
British Standard

Determination of the specific surface area of powders

Part 1. Recommendations for gas adsorption (BET) methods

Détermination de la surface spécifique des poudres
Partie 1. Méthodes d'adsorption gazeuse — Recommandations

Bestimmung der spezifischen Oberfläche von Pulvern
Teil 1. Empfehlungen für Gasadsorptions-BET-Verfahren

Foreword

This Part of BS 4359, prepared under the direction of the Chemical and Petroleum Engineering Standards Committee, supersedes BS 4359 'Method for the determination of specific surface of powders' Part 1 : 1969 'Nitrogen adsorption (B.E.T. method)' which is withdrawn.

This revision is based on the systematic study of the methods and the comparison of the results from various sources during the last 12 years. It is one of a series that describes methods for the determination of the specific surface area of powders. The other standards in this series are:

Part 2. Recommended air permeability methods

Part 3. Calculation from the particle size distribution

No single method for the measurement of specific surface area can be recommended to cover the many different types of powders encountered and the circumstances in which they are used, but it is possible to formulate recommended procedures that may be applied to the majority of cases. The purpose of these standards is to obtain uniformity in procedure for any one of the methods selected, in order to facilitate comparisons between determinations made in different laboratories. Standardization between laboratories is best established by the use of certified reference materials, for example those of the National Physical Laboratory*.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

* Reference materials certified with respect to nitrogen BET specific surface area are available from the Office of Reference Materials, National Physical Laboratory, Teddington, Middlesex TW11 0LW.

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Recommendations

0 Introduction

Accurate sampling of particulate material is a prerequisite for the determination of specific properties of powders, especially when using methods in which the test sample may be relatively small in amount. Procedures are described in BS 3406 : Part 1* for obtaining a test sample as representative of the laboratory sample as is possible.

The value obtained for the specific surface area of a powder depends upon the method of measurement, e.g. the value obtained by gas adsorption will generally be higher than that obtained by permeametry.

Adsorption methods are based on the deposition of a layer of adsorbate on the sample. They take the total surface of each particle into account, including any open pores accessible to the adsorptive (see figure 1). These methods yield results that bear a closer relationship to the surface reactivity of a powder than permeametry.

The permeametry method is based on the flow of a fluid through a packed powder bed. It measures the overall area of the particles without taking into account any closed or 'cul-de-sac' pores that may be present (see figure 2). It is a simple and practical method that is highly suitable for production control. The result is not always representative of the surface reactivity of the powder.

There is an obvious virtue in co-ordinating the conditions of test with the conditions of use. For instance, a powder to be used as an adsorbent is best tested by an adsorption method. The standards in this series are intended to be widely applicable methods for obtaining reference data or for carrying out routine checks. Consequently, the experimental and computational procedures described in this Part are based on the use of nitrogen gas as the adsorptive, and the assumption that the shapes of the adsorption

isotherms do not differ greatly from that shown in figure 3. In practice, other gases and other forms of apparatus may be used for obtaining reference data, provided that they can be shown to yield experimental results that can be correlated with those obtained in accordance with the recommendations of this standard.

For samples of low surface area (below about $1.0 \text{ m}^2 \cdot \text{g}^{-1}$), there are advantages to be gained by using gases that have a low saturation vapour pressure at the temperature of liquid nitrogen, so that the dead space correction is considerably reduced. Special forms of apparatus will be required in such cases. A list of other gases is given in appendix A. Continuous flow systems may also be used for measurements of low surface area.

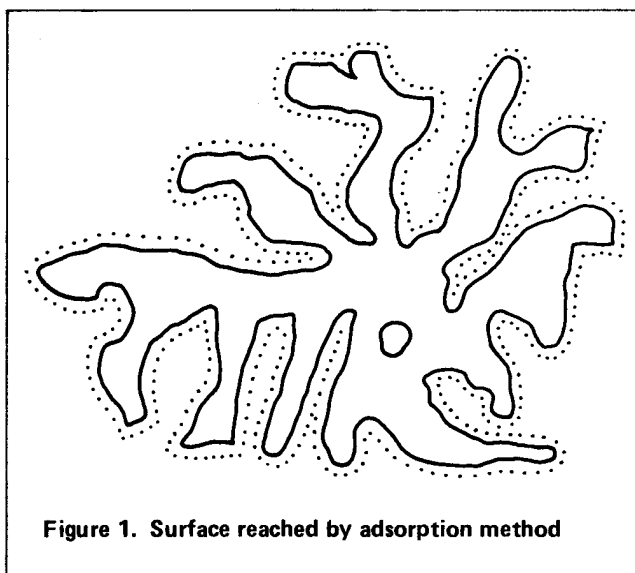


Figure 1. Surface reached by adsorption method

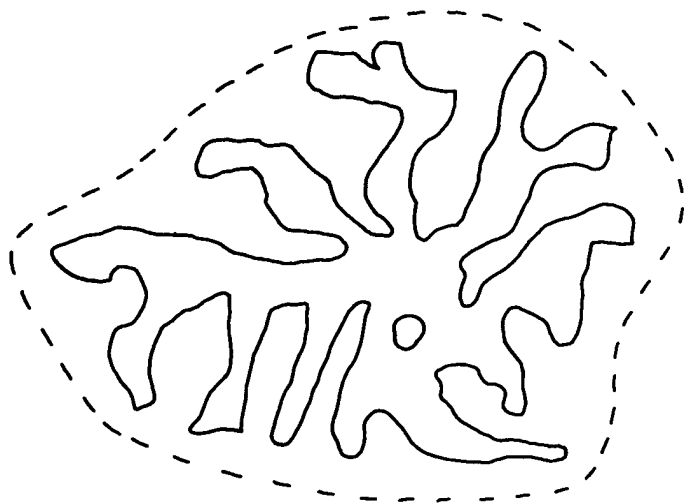


Figure 2. Surface reached by permeametry method

* A revision of BS 3406 : Part 1 is being prepared that will include guidance on procedures for obtaining the gross and laboratory samples.

1 Scope

This Part of BS 4359 gives recommendations for three methods, including the procedures for the necessary outgassing, for determining the specific surface area of a powder by measuring the amount of gas that would cover the surface with a single layer of adsorbed gas molecules. The principle of each method is outlined, and forms of apparatus are described, together with the necessary precautions and method of use. A method is given for recording the data and calculating the results in a tabular form in order to simplify the calculations.

Using the design conditions for the static volumetric multipoint method given in this standard the uncertainty in the monolayer amount (n_m^s) due to experimental reasons is less than $\pm 3\%$.

NOTE. The titles of the publications referred to in this standard are listed on the inside of the back cover.

2 Definitions

For the purposes of this