1% HNO₃ (v/v);**
- **Solution for mass calibration at 10 µg/L in 1% HNO₃ (v/v);**
- **Internal standard solution at 200 µg/L in 1% HNO₃ (v/v);**
- **Intermediate concentration working solutions for the preparation of calibration solutions;**

Prepare, if necessary, one or more solutions at intermediate concentrations by introducing precisely by pipette the necessary volume of the multi-element stock solution into a graduated flask of suitable volume containing a quantity of 1% HNO₃ (v/v). Fill to approximately 90% of the volume of the flask with 1% HNO₃ (v/v), cap and then shake to mix. Allow to cool at ambient temperature, fill to the mark with this same acid solution e.g. 1% HNO₃ (v/v), cap and mix well.

- **Multi-element calibration solutions in 1% HNO₃ (v/v);**
From the multi-element working solutions at intermediate concentrations prepared for calibration, prepare a series of calibration solutions covering the range of concentrations of each of the elements in the analytical method by introducing precisely by pipette the appropriate volume into a graduated flask of suitable volume containing a quantity of 1% HNO₃ (v/v). Fill to approximately 90% of the volume of the flask with 1% HNO₃ (v/v), cap and then shake to mix. Allow to cool at ambient temperature, fill to the mark with this same acid solution e.g. 1% HNO₃ (v/v), cap and mix well. It is recommended that at least three calibration solutions be prepared. Also prepare a calibration blank solution.
- **Intermediate concentration working solutions for the preparation of calibration control and control on filter solutions;**

Prepare, if necessary, one or more intermediate concentration solutions by introducing precisely by pipette the necessary volume of the multi-element stock solution into a graduated flask of suitable volume containing a quantity of 1% HNO₃ (v/v). *The multi-element stock solution must ideally come from a different manufacturer than the one used for preparing the calibration solutions, or from a different lot from the same manufacturer or, ultimately, should be prepared separately.* Fill to approximately 90% of the volume of the flask with 1% HNO₃ (v/v), cap and then shake to mix. Allow to cool at ambient temperature, fill to the mark with this same acid solution e.g. 1% HNO₃ (v/v), cap and mix well.

- **Multi-element calibration control and control on filter solutions in 1% HNO₃ (v/v);**
Two calibration control solutions and one filter spiking solution are necessary (see section 7.5). From the multi-element working solutions at intermediate concentrations, prepare the solutions by introducing precisely by pipette the necessary volume into a graduated flask of suitable volume containing a quantity of 1% HNO₃ (v/v). Fill to approximately 90% of the volume of the flask with 1% HNO₃ (v/v), cap and shake to mix. Allow to cool at ambient temperature, fill to the mark with this same acid solution e.g. 1% HNO₃ (v/v), cap and mix well.
- **Stock solution of 1% Triton X-100 (v/v) in 1% HNO₃ (v/v);**
- **Rinsing solution of 0.001% Triton X-100 (v/v) in 3% HNO₃ (v/v).**

7.2 Preparation of samples

NOTE 11 – Samples must be prepared under a hood.

NOTE 12 – Single use nitrile gloves should be worn during preparation of the samples, in order to avoid any possibility of contamination by hands and to protect them against contact with toxic and corrosive substances.

NOTE 13 – Note in the laboratory records any relevant remark about the state of the sample and/or observed during solubilization of the sample.

- Open the cassettes and transfer each filter, using a pair of clean tweezers, into a digestion beaker numbered with the number of the corresponding sample. Follow the same procedure for the field blanks and quality controls on filter;
NOTE 14 – If there is a loss of dust during transfer into the digestion container, an appropriate note is added to the laboratory records in order to put this observation in writing, and the client is informed about it in the analytical report.
 - Rinse with 6 mL (3 x 2 mL) of the mixture of concentrated HNO₃ and HClO₄ (4:1), the inside surfaces of the cassette (inlet section), to carry any particles adhering to them into the corresponding beaker;
 - Let the beakers stand for a minimum of 30 minutes;
 - Place the beakers on a hot plate at 150°C, and then evaporate by shaking until approximately 1 mL of acid remains;
NOTE 15 – If the solution darkens as it evaporates, slowly add concentrated HNO₃ dropwise until the solution becomes colourless or slightly yellowish. **Attention:** splashes can occur if the concentrated HNO₃ is poured too quickly, leading to losses of sample.
 - Remove the beakers from the hot plate and allow the solutions to cool;
 - Slowly add 1 mL of H₂O₂ to each beaker and let stand for 5 minutes;
 - Place the beakers again on the plate and evaporate until approximately 1 mL remains;
 - Remove the beakers from the hot plate and allow the solutions to cool well;
 - Slowly add 5 mL of concentrated HCl by rinsing the inside of each beaker;
- NOTE 16 – This step produces a release of irritant vapours.

