

Australian Standard™

**Recommended practice for chemical
analysis by atomic absorption
spectrometry**

Part 2: Graphite furnace spectrometry

This Australian Standard was prepared by Committee CH/16, Spectroscopy. It was approved on behalf of the Council of Standards Australia on 29 October 1999 and published on 5 December 1999.

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STANDARDS AUSTRALIA

RECONFIRMATION

OF

AS 2134.2—1999

**Recommended practice for chemical analysis by atomic absorption spectrometry
Part 2: Graphite furnace spectrometry**

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NOTES

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Part 2: Graphite furnace spectrometry

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PREFACE

This Standard was prepared by the Standards Australia Committee CH/16, Spectroscopy, to supersede AS 2134.2—1989.

This Standard will be Part 2 of a series comprising:

AS

2134 Recommended practice for chemical analysis by atomic absorption spectrometry

2134.1 Part 1: Flame atomic absorption spectrometry

2134.2 Part 2: Graphite furnace atomic absorption spectrometry

2134.3 Part 3: Vapour generation atomic absorption spectrometry

The objective of this Standard is to set out recommended practices for the operation of graphite furnace spectrometers used in chemical analysis. The Standard includes a description of instrumentation, optimization procedures, calibration, test procedures and information on factors affecting atomic absorption. A section on analytical quality assurance has been added to the Standard.

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STANDARDS AUSTRALIA

Australian Standard

Recommended practice for chemical analysis by atomic absorption spectrometry

Part 2: Graphite furnace spectrometry

SECTION 1 SCOPE AND GENERAL

1.1 SCOPE This Standard sets out recommendations for instrumentation and operating techniques suitable for chemical analysis by graphite furnace atomic absorption spectrometry (GFAAS) and includes a summary of testing procedures and requirements for safe operation. While this Standard is written primarily for a graphite furnace, the principles are applicable to alternative types of electrothermal atomization; and while written substantially for liquid sample introduction, the principles discussed are of application to solid sample introduction.

NOTES:

- 1 Flame atomization and vapour generation techniques are dealt with in Parts 1 and 3 of the AS 2134 series of Standards.
- 2 This Standard should be read in conjunction with the instrument manufacturer's recommendations.
- 3 A flowsheet on the procedure for the acceptance of analytical values for test sample is shown in Appendix A.

1.2 PRINCIPLE GFAAS relies upon—

- (a) heating a sample sufficiently to produce free atoms;
- (b) free atoms of an element being able to absorb energy only at certain discrete wavelengths (usually resonance wavelengths: refer to Appendix B; and
- (c) the energy absorbed being a function of the concentration of the absorbing atoms.

The technique described in this Standard involves the introduction of a sample, usually a solution of the sample, into a graphite furnace, heating of the furnace by an electric current and measurement of the absorption of energy at a specified wavelength.

1.3 REFERENCED DOCUMENTS The documents below are referred to in this Standard:

AS

2134 Recommended practice for chemical analysis by atomic absorption spectrometry

2134.1 Part 1: Flame atomic absorption spectrometry

2134.3 Part 3: Vapour generation atomic absorption spectrometry

2162 Verification and use of volumetric apparatus

2162.1 Part 1: General—Volumetric glassware

2850 Chemical analysis—Interlaboratory test programs—For determining precision of analytical method(s)—Guide to the planning and conduct

2929 Test methods—Guide to the format, style and content

BS

5703 Guide to data analysis and quality control using cusum techniques (series)

1.4 DEFINITIONS For the purpose of this Standard the definitions in Appendix B apply

SECTION 2 INSTRUMENTATION

2.1 GENERAL An instrument for graphite furnace atomic absorption spectrometry consists essentially of the following components:

- (a) A source of radiation which emits the required atomic spectrum of the analyte element (Clause 2.2).
- (b) A graphite furnace with temperature control (Clause 2.3).
- (c) A sample introduction system (Clause 2.4).
- (d) An optical system incorporating a device for isolating essentially monochromatic radiant energy (Clause 2.6).
- (e) A measurement system which usually consists of a detector, amplifier and a display, and a means for background correction (Clause 2.7).

