

Australian/New Zealand Standard™

AS/NZS 3580.9.15:2014

Methods for sampling and analysis of ambient air

Method 9.15: Determination of suspended particulate matter—Particulate metals high or low volume sampler gravimetric collection—Inductively coupled plasma (ICP) spectrometric method

PREFACE

This Standard was prepared by the joint Standards Australia/Standards New Zealand Committee EV-007, Methods for Examination of Air, to supersede AS 2800—1985, *Ambient air—Determination of particulate lead—High volume sampler gravimetric collection—Flame atomic absorption spectrometric method*.

Reference was made to the US Environmental Protection Agency, *Compendium of methods for the determination of inorganic compounds in ambient air, including Chapter IO-3.4 Determination of metals in ambient particulate matter using inductively coupled plasma (ICP) spectroscopy* and European Standard, EN 14902, *Ambient air quality—Standard method for the measurement of Pb, Cd, As and Ni in the Pm10 fraction of suspended particulate matter*, in preparing this Standard.

The objective of this Standard is to provide regulatory and testing bodies with a standard method for the determination of the concentrations of metals present in suspended particulate matter in ambient air.

FOREWORD

Both natural and anthropogenic processes and sources emit metals and their compounds into the air. Metals occur naturally in soil and rocks and can be released into air as particulate matter through weathering, mining activities and wind-blown dust. Anthropogenic sources of particulate metals include mineral processing, incineration and combustion of fuels containing metals. Some metals, upon inhalation or ingestion, can lead to a range of health effects such as cancer, neurotoxicity and reproductive toxicity.

METHOD

1 SCOPE

This Standard sets out a method for the determination of particulate metals collected from ambient air by either a high or low volume sampler using inductively coupled plasma/atomic emission spectroscopy (ICP-AES) or inductively coupled plasma/mass spectrometry (ICP-MS).

This method is applicable to the determination of hydrochloric/nitric acid-soluble metals present in particulate matter. While dilute nitric acid is the preferred matrix for ICP-MS analysis, as this reduces polyatomic interferences, a hydrochloric/nitric acid mixture is specified as it has been shown to be a better matrix for extraction of metals from quartz filters (US EPA IO-3.5).

This method is suitable for the determination of the following metals: aluminium, arsenic, antimony, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, selenium, thallium, tin, titanium, vanadium and zinc. Other elements may be determined by this method if adequate performance is demonstrated.

Concentrations greater than or equal to 1 nanogram per cubic metre (ng/m³) may be determined for samples collected by a high volume sampler over a 24 h sampling period, with subsequent analysis by ICP-MS.

Metals present in the vapour phase and volatile metal compounds are not effectively collected by the filter-based methods used to obtain samples for determination by this procedure.

2 REFERENCED DOCUMENTS

The following documents are referred to in this Standard.

AS

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|--------|--|
| 2162 | Verification and use of volumetric apparatus |
| 2162.1 | Part 1 : General—Volumetric glassware |
| 2162.2 | Part 2 : Guide to the use of piston-operated volumetric apparatus (POVA) |
| 2164 | Laboratory glassware—One-mark volumetric flasks |
| 2166 | Laboratory glassware—One-mark pipettes |
| 3641 | Recommended practice for atomic emission spectrometric analysis |
| 3641.1 | Part 1 : Principles and techniques |
| 3641.2 | Part 2 : Inductively coupled plasma excitation |
| 4873 | Recommended practice for inductively coupled plasma-mass spectrometry (ICP-MS) |
| 4873.1 | Part 1 : Principles and techniques |
| 4873.2 | Part 2 : Quantitative determination—Water |

AS/NZS

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3580.1.1 Part 1.1 Guide to siting air monitoring equipment

3580.9.3 Method 9.3: Determination of suspended particulate matter—Total suspended particulate matter (TSP)—High volume sampler gravimetric method