- Place the beakers again on the hot plate at 150°C and then evaporate to dryness by shaking;
NOTE 17 – Do not allow the residues to carbonize.
- Remove the beakers from the hot plate and allow them to cool;
- Carefully rinse the walls of each beaker with several mL of 1% HNO₃ v/v;
- Place the beakers again on the plate and heat for a few minutes while shaking to redissolve the residue;
- Transfer the contents to a graduated test tube. Rinse the beaker 3 times with a few mL of 1% HNO₃ by transferring quantitatively after each rinse;
- Place the plugs in the test tubes and allow to cool at ambient temperature;
- Fill the test tubes to 10 mL with 1% HNO₃, plug and then store for later analysis;

NOTE 18 – The digestion method does not always allow the sample to completely dissolve. The remaining undigested material is then eliminated from the sample solution by filtration. An appropriate note is added to the laboratory records in order to put this observation in writing, and the client is informed about it in the analytical report.

7.3 Verification of the ICP-MS performance criteria

Before activating the plasma, certain parts of the instrument should be visually checked: excessive deposits on the cones, cleanliness of the torch, and mainly the introduction tube and integrity of the tubing peristaltic pump. The cones should also be changed and/or cleaned when the deposits are considered excessive, when the sensitivity is insufficient, or when the level of polyatomic ions and/or doubly charge ions is too high.

The manufacturer's recommendations for turning on the instrument must be followed, for example, regarding compliance with the required laboratory environmental conditions, requirements relating to electrical power, to cooling water, to exhaust ventilation, warm-up time, etc.

Once the visual checks have been done, activate the plasma and allow the instrument to warm up for a minimum of 30 minutes before using it. The calibration blank solution should be aspirated into the plasma during the warm-up period in order to avoid changing the conditions of the plasma during the analysis.

Parameterize the instrument in accordance with the manufacturer's specifications for performance verification and begin the application. The performance results must be equal to or better than the manufacturer's; otherwise, the different parameters of the ICP-MS must be adjusted and the verification restarted. The instrument must be adjusted to reduce interferences (oxide formation, formation of doubly charged ions, for example) to a minimum and to obtain sufficient sensitivity.

The instrument's performances are checked daily, before sample analysis, by aspiration of a prescribed tuning solution of the elements. Mass calibration and alignment of the two detectors (linear response) must be done as often as required by the manufacturer or according to the instrument's performance history.

7.4 Calibration

The instrument is calibrated by measuring, in increasing order of concentration, the intensity of the different standards of known concentrations. Once the standards have been analyzed, the data acquisition software produces a calibration curve, of type $mx+b$, of the concentration of the element as the ordinate and the signal as the abscissa. Typically, one calibration blank solution and three standard solutions are analyzed to produce the calibration curve. Calibration with more than five solutions is rarely necessary. It is recommended that the signal originating from the calibration blank solution be subtracted from the other calibration solutions.

The correlation coefficient (r), which translates the adjustment of the estimates of the linear regression equation, should be greater than 0.995. If r is less than this value, the calibration standards should be reanalyzed or redone to reach this value. It may be possible to eliminate one calibration point and to treat the data again to obtain a correlation coefficient > 0.995 , but one should comply with the minimum number of 4 calibration points (the calibration blank solution and three standard solutions).

All the calibration solutions, control solutions, internal standard solution and samples are sent to the nebulizer by a peristaltic pump with several channels.