2.2 SOURCES OF RADIATION

2.2.1 Line sources—Hollow-cathode lamp

2.2.1.1 Principle of operation A hollow-cathode lamp has a cathode constructed of, or containing, the analyte element in order to produce a sharp spectrum of that element. It is generally operated to give a pulsed signal by electronic modulation of the lamp or mechanical chopping of the radiant beam. The amplifier used for measurement is designed to respond only to the frequency of the modulated signal, so that radiation emitted from the furnace does not significantly alter the signal measured at any time during the analysis.

2.2.1.2 Operating current The hollow-cathode lamp should be operated according to the manufacturer's recommendations. Lower currents may improve sensitivity but may also result in a decrease in signal-to-noise ratio. Higher currents increase the possibility of self-absorption in the lamp which contributes to non-linearity of the calibration graph. In practice, the operating current chosen should provide the optimum signal-to-noise ratio.

2.2.1.3 Stability and testing The hollow-cathode lamp should be periodically tested to ensure that the signal intensity and stability are maintained.

2.2.1.4 Multi-element type Combination (or multielement) lamps are available so that a single lamp may serve as a convenient light source for two or more elements. The single-element lamps are to be preferred as the intensity of radiation of the line for a particular element will be greater at a given operating current.

Combinations of elements which produce relatively intense spectral lines close to the wavelengths of the normally utilized resonance lines should be avoided. Such nearby lines may necessitate the selection of unusually narrow spectral bandwidths with the monochromator, thus causing a deterioration of the signal-to-noise ratio, and hence, precision.

2.2.2 Line sources—other lamps Other types of lamp may be used as an alternative provided that they meet or exceed the same criteria of stability, signal intensity and line width as hollow-cathode lamps. Electrodeless discharge lamps and boosted discharge hollow-cathode lamps, which are commercially produced, provide suitable line sources for some elements.

NOTE: Some modern hollow-cathode lamps have electronic coding to enable the instrument to recognize the element(s).

2.2.3 Continuum sources Continuum light sources are used for background correction and should conform to adequate standards of intensity and stability. For correction in the ultraviolet region of the spectrum, deuterium lamps are commonly employed, while for the visible region of the spectrum, tungsten lamps or quartz-halogen lamps should be used (see also Clause 3.4).

2.3 GRAPHITE FURNACE SYSTEM

2.3.1 Basic construction The fundamental part of a graphite furnace atomizer is a graphite tube, approximately 6 mm in diameter and 30 mm in length, which is heated by a power supply, the function of which is to provide a low voltage, high power waveform which may be controlled to give the required temperature for the required time for the drying, pyrolysis and atomizing steps. A centrally located sample-introduction hole of diameter 1 mm to 1.5 mm allows the sample solution to be placed in the tube.

Tubes should be made from very pure graphite to prevent contamination which could adversely affect trace analysis. In common practice, tubes consist of ordinary graphite which has generally been coated with a thin layer of pyrolytic graphite. Tubes composed entirely of pyrolytic graphite are also available. Pyrolytic graphite is chemically more resistant and less permeable, thus minimizing the soaking-in of the sample solution and the loss of atomic vapour by diffusion through the tube walls. As a result of these properties, absorption peaks are both larger and sharper when pyrolytically coated tubes are used in preference to amorphous graphite tubes. Pyrolytic graphite tubes also provide longer operational life.

A platform made from pyrolytic graphite may be placed horizontally within the tube and the sample dispensed into a trough-like depression in the platform. A probe device also may be inserted into the tube.

Some pyrolytic graphite tubes have an integrated platform design.