3580.9.6 Method 9.6: Determination of suspended particulate matter—PM₁₀ high volume sampler with size selective inlet—Gravimetric method3580.9.9 Method 9.9: Determination of suspended particulate matter—PM₁₀ low volume sampler—Gravimetric method3580.9.10 Method 9.10: Determination of suspended particulate matter—PM_{2.5} low volume sampler—Gravimetric method3580.9.14 Method 9.14: Determination of suspended particulate matter—PM_{2.5} high volume sampler with size selective inlet—Gravimetric method

EN

14902 Ambient air quality—Standard method for the measurement of Pb, Cd, As and Ni in the Pm10 fraction of suspended particulate matter

ISO

3696 Water for analytical laboratory use—Specification and test methods

ISO/IEC

Guide 98-3: Uncertainty in measurement Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)

US EPA

Compendium of methods for the determination of inorganic compounds in ambient air

Chapter IO-3 Chemical species analysis of filter-collected suspended particulate matter (SPM) overview

Chapter IO-3.1 Selection, preparation and extraction of filter material

Chapter IO-3.5 Determination of metals in ambient particulate matter using inductively coupled plasma/mass spectroscopy (ICP-MS)

3 DEFINITIONS

For the purpose of this Standard, the definitions below apply.

3.1 Atomic mass unit (amu)A mass equal to 1/12 the mass of one atom of the most abundant form of carbon, the ¹²C isotope.

NOTE: 1 amu is equivalent to 1 unified atomic mass unit (u) or 1 dalton (Da).

3.2 Calibration blank solution

A solution prepared in the same way as the calibration solution but without adding the analyte.

3.3 Calibration check solution

A solution of similar composition as one of the calibration solutions, but prepared with stock standard solutions from a different source.

3.4 Calibration standard solution

A solution used to calibrate the instrument, prepared from a stock standard solution.

3.5 Field blank filter

A filter that is taken through the same procedure as a sample filter, except that no air is drawn through it.

3.6 Field blank solution

A solution prepared from a field blank filter by the sample preparation process.

3.7 Inductively coupled plasma

A stream of partially ionized gas sustained by a radiofrequency (RF) field created by an induction coil.

3.8 Instrument optimization solution

A solution used to determine acceptable instrument performance prior to calibration and sample analysis.

3.9 Interference check solution

A solution used to determine interference correction factors for elements which are subject to spectral overlap problems. The solution contains the target analyte with a mixture of other analytes that are expected to be in the samples and any potential interfering elements.

3.10 Internal standard

Pure analyte(s) not found in measurable concentrations in the test sample that are added to a sample, extract or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. Internal standards are used primarily to correct for solution matrix effects and instrument drift. Internal standards may be added directly to the test solution or by instrument on-line addition immediately prior to analysis.

3.11 Laboratory blank filter

An unused filter that does not leave the laboratory. This filter is taken from the same batch as used for sampling.

3.12 Laboratory blank solution

A solution prepared from a laboratory blank filter by the sample preparation process.

3.13 Measurement uncertainty

A variable associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand.

NOTE: The variable may, for example, be a standard deviation (or given multiple of it), or the half-width of an interval having a stated level of confidence. ISO/IEC Guide 98-3 provides a basis of evaluating uncertainty in the measurement system output.

3.14 Method detection limit (MDL)

The minimum concentration of an analyte that can be identified and quantified with a defined statistical probability for defined maximum matrix element concentrations.

3.15 Method quality control solution

A solution prepared by addition of a known amount of certified reference material to a laboratory blank filter followed by the sample preparation process.

3.16 Reagent blank solution

A solution that contains all the reagents used during analysis of the sample, but without the sample and filter matrix.

3.17 Rinse blank solution

A solution used to flush the instrument between samples to reduce memory effects.

3.18 Standardizing solution

A solution used to correct for any variation in ICP-AES instrument measured wavelength intensities over time.

3.19 Stock standard solution

A solution used for the preparation of calibration solutions, containing one or more of the analytes of interest at concentrations traceable to national or International Standards.