The internal standard solution is added and mixed with all the solutions before analysis using a T connection and the peristaltic pump. The mixture is then sent to the nebulizer. The sample/internal standard mixture ratio is 5 to 1.

Before and after each analysis, the system tubing is rinsed with a mixed solution of 0.001% Triton X-100 and 3% HNO_3 (v/v). The instrument's main analytical parameters are indicated in the tables below.

| PARAMETERS | VALUE |
|------------------------------------|----------------------|
| Plasma power (Watts) | 1200 |
| Argon flow rate (L/min) | 15 |
| Flow rate of auxiliary gas (L/min) | 1.2 |
| Gas flow to nebulizer (L/min) | ~ 0.9 |
| Acquisition mode | Peak hopping |
| Sweeps (per reading) | 10 |
| Readings (per replicate) | 1 |
| Replicates | 3 |
| Mode of analysis | Standard and DRC |
| Calibration | External calibration |
| Detector mode | Pulse |

| Isotope | Correction equations | Internal standard | Mode | Flow (mL) | Rpa ¹ | Rpq |
|-------------------|--|-------------------|---------------------|-----------|------------------|------|
| ²⁷ Al | | Sc | Standard | 0 | 0.015 | 0.25 |
| ¹¹⁴ Cd | -0.027250*Sn118 | In | Standard | 0 | 0 | 0.25 |
| ⁵² Cr | | Ge | Standard | 0 | 0 | 0.25 |
| ⁵⁹ Co | | In | DRC-NH ₃ | 0.4 | 0.046 | 0.6 |
| ⁶³ Cu | | Ge | Standard | 0 | 0 | 0.25 |
| ⁵⁷ Fe | | Ge | Standard | 0 | 0 | 0.25 |
| ²⁶ Mg | | Sc | Standard | 0 | 0 | 0.25 |
| ⁵⁵ Mn | | Ge | Standard | 0 | 0.0127 | 0.25 |
| ⁶⁰ Ni | | In | DRC-NH ₃ | 0.4 | 0 | 0.75 |
| ²⁰⁸ Pb | 1*Pb ²⁰⁶ +1*Pb ²⁰⁷ | Bi | Standard | 0 | 0 | 0.25 |
| ⁵¹ V | | In | DRC-NH ₃ | 0.4 | 0 | 0.6 |
| ⁶⁶ Zn | -0.035297*Ni ⁶⁰ | Ge | Standard | 0 | 0 | 0.25 |

¹ The Rpa value can vary in relation to system optimization. It is important to limit the count number of the last curve point to 2,000,000 cps so as not to saturate the detector in pulse mode.

7.5 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 meet the criteria established for this control, and any exceedence or deviation must be documented, and the appropriate actions planned by the quality system must be undertaken.

The commercial solution used for preparing the calibration control solutions, minimum reported value and quality control on filter must ideally come from a different manufacturer than the one used for preparing the calibration solutions, or from a different lot from the same manufacturer or, ultimately, from a different intermediate solution from the same manufacturer.

Initial calibration verification (ICV) solution. The calibration controls are solutions that are analyzed just after instrument calibration. Two solutions are recommended and their concentrations are approximately 25% (ICV-L) and 75% (ICV-H) of the concentration of the highest standard.

Initial calibration blank verification solution (IBV). The IBV control is the same solution as the calibration blank solution. It is analyzed after the two (2) ICV controls and the results must be comparable to the results obtained in the analysis of the calibration blank solution.

Minimum reported value (MRV). The MRV control is a control solution analyzed after the initial calibration controls. This control verifies the instrument's response at the analytical method's minimum reported value.

Calibration control solution (CCV). The CCV control is the same solution as the calibration solution representing approximately the concentration at the midpoint of the calibration curve. The CCV is analyzed sequentially every 10 samples.

Continuing calibration blank solution (CCB). The CCB control is the same solution as the calibration blank solution and is analyzed after each CCV. The results of the CCBs must be comparable to the results of the calibration blank solution.

Quality control on filter (QC). These control samples are filters spiked with the different elements to be determined. They are subjected to all of the preparation and analytical steps as a sample. Two control samples are digested and analyzed as samples in the analytical sequence. The results are used to estimate the accuracy of the analytical method and the replicability (precision) between the two controls.