2.3.2 Use of the furnace The furnace tube is arranged such that the light beam from the line source passes through its centre without attenuation by the tube walls, or platform if used. When a small volume of test solution is placed in the tube, the passage of a controlled electrical current via graphite contacts (which also support the tube) permits the heating of the tube. The three principal stages of the controlled heating cycle are—

- (a) drying, to volatilize solvent;
- (b) pyrolysis, to eliminate potentially interfering species and convert the analyte into a suitable form; and
- (c) atomization.

By heating to a temperature sufficient to cause atomization (usually 2000°C to 3000°C), a transient population of atoms is generated in the furnace, causing a transient absorbance signal.

The tube itself may be partly enclosed in a suitable manifold construction. This permits the tube to be both surrounded by and filled with an inert gas, such as argon or nitrogen (see Clause 3.2.4), which protects the tube from combustion and ensures a better environment for the atomization process.

Some systems allow automatic selection between alternative purge gases. For example, air or oxygen may be introduced to aid ashing or oxidation of the test sample constituents during the pyrolysis stages.

2.4 SAMPLE INTRODUCTION SYSTEM

2.4.1 Liquid sample introduction In graphite furnace atomic absorption, a liquid sample is introduced directly into a graphite furnace or onto a graphite platform or probe device. The solution introduced may be a blank test solution, a calibration solution, a chemical (or matrix) modifier solution or a test solution. A combination of some or all of these solutions may also be dispensed into the graphite furnace.

The total volume of the liquid sample, which may be aqueous or organic, can vary from 1 µL to 100 µL. The solution may be introduced manually using a suitable micropipettor, or automatically by a motor-driven syringe. Alternatively, the solution may be introduced into the graphite tube for a predetermined time as an aerosol generated by a nebulizing device.

2.4.2 Solid sample introduction Where a facility is available for direct introduction of solid samples into a furnace, such as a specially constructed tube to contain a microboat, samples should be placed in the microboat so as to avoid blocking the light from the hollow-cathode lamp source. It should be possible to insert and replace the microboat reproducibly. Particular care is required to avoid contamination during the manipulation of the microboat, particularly during the sample weighing procedure.

Should the sample material be heterogeneous and its particle size greater than that in the residue remaining after evaporation of a liquid sample, then increased interferences may be experienced during atomization of the analyte resulting in decreased accuracy.

2.4.3 Manual sample introduction A suitable micropipettor is used to deposit the solution into the graphite tube or onto the graphite platform or probe device. Care should be taken to ensure that the dispensed solution does not overflow the designed location in the graphite tube. Care should also be taken to ensure that the micropipettor tip does not become contaminated by contact with any object or move or displace any of the graphite components. Only one solution should be dispensed from the micropipettor at one time, however more than one solution may be introduced prior to the analytical measurement. Either the first solution may be dried prior to subsequent solution introduction, or the solutions may be allowed to mix.

2.4.4 Automatic sample introduction More commonly, automatic sample introduction is used; by this technique a predetermined volume of solution is deposited into the graphite tube or onto the graphite platform or the probe device. The automatic sampler may deliver a blank test solution, a calibration solution, a chemical (or matrix) modifier solution or a test solution. A combination of some or all of these solutions may also be dispensed at the one time.

The programmed addition of increasing volumes of a single calibration solution can be used to prepare a calibration graph automatically. Suitable volumes of a zero calibration solution (see Clause 4.4.1) should be added to each volume of the calibration solution, to ensure the total volume dispensed is the same in each case.

The programmed addition of increasing volumes of a single calibration solution together with a constant volume of a sample solution can be used to prepare an analyte additions calibration graph automatically (see Clause 4.5.4). Suitable volumes of zero calibration solution should be added to ensure that the same total volume is maintained.

By programming the repeated introduction of volumes of the one solution, with drying and perhaps pyrolysis, it is possible to increase the analytical response for that solution.

