

# Australian Standard<sup>®</sup>

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## Methods for sampling and analysis of ambient air

### Method 3.1: Determination of acid gases—Titrimetric method

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#### PREFACE

This Standard was prepared by the Standards Australia Committee on Methods for Examination of Air to supersede AS 2509 — 1981, *Ambient air —Determination of acid gases (expressed as sulphur dioxide)*.

In the preparation of this Standard, consideration was given to BS 1747, *Measurement of air pollution*, Part 3: *Determination of sulphur dioxide*, and to ISO 4219, *Air quality—Determination of gaseous sulphur compounds in ambient air—Sampling equipment*. Acknowledgement is made of the assistance obtained therefrom.

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#### FOREWORD

Because of their widespread distribution, acid gases, of which sulfur dioxide is often the main constituent, have long been regarded as a principal gaseous pollutant and the need is recognized for investigations at various sites, including atmospheric measurement of the day-to-day variations in concentration.

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#### METHOD

**1 SCOPE.** This Standard sets out a titrimetric method for the determination of acid gases (expressed as sulfur dioxide) in ambient air. The method is applicable to ambient air in which the sulfur dioxide concentration ranges from approximately 0.007 p.p.m to 3.5 p.p.m by volume (20 µg/m<sup>3</sup> to 10 000 µg/m<sup>3</sup>).

The method is suitable for determining acid gases in the atmosphere, preferably as an average over a 24 h period at a particular location. However, it is emphasized that the method is not specific for sulfur dioxide.

NOTE: In order to avoid interference from suspended matter, a filter is specified as an integral part of the apparatus; the filter also enables suspended matter to be measured separately within a limited size range.

**2 REFERENCED DOCUMENTS.** The following documents are referred to in this Standard:

|      |                                                      |
|------|------------------------------------------------------|
| AS   |                                                      |
| 2162 | Code of practice for the use of volumetric glassware |
| 2165 | Burettes and bulb burettes                           |
| 2922 | Ambient air—Guide for the siting of sampling units   |
| BS   |                                                      |
| 2461 | Specification for gas washing bottles                |

**3 PRINCIPLE.** Sulfur dioxide, with varying, but normally much smaller amounts of other acid and alkaline gases (see Note 1), is absorbed in a solution of hydrogen peroxide. The resulting net acidity of the solution is titrated to pH 4.5 with standard alkali.

NOTES:

1. Acid mists will mainly be retained on the filter paper in the smoke filter (see Figure 1) and will not affect the results appreciably.

If it is desired to make a correction for ammonia, it is necessary to measure the concentration by some independent method. The correction seldom reaches  $+25 \mu\text{g}/\text{m}^3$  except in farming areas or in certain indoor locations, where the concentration of ammonia may be sufficient to neutralize all the sulfur dioxide and produce a negative result.

2. At pH 4.5 there is no interference from dissolved carbon dioxide arising from normal atmospheric concentrations or from the reagents used.

#### 4 REAGENTS.

**4.1 General requirements.** Unless otherwise specified, use only reagents of analytical reagent grade and distilled water or water of equivalent purity. The water used to prepare standard solutions shall be carbon dioxide free.

**4.2 Hydrogen peroxide stock solution.** Dilute 10 mL of hydrogen peroxide, 30% *m/V* (known as 100 vol) to 1 L with water and mix well. Adjust the pH of the solution to pH 4.5 by adding either hydrochloric acid (4.3.1) or sodium hydroxide solution (4.3.2), using a pH meter to determine the end-point.

The stock solution should be contained in a stoppered borosilicate glass or polyethylene bottle and stored in a cool, dark place; any residual solution should be discarded after 2 weeks.

#### 4.3 Standard solutions.

**4.3.1 Hydrochloric acid solution** (0.004 mol/L). Pipette 20 mL of hydrochloric acid ( $\rho_{20}$  1.16 g/mL to 1.18 g/mL) into a 1 L volumetric flask and dilute to volume with water. Pipette 20 mL of this solution into a separate 1 L volumetric flask and dilute to volume with water. Standardize this solution against sodium tetraborate using the procedure described in Appendix A.

NOTE: It is advisable not to use standard solutions for more than three months without checking their concentration. Where the concentration of sulfur dioxide is high, it may be convenient to use a 0.01 mol/L solution and to modify the calculation accordingly; in this case, smaller burettes may be convenient for the titration procedure. It is also permissible to use a standardized solution of sulfuric acid, in place of hydrochloric acid.

**4.3.2 Sodium carbonate solution** (0.002 mol/L). Dissolve  $0.212 \pm 0.0001$  g of anhydrous sodium carbonate (previously dried at  $110^\circ\text{C}$  for 1 h) in water. Transfer to a 1 L volumetric flask and dilute to volume with water. Standardize this solution against standard hydrochloric acid solution (4.3.1), titrating to a methyl red end-point.

NOTE: It is advisable not to use standard solutions for more than three months without checking their concentrations. Where the concentration of sulfur dioxide is high, it may be convenient to use a 0.005 mol/L solution and to modify the calculation accordingly; in this case, smaller burettes may be convenient for the titration procedure. It is also permissible to use a standardized solution of sodium tetraborate in place of sodium carbonate solution.

**4.3.3 Sodium hydroxide solution** (0.01 mol/L). Dissolve  $0.4 \pm 0.001$  g of sodium hydroxide in water. Cool, transfer to a 1 L volumetric flask and dilute to volume with water. Store in a plastics container. Standardize this solution against potassium hydrogen phthalate using the procedure described in Appendix A.

#### 4.4 Indicator.

**4.4.1 Mixed indicator solution.** Mixed indicator having a colour change at pH 4.5. A suitable indicator can be prepared by mixing 20 mL of Solution A with 20 mL of Solution B and diluting to 250 mL with water.

NOTE: BDH 4.5 indicator solution is suitable, giving a neutral steel-grey colour at pH 4.5. This indicator should not be added to the hydrogen peroxide solution before it is used for absorbing the sample. This coloured indicator solution does not react with hydrogen peroxide, but certain other types of indicator may.

**Solution A.** Dissolve 2 g of thymol-sulfonephthalein (thymol blue RAL) in 45 mL of 0.1 mol/L sodium hydroxide solution, warming if necessary to assist dissolution, and dilute to 1 L with water.

**Solution B.** Dissolve 2 g of tetrabromophenolsulfonephthalein (bromophenol blue RAL) in 30 mL of 0.1 mol/L sodium hydroxide solution, warming if necessary to assist dissolution, and dilute to 1 L with water.

Solutions A and B shall be kept in the dark.

NOTE: This mixed indicator solution is used on the basis of 0.1 mL of indicator solution to 50 mL of hydrogen peroxide stock solution (4.2). The colours obtained are yellow at pH  $<4$ , pale lilac at pH 4.5, and blue-violet at pH  $>5$ .

#### 5 APPARATUS.

**5.1 General.** Volumetric glassware shall comply with AS 2165 and its use shall comply with AS 2162.

#### 5.2 Sampling train.

NOTE: Items (a) to (g) below are listed in the order in which they appear in the diagram of the sampling train illustrated in Figure 1.

The sampling train shall consist of the following apparatus:

- (a) *Funnel*—60 degrees, glass, diameter 40 mm. The funnel stem shall be 6 mm to 8 mm internal diameter, and shall be joined to the remainder of the apparatus by 6 mm to 8 mm internal diameter tubing without sharp bends or abrupt changes in internal diameter.
- (b) *Connecting tubing*—of internal diameter 6 mm to 8 mm and having a smooth internal surface.

The tubing between the air intake and the absorber shall be made of one of the following materials (in order of decreasing effectiveness):

- (i) Polytetrafluoroethylene (PTFE).

NOTE: PTFE tubing should not be exposed to sunlight, it should be protected by an opaque covering.

- (ii) Glass. Glass tubing may be connected using butt-joints with polyvinyl chloride (PVC) tubing; however the glass becomes dirty with use and requires regular cleaning.

NOTE: PVC tubing is liable to decomposition with release of hydrochloric acid when exposed to sunlight and heat, and its use should be restricted to joints.

- (iii) Stainless steel. It is difficult to obtain stainless steel tubing having a surface texture clean enough for sampling purposes. Absorption of sulfur dioxide from air passing through stainless steel tubing tends to vary with different batches of tubing.

NOTE: Cleaning agents used for tubing should be sulfur-free.

- (c) *Smoke filter unit*—a suitable assembly as shown in Figures 2 and 3.

NOTE: As anodized aluminium and certain aluminium alloys have been found to absorb or to react with sulfur dioxide, it is advisable to protect the surface of an aluminium filter with a coating of acid-resistant lacquer, or to use a filter unit made from a demonstrably unreactive (toward acid gases) material such as brass, PTFE or stainless steel. PVC is unsuitable.

- (d) *Filter paper*—Whatman No 1 or equivalent or PTFE filter papers.

NOTE: The use of Whatman No 1 filter paper is essential if the determination of suspended matter by filter paper soiling is also to be carried out.

- (e) *Gas washing bottles*—150 mL capacity, of colourless borosilicate glass, complying with BS 2461.

NOTE: Particular care is necessary to ensure that the washing bottles contain no free alkali, e.g. bottles should be washed by filling with hydrochloric acid (1 volume of acid (g<sub>20</sub> 1.16 g/mL to 1.18 g/mL) diluted with 1 volume of water), allowing to stand for 24 h, washing out and filling with water, allowing to stand for a further 24 h and then rinsing thoroughly. The washing bottles should then be filled with hydrogen peroxide stock solution (4.2) and the pH checked after 24 h; if the pH changes by more than 0.1, the treatment described above should be repeated.

- (f) *Vacuum pump*—conveniently of the diaphragm type, nominal capacity 0.08 m<sup>3</sup>/h (80 L/h), capable of drawing between 1.5 m<sup>3</sup> and 2.25 m<sup>3</sup> of air through the apparatus in 24 h.

- (g) *Gas meter*—a dry gas meter capable of measuring the volume of air sampled to an accuracy within  $\pm 2\%$  at the sampling flow rate used.

#### NOTES:

1. The dry gas meter provides a means for measuring the volume of air sampled by an integrating method.
2. Calibration of dry gas meters can be carried out by comparison with a laboratory wet gas meter which itself has been subjected to primary calibration within the preceding 2 years.
3. If the pressure drop across the system is expected to be large, it may be necessary to arrange for the gas meter to follow a leakproof pump. This spatial order minimizes risk of damage to the gas meter, and avoids the need for correction for reduced pressure.
4. Unless the gas meter is protected internally against corrosion, a moisture trap containing a suitable desiccant, e.g. flake calcium chloride, may be required (see Figure 1) to prevent condensation of moisture in the meter. The gas meter should, however, be installed in surroundings where extremes of temperature are unlikely to occur, e.g. in cold weather advantage may be taken of the heat generated by the pump by placing a suitable enclosure round the meter, while in warm weather the enclosure can be readjusted to exclude the pump.

**5.3 pH meter**—(optional) calibrated at pH 7 and pH 4.5 and capable of measuring accurately to within 0.01 pH units.

## 6 SAMPLING.

**6.1 Location.** The sampling site shall be selected in accordance with AS 2922.

NOTE: Dense vegetation and local sources of pollution (such as a low-level chimney or an exhaust vent) affect the concentration of acid gases in their respective vicinities.

**6.2 Installation of sampling train.** The items of apparatus shall be installed in accordance with the arrangement shown in Figure 1 and the following procedure:

- (a) Install the equipment in an environment such that decomposition of hydrogen peroxide will not occur.

NOTE: Prolonged exposure of hydrogen peroxide to sunlight and elevated temperatures can cause decomposition.