The two filters are spiked with 50 µL of the control solution for filters. The mass (µg) of the different elements deposited on the filter represents approximately 50% of the value of the final calibration point.

Laboratory reagent blank (LRB). The LRB control is a sample solution that contains only the reagents. It is subjected to all the preparation and analytical steps as a sample. It is used to verify whether the preparation steps result in contamination of the samples. Three (3) reagent blanks are digested per analytical sequence.

7.6 Analysis

Once the calibration curve has been established, the reagent blanks, controls and samples are successively analyzed, and the concentration of the different elements present is determined by comparison with the calibration curve.

The concentration of the different elements determined in the sample must fall within the analytical method's working range. If the concentration in the sample is higher than the highest concentration in the working range, the sample is appropriately diluted to match the matrix and analyzed again while taking the dilution factor into account in the calculations.

Furthermore, if the concentration of an element greatly exceeds the concentration of the most concentrated sample, it becomes necessary to verify the elimination of the different elements in the tubing (memory effect) by analyzing the calibration blank solution. The result must be similar to the result obtained for the initial calibration blank solution. A longer rinsing time generally corrects this situation.

When the internal standard's signal varies by more than $\pm 25\%$ for a sample, it is important to verify whether dilution of this sample significantly affects the previous obtained result.

The analyses are performed according to the following proposed sequence:

| Sample | Type of sample |
|------------------------|---|
| 1% HNO ₃ | Rinsing of the injection loop (3X) |
| S0 | Calibration blank solution |
| S1 | Standard #1 |
| S2 | Standard #2 |
| S3 | Standard #3 |
| S4 | Standard #4 |
| S5 | Standard #5 |
| ICV-L (at 20% of S5) | Initial calibration verification solution |
| ICV-H (at 80% of S5) | Initial calibration verification solution |
| IBV | Initial blank verification |
| MRV | Control solution at the MRV |
| QC1 | Digested spiked filter |
| QC2 | Digested spiked filter |
| LRB #1 | Reagent blank #1 |
| LRB #2 | Reagent blank #2 |
| LRB #3 | Reagent blank #3 |
| 5 samples | |
| CCV | Continuing calibration verification |
| CCB | Continuing calibration blank |
| 10 samples | |
| CCV and CCB | Continuing calibration controls |
| S0 to S5 | Calibration blank and standards #1 to #5 |
| ICV-L, ICV-H, IBV, VMR | Initial calibration controls |
| 10 samples | |
| CCV and CCB | Continuing calibration controls |
| 10 samples | |
| CCV and CCB | Continuing calibration controls |
| S0 to S5 | Calibration blank and standards #1 to #5 |
| ICV-L, ICV-H, IBV, VMR | Initial calibration controls |
| 10 samples | |
| CCV and CCB | Continuing calibration controls |
| 10 samples | |
| CCV and CCB | Continuing calibration controls |
| Etc. | |
| MRV | Control solution at the MRV |
| CCV and CCB | Continuing calibration controls |
| 1% HNO ₃ | Rinsing of the injection loop (3X) |

8. CALCULATIONS

Calculation of the concentration of the different elements in the air at ambient conditions is done using the following equation:

$$C = [(C_1 \times V_1 \times F) - (C_0 \times V_0)] / V_e$$

| | | |
|-------|----------------|---|
| Where | C | is the calculated concentration of the element in the sample, in mg/m ³ |
| | C ₁ | is the concentration of the element in the sample, in µg/L |
| | V ₁ | is the final volume of the sample, in litres (L) |
| | F | is the dilution factor (F=1 for no dilution) |
| | C ₀ | is the average concentration of the element in the digestion blanks ¹ (reagent blanks and/or filters), in µg/L |
| | V ₀ | is the final volume of the sample, in litres (L) |
| | V _e | is the sampling volume, in litres (L) |

¹ The results of the digestion blanks are results originating from laboratory reagent blank or filter blanks obtained by following the same analytical process as the sample. The results obtained for the samples are not corrected for the results of the field blanks. The results of the field blanks are reported as total mass (µg).