The major advantages of automatic, compared with manual, sample introduction are that improved precision generally results and that the graphite furnace can operate unattended for prolonged periods of time.

2.4.5 Temperature of furnace for sample introduction With aerosol deposition systems the graphite furnace should be maintained at an elevated temperature sufficient to rapidly dry the solvent and provide reproducible deposition of the residue on the tube walls.

Similarly, for either manual or, especially, automatic introduction it may be advantageous with some liquid samples to maintain the furnace at an elevated temperature during the complete deposition sequence. By this means the effective furnace heating cycle time may be significantly reduced. The selected temperature should be close to, but below, the solvent boiling temperature. The rate of sample solution delivery may be adjusted to ensure the smooth evaporation of solvent.

2.5 SAFETY PRECAUTIONS

2.5.1 Safety hazards requiring precautions Potential hazards which exist with GFAAS and which require precautions include—

- (a) production of toxic gaseous by-products from solutions placed within the furnace;
- (b) vapours emitted from solutions in open vessel which are presented for automated analysis;

- (c) ultraviolet and visible radiation emitted by the hot graphite;
- (d) use of compressed gases;
- (e) surfaces or components at high temperatures in the vicinity of the furnace; and
- (f) high magnetic field strength with Zeeman GFAAS.

2.5.2 Fume hoods It is strongly recommended that an efficient mechanical ventilation system be installed to exhaust toxic elements and compounds issuing from the furnace. It should be heat and corrosion resistant. The intake of the exhaust system should be placed directly above the furnace. The exact position of the intake and the exhaust capacity of the system should be in accordance with the instrument manufacturer's specification.

Care should be taken to minimize the vapours emanating from the solutions being analysed by keeping vessels covered.

2.5.3 Radiation safety Radiation from the heated graphite should never be viewed either directly or by reflection in a mirror.

2.5.4 Compressed gases Gas cylinders should always be stored upright and held securely in place. Use only the gas type and the operating pressure recommended by the instrument manufacturer.

Always handle gas cylinders in accordance with recommended procedures.

2.5.5 Heated surfaces Some surfaces of components in the vicinity of the heated graphite furnace may become hot. Zeeman graphite furnaces which employ electrical coils to produce the magnetic field can generate heat in the coils.

2.5.6 Magnetic fields With Zeeman GFAAS, a strong magnetic field exists in the vicinity of the magnet while it is operating. Some instruments use permanent magnets. It should be ensured that articles which may be affected by magnetic fields (i.e. heart pacemakers, magnetic storage media, some electronic equipment) are kept at a safe distance (at least 300 mm) from the magnetic source.

2.6 MONOCHROMATOR

2.6.1 Resolution The desirable resolution will vary with the element and the light source being used. In general, the monochromator should have an operating range between 185 nm and 900 nm and be capable of resolving lines such as the cobalt resonance line at 240.73 nm and the non-resonance line at 241.05 nm and the sodium resonance lines at 589.00 nm and 589.59 nm.

2.6.2 Wavelength stability The monochromator wavelength setting should not drift. However, if a wavelength setting is to be maintained over a period of several hours, it should be checked periodically and re-set if necessary. Airconditioning is recommended to ensure stability of settings, especially in extreme climatic conditions.

2.6.3 Slit width The slit width setting is expressed as the spectral bandwidth in nanometres. The slit width should be set to a maximum consistent with an acceptable signal-to-noise ratio and resolution of the required absorption line from nearby lines.

2.6.4 Slit height The heated graphite tube emits radiation with an intensity that is temperature dependent. Such radiation may cause a spurious signal if it reaches the detector of the spectrometer.

The graphite tube should always be aligned to maximize the source light throughput and to minimize the possibility of incandescent light from the hot graphite reaching the photomultiplier tube.

In some instances, it is recommended that a reduced slit height is used. This will ensure that the detector observes only a small vertical zone within the graphite tube. Instances when this may be desirable include—

- (a) when a platform or probe device is used;