3.20 U_{95}

A measurement of uncertainty at a confidence interval of 95% according to ISO/IEC Guide 98-3.

4 PRINCIPLE

Airborne particulate matter is collected by a high or low volume sampler in accordance with the procedure described in the appropriate sampling method standard. A representative portion of the filter is digested in a hydrochloric/nitric acid mixture to extract metals and metal compounds from the collected particulate matter, with the metals determined by ICP-AES or ICP-MS. The concentration of particulate metals in ambient air is then calculated by dividing the mass of metal present on the filter by the volume of air sampled.

In ICP-AES analysis, the atoms or ions of elements in the sample are excited in an argon plasma. When the excited atoms or ions return to their ground state, each element emits light with wavelengths characteristic of that element. The spectra are dispersed by a grating spectrometer and the wavelength intensity monitored by photomultiplier tubes or solid state detectors. The wavelengths detected and their intensities indicate the presence and amounts of particular elements. ICP-AES analysis is best suited to samples collected by high volume sampler.

Analysis by ICP-MS also uses an argon plasma torch to generate elemental ions for subsequent separation and identification by mass spectrometry. The number of ions detected in a given time is proportional to the concentration of the element of interest. This technique can determine isotopes of an element. Samples collected by either high or low volume sampler are suitable for ICP-MS analysis.

5 SAFETY PRECAUTIONS

Analytical plasma sources emit radiofrequency radiation in addition to intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards. More detailed safety information pertaining to the use of ICP instrumentation can be found in AS 3641.2 and AS 4873.1.

6 REAGENTS

6.1 General requirements

Owing to the high sensitivity of ICP-MS in particular, high-purity reagents should be used wherever possible to minimize background contaminants. All acids used for extraction and analysis shall be of high-purity grade. All water used in the preparation of solutions shall be Grade 1 water in accordance with ISO 3696.

NOTE: It is recommended that the water used be obtained from a water purification system that delivers ultrapure water having a resistivity of 18 M Ω .cm or greater at 25°C.

6.2 Concentrated hydrochloric acid (HCl)

High purity grade, specific density (ρ_{20}) 1.16 to 1.18 g/mL, mass fraction between 32% and 37%.

6.3 Concentrated nitric acid (HNO₃)

High purity grade, specific density (ρ_{20}) 1.42 g/mL, mass fraction approximately 70%.

6.4 Nitric acid (HNO₃) for cleaning solution

Reagent grade, specific density (ρ_{20}) 1.42 g/mL, mass fraction approximately 70%.

6.5 Solutions

6.5.1 General

WARNING: CONCENTRATED HYDROCHLORIC AND NITRIC ACIDS ARE CORROSIVE AND OXIDIZING, AND THEIR FUMES ARE IRRITANTS. AVOID EXPOSURE BY CONTACT WITH THE SKIN OR EYES, OR BY INHALATION OF FUMES. USE SUITABLE PERSONAL PROTECTIVE EQUIPMENT (INCLUDING GLOVES, FACE SHIELD OR SAFETY SPECTACLES) WHEN WORKING WITH CONCENTRATED OR DILUTE ACID. PREPARE ALL SOLUTIONS IN A WELL-VENTILATED FUME HOOD. ADD CONCENTRATED ACID SLOWLY AS MIXING RESULTS IN AN EXOTHERMIC REACTION.

6.5.2 Metals extraction solution (16% HCl/6% HNO₃)

To approximately 700 mL of water (Clause 6.1) cautiously add, with stirring, 160 mL of concentrated hydrochloric acid (Clause 6.2) and 60 mL of concentrated nitric acid (Clause 6.3). Cool, transfer to a 1 L volumetric flask and dilute to the mark with water (Clause 6.1). Mix thoroughly. This solution shall be prepared freshly on use.

6.5.3 Diluent for working solutions preparation/rinse blank solution (2% HNO₃)

To approximately 800 mL of water (Clause 6.1) cautiously add, with stirring, 20 mL of concentrated nitric acid (Clause 6.3). Cool, transfer to a 1 L volumetric flask and dilute to the mark with water (Clause 6.1). Mix thoroughly.