9. PERFORMANCE PARAMETERS

9.1 Limit of detection, limit of quantification and minimum reported value (MRV)

The method detection limit (MDL) and quantification limit (MQL) were evaluated (n=10) for a final volume of 10 mL and are reported in Appendix 1. The minimum reported value (MRV) is the minimum amount of a contaminant that is quantified in the IRSST laboratory. The MRV is greater than or equal to the MDL. It takes into account one or more of the following aspects: linearity of the method under the experimental conditions used, the recovery efficiency, and the relevance of the determination at low concentration levels.

9.2 Recovery

The dissolution procedure was evaluated by subjecting a series of spiked membranes (n=28, 4 concentration levels, 7 membranes per level) to the entire analytical procedure with a soluble form of the different elements in the method. Appendix 1 contains the different recovery percentages obtained for each of these elements.

9.3 Reliability

The replicability and repeatability values were determined in the laboratory from the 44 spiked membranes subjected to the entire analytical procedure (4 concentration levels, 11 membranes per level). These values represent the **precision** of the method.

9.4 Accuracy

The accuracy of the analytical method was evaluated ($n=10$) for each of the elements in the analytical method (see Appendix 1). Accuracy is also verified with each series of analyses by means of a membrane spiked with different metals. The results obtained are compiled in the context of the intra-laboratory quality control.

9.5 Measurement uncertainty

Analytical measurement uncertainty was calculated with the results obtained from 28 spiked membranes (4 concentration levels, 7 membranes per level) subjected to the entire analytical procedure. This value corresponds to the analytical method's coefficient of variation (CV_A) (see Appendix 1).

Also, the expanded measurement uncertainty (CV_E) for the entire determination and sampling was calculated by taking into account a CV estimated at 5% for the sampling, and a probability threshold of 95%.

10. REFERENCES

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9. EPA, *Test Method for Evaluating Solid Waste, Physical/Chemical Methods*, Method 200.8.
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Appendix 1 – Performance parameters

| | MDL | SQL | MRV ¹ | Replicability | Repeatability | Accuracy | Recovery | CV _a | CV _E |
|-----------|-------|-------|------------------|---------------|---------------|----------|----------|-----------------|-----------------|
| | µg/L | µg/L | µg | % | % | % | % | % | % |
| Al | 7.8 | 26.1 | 10 | 1.5 | 2.7 | 94.6 | 97.7 | 3.8 | 12.4 |
| Cd | 0.015 | 0.051 | 0.05 | 0.72 | 0.77 | 98.7 | 100.7 | 1.6 | 10.3 |
| Co | 0.009 | 0.030 | 0.04 | 0.61 | 1.1 | 99.0 | 102.1 | 0.94 | 10.0 |
| Cr | 0.38 | 1.3 | 1 | 1.5 | 3.0 | 100 | 96.6 | 3.2 | 11.7 |
| Cu | 0.26 | 0.88 | 0.4 | 1.8 | 2.6 | 98.2 | 99.2 | 4.2 | 12.8 |
| Fe | 3.3 | 11.1 | 10 | 1.0 | 1.3 | 99.3 | 102.6 | 2.3 | 10.8 |
| Mg | 0.84 | 2.8 | 2 | 1.1 | 2.3 | 98.5 | 100.9 | 2.6 | 11.0 |
| Mn | 0.14 | 0.46 | 1 | 1.9 | 2.4 | 98.4 | 96.6 | 4.1 | 12.7 |
| Ni | 0.13 | 0.43 | 2 | 0.73 | 2.5 | 93.5 | 98.2 | 1.8 | 10.4 |
| Pb | 0.27 | 0.89 | 0.1 | 2.1 | 2.7 | 98.5 | 101.5 | 6.0 | 15.3 |
| V | 0.005 | 0.016 | 0.1 | 0.88 | 3.0 | 94.0 | 95.6 | 2.2 | 10.7 |
| Zn | 0.88 | 2.9 | 1 | 1.9 | 2.8 | 95.3 | 100.2 | 4.9 | 13.8 |

¹ Minimum reported value, it takes into account the final volume of 10 mL and the 1:10 dilution of the samples during the analysis.