

Analytical Method

Determination of airborne metal concentrations by ICP-MS – Sampling using Solu-Sert™ filter capsules

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**ANALYTICAL
METHOD**

MA-394A



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SUBSTANCES	CAS No.	STANDARD ¹ (TWAEV ²)
Aluminum, welding fumes	7429-90-5	5 mg.m ⁻³
Arsenic, elemental and inorganic compounds	7440-38-2	0.1 mg.m ⁻³
Cadmium, elemental and compounds	7440-43-9	0.025 mg.m ⁻³
Chromium, metal	7440-47-3	0.5 mg.m ⁻³
Cobalt, elemental and inorganic compounds	7440-48-4	0.02 mg.m ⁻³
Copper, fumes	7440-50-8	0.2 mg.m ⁻³
Iron(III) oxide, fumes and dust	1309-37-1	5 mg.m ⁻³
Magnesium oxide, fumes	1309-48-4	10 mg.m ⁻³
Manganese, fumes, dust and compounds	7439-96-5	0.2 mg.m ⁻³
Nickel, metal	7440-02-0	1 mg.m ⁻³
Lead and its compounds in solution	7439-92-1	0.5 mg.m ⁻³
Vanadium(V) oxide, fumes and respirable dust	1314-62-1	0.05 mg.m ⁻³
Zinc chloride, fumes	7646-85-7	1 mg.m ⁻³

¹ Quebec's regulation respecting occupational health and safety (*"Règlement sur la santé et la sécurité du Travail du Québec"*)

² Time-weighted average exposure value

APPLICABILITY

This method applies to all metal compounds and metal oxides that can be put into a solution by acid digestion.

Ranges:

SUBSTANCE	RANGE	SUBSTANCE	RANGE
ALUMINUM	0.028 to 11,1 mg.m ⁻³	MAGNESIUM	0.056 to 2,2 mg. m ⁻³
ARSENIC	0.00028 to 0,017 mg.m ⁻³	MANGANESE	0.00056 to 1,1 mg.m ⁻³
CADMIUM	0.00014 to 0,056 mg.m ⁻³	NICKEL	0.0011 to 2,2 mg.m ⁻³
CHROMIUM	0.0056 to 1,1 mg.m ⁻³	LEAD	0.00056 to 0,11 mg.m ⁻³
COBALT	0.00022 to 0,044 mg.m ⁻³	VANADIUM	0.00056 to 0,11 mg.m ⁻³
COPPER	0.0022 to 0,44 mg.m ⁻³	ZINC	0.0056 to 1,1 mg.m ⁻³
IRON	0.028 to 11,1 mg.m ⁻³		

N.B.: These values are based on a recommended sampling volume of 180 liters, a dissolution in a volume of 10 mL, and 1/10 dilution of the sample.

Coefficient of determination (r^2) > 0.9980 or Correlation coefficient r > 0.999

LIMITATIONS AND INTERFERENCES

- The concentrations obtained depend on the method's capacity to solubilize the metals present in the samples.
- There are two types of interferences for this method: spectral and non-spectral.
 - Non-spectral interferences, or matrix effects, originate in the matrix composition and result in the physical suppression of the analyte signal. This occurs when the matrix has too much dissolved salt or acid. The matrix effect can be reduced or eliminated by using an internal standard and/or diluting the sample if possible.
 - There are two types of spectral interference: isobaric and polyatomic. Isobaric interferences are avoided through the selection of isotopes. Polyatomic interferences are reduced or eliminated through the use of a collision/reaction cell in collision mode.

SAMPLING

1) Sampling system

Media	Solu-Sert™ 25 mm and 37 mm (0.8 µm MCE filter membrane encapsulated in a cellulose shell)
Device	2-piece polypropylene cassette with cellulose support pad

Notes : A control sample containing a filter from the same lot number must be set aside. See reference [1] for the frequency and number of control samples.

Due to the hygroscopic properties of cellulose, Solu-Sert™ filters are not recommended for gravimetric analysis.

2) Recommended sampling conditions

Flow : 1.5 L.min⁻¹ (ajustable from 1,5 to 4 L.min⁻¹)

Sampling time : 120 min

Sampling volume : 180 liters (L)

3) Tested and validated conservation time

Stable at ambient temperature

4) Storage

At ambient temperature

Maximum storage time : Not determined

5) Details

Remove the caps from the cassette and connect the upper part (red cap) to the pump through a flexible tube.

Perform the sampling according to the recommended flow and sampling time.

After sampling, put the caps back on the cassette and package it for shipping.

For more information on sampling, see the *Sampling Guide for Air Contaminants in the Workplace* [1].

REAGENTS AND STANDARDS

- Nitric acid, TraceMetal™ grade (CAS 7697-37-2)
- Perchloric acid, TraceMetal™ grade (CAS 7601-90-3)
- Hydrochloric acid, TraceMetal™ grade (CAS 7647-01-0)
- Hydrogen peroxide, Suprapur® (CAS 7722-84-1)
- Multi-element internal standards commercial solution
- Multi-element commercial solution adjusted to calibration curve concentrations
- Multi-element commercial solutions adjusted to Quality Control standards concentrations
- Argon (purity > 99.998%), helium (purity > 99.9999%)

EQUIPMENT

- Filter tongs with corrosion-resistant tips
- 50-mL Teflon digestion beakers
- Leakproof graduated flasks of appropriate volume for the preparation of standard or control solutions
- 13 mL and 15 mL single-use graduated test tubes
- Eppendorf pipette with Combitip for the addition of concentrated acids
- Centrifuge with accessories for 15-mL test tubes
- Electronic pipettes with disposable tips
- Stirring hot plate
- ESI SC-4 DX sampler with prepFAST S400V autodilution system
- Inductively coupled plasma mass spectrometer (ICP-MS), Perkin Elmer Nexion 350D

Comments:

- All Teflon beakers used to digest samples must be subjected to a decontamination cycle including a concentrated nitric acid bath.
- Aqueous solutions of concentrated perchloric acid are highly oxidizing. They can react explosively with many products such as alcohols, glycols, ketones, ethers, glycerol, hypophosphites (phosphinates), sulfoxides, steel, bismuth, antimony, etc.
- Dehydrating agents such as sulfuric acid, diphosphorous pentoxide and acetic anhydride cause the formation of dichlorine heptoxide (perchloric acid anhydride), an explosive compound.

SAMPLE PREPARATION

Number of preparatory steps: 2

Step 1	Acid digestion of samples (Solu-Sert™ + collected particles). Samples are retrieved and filled to 10 mL with 1% nitric acid.
Step 2	Samples are systematically diluted 1/10 in a 1% nitric acid matrix.

Comments:

All quality control (QC) samples are subjected to the same procedure as the other samples. Prepare an appropriate number of blanks for estimating the contamination level of the reagents and of the digestion step.

ANALYTICAL CONDITIONS

Analytical technique	: Inductively coupled plasma mass spectrometer (ICP-MS)
Injector	: 1.5 mL injection loop
Pump	: Peristaltic pump set to 6 rpm
Auto-sampler	: ESI SC-4 DX
Auto-dilution system	: PrepFast S400V. Automated dilution of calibration curves and QC solutions. Auto-dilution of out-of-range samples.
Eluant	: 1% nitric acid
Isotope analyzed	: ²⁴ Mg, ²⁷ Al, ⁵¹ V, ⁵² Cr, ⁵⁵ Mn, ⁵⁷ Fe, ⁵⁹ Co, ⁶⁰ Ni, ⁶³ Cu, ⁶⁶ Zn, ⁷⁵ As, ¹¹¹ Cd, ^{206,207,208} Pb
Internal standard	: ⁴⁵ Sc, ⁸⁹ Y, ⁷² Ge, ¹⁵⁹ Tb
Analysis mode	: KED (Kinetic Energy Discrimination). Helium, an inert gas, is used for reducing or eliminating polyatomic interferences
Helium gas flow	: 3.9 and 4.9 L.min ⁻¹
Detector	: SimulScan™ dual-stage (pulse counting or analog)
Plasma torch power rating	: 1600 Watts
Argon gas flow	: 16 L.min ⁻¹
Flow at nebulizer	: ≈ 1 L.min ⁻¹

CALIBRATION

The concentrations in the sample extract are determined by a $Y = AX$ type equation.

Comments:

The concentrations determined in the sample must be within the calibration range of this analysis method. If one or more elements have concentrations that exceed the upper limit of the range, the sample is diluted appropriately with matrix-matching, then the analysis is repeated and the dilution factor is taken into account in the calculations. Consequently, the reported limit (RL) will be adjusted as a function of the additional dilution.

CALCULATIONS AND EXPRESSION OF RESULTS

Calculation of the concentration of a target element (metal) in the air sample:

$$C = \frac{(Q_{éch} \times F \times V_{éch}) - C_f - (Q_{3b} \times F_b \times V_b)}{V_{air}}$$

Where:

C	=	Concentration of the element in the air sample, in mg.m⁻³
Q _{éch}	=	Concentration of the element in the sample solution, in µg.L⁻¹
V _{éch}	=	Volume to which the sample was filled, in L
F	=	Total dilution factor (if no dilution, F=1)
C _f	=	Element contamination on filters, in µg
Q _{3b}	=	Average concentration of the element in the digestion blanks, in µg.L⁻¹
V _b	=	Volume to which the solution blanks were filled, in L
F _b	=	Dilution factor of blanks (if no dilution, F=1)
V _{air}	=	Volume of air sampled, in L

Comments :

- The element concentrations in the solution blanks are obtained by averaging the results from analysis of all digestion blanks. The average contamination of these blanks is subtracted if that value exceeds the method quantification limit (MQL) and is greater than $0.5 \times RL$ for the element in question.
- Before the filters are made available, their contamination is evaluated in the laboratory and statistically determined. Filter contamination C_f is taken into account when the element quantity (e.g., Fe) exceeds 5% of RL. If the element quantity is less than 5% of RL, C_f = 0.
- The results obtained for the samples are not corrected with the results of the field blanks.

METHOD EVALUATION

Note: The validation data show the method's performance at the time of publication. For updated values, see the IRSST website.

Detection limit and Quantification limit

COMPOUND OR ELEMENT	DETECTION LIMIT (µg.L ⁻¹)	QUANTIFICATION LIMIT (µg.L ⁻¹)
Aluminum	1.4	4.6
Arsenic	0.056	0.19
Cadmium	0.022	0.074
Chromium	2.7	9.0
Cobalt	0.041	0.14
Copper	0.47	1.6
Iron	1.5	5.1
Magnesium	5.5	18.5
Manganese	0.12	0.41
Nickel	0.31	1.0
Lead	0.11	0.37
Vanadium	0.11	0.35
Zinc	1.0	3.5

Precision

COMPOUND OR ELEMENT	REPLICABILITY (%)	REPEATABILITY (%)
Aluminum	3.0	3.3
Arsenic	2.7	3.5
Cadmium	2.4	3.3
Chromium	4.2	3.9
Cobalt	2.6	3.3
Copper	3.2	3.1
Iron	2.3	2.3
Magnesium	3.3	2.6
Manganese	2.9	3.2
Nickel	2.6	3.8
Lead	2.3	2.1
Vanadium	3.3	3.5
Zinc	2.8	3.1

Accuracy

COMPOUND OR ELEMENT	ACCURACY (%)
Aluminum	97.6
Arsenic	97.2
Cadmium	97.0
Chromium	97.8
Cobalt	99.6
Copper	99.2
Iron	99.9
Magnesium	98.6
Manganese	99.3
Nickel	99.4
Lead	98.8
Vanadium	96.7
Zinc	99.4

Recovery

COMPOUND OR ELEMENT	RECOVERY (%)
Aluminum	102.9
Arsenic	97.3
Cadmium	99.9
Chromium	98.2
Cobalt	100.5
Copper	98.4
Iron	100.3
Magnesium	99.4
Manganese	100.2
Nickel	102.7
Lead	98.7
Vanadium	97.8
Zinc	100.1

Measurement uncertainty

Note: The validation data show the method's performance at the time of publication. For updated values, see the IRSST website.

Analytical measurement uncertainty (CV_a) was calculated using the individual results of samples subjected to the entire analytical procedure. It does not take into account a probability threshold (confidence level of 95%, for example) or the contribution of sampling uncertainty.

COMPOUND OR ELEMENT	$CV_a(\%)$
Aluminum	3.2
Arsenic	3.0
Cadmium	2.9
Chromium	4.9
Cobalt	2.8
Copper	3.9
Iron	2.7
Magnesium	4.7
Manganese	3.4
Nickel	3.3
Lead	2.6
Vanadium	3.7
Zinc	3.4

For more information on calculation of uncertainties, see *Document Explicatif pour éléments de validation de méthodes, I-G-041*, produced by the IRSST Laboratory Division.

REFERENCES

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