6.5.4 Nitric acid cleaning solution (5% HNO₃)

To approximately 700 mL of water (Clause 6.1) cautiously add, with stirring, 50 mL of concentrated nitric acid (Clause 6.4). Cool and make up to 1 L with water (Clause 6.1). Mix thoroughly.

6.5.5 Calibration blank solution (1% HNO₃)

To approximately 800 mL of water (Clause 6.1) cautiously add, with stirring, 10 mL of concentrated nitric acid (Clause 6.3). Cool, transfer to a 1 L volumetric flask and dilute to the mark with water (Clause 6.1). Mix thoroughly.

6.6 Stock standard solutions

Stock standard solutions (single element or multi-element) can be obtained from commercial suppliers or prepared from high-purity grade chemicals or metals. If commercial stock standard solutions are utilized, these shall be supplied with certified concentrations traceable to national or international standards. All commercial stock standard solutions shall be validated by comparison of new data with data from the previous standard used. Stock standard solutions shall only be used within the laboratory's established expiry date. Stock standard solutions prepared in-house shall be stored in new acid-washed polytetrafluoroethylene (PTFE), high density polyethylene (HDPE) or polypropylene containers.

NOTE: AS 4873.2 contains preparation details for in-house stock standard solutions.

6.7 Working solutions

6.7.1 Calibration standard solutions

Instrument calibration standard solutions shall be prepared from a stock standard solution (Clause 6.6) diluted with diluent (Clause 6.5.3) to the manufacturer's specified calibration range. At least three calibration standard solutions covering the range appropriate for the method shall be prepared.

6.7.2 Calibration check solutions

Calibration check solutions shall be prepared from a different stock standard solution (Clause 6.6) to that used for the calibration standard solutions (Clause 6.7.1) by dilution with diluent (Clause 6.5.3). Often two or three calibration check solutions are prepared to cover the method measurement range (i.e. low, mid and high concentrations).

6.7.3 Instrument optimization solution

Instrument optimization solution shall be prepared in accordance with the instrument manufacturer's specifications.

6.7.4 Internal standards solution

The internal standards solution shall be prepared by dilution of stock standard solutions (Clause 6.6) with diluent (Clause 6.5.3) to produce a solution that is appropriate to the acid matrix and specific instrument.

6.7.5 Interference check solution

The interference check solution shall be prepared by dilution of stock standard solutions (Clause 6.6) with diluent (Clause 6.5.3) to produce a solution that is appropriate to the acid matrix and specific instrument.

6.7.6 Standardizing solutions

Standardizing solutions shall be prepared by dilution of stock standard solutions (Clause 6.6) with diluent (Clause 6.5.3). Standardizing solutions should have concentrations covering all elements in both the lower (less than 10%) and the upper (greater than 75%) sections of the concentration range. A suite of solutions may be required to cover all elements.

6.8 Argon

High purity grade (99.99%).

NOTE: When analyses are conducted frequently, liquid argon is more economical and requires less frequent replacement of tanks than compressed argon in cylinders.

6.9 Certified reference material (CRM)

Particulate matter containing known concentrations of metals with a sample matrix that is as representative as possible of the sampled ambient particulate matter.

NOTE: NIST 1648a 'Urban particulate matter' from the National Institute of Standards and Technology, USA is an example of a suitable product available commercially.

7 APPARATUS

7.1 Filters

Filters with a low and consistent metal content shall be used. Binderless quartz or pure borosilicate glass fibre filters are commonly used with high volume samplers. PTFE filters (with or without a plastic supporting ring) are commonly used with low volume samplers. Filter dimensions and particle collection efficiency shall be as described in the relevant sampling method standard, i.e. AS/NZS 3580.9.3, AS/NZS 3580.9.6, AS/NZS 3580.9.9, AS/NZS 3580.9.10 or AS/NZS 3580.9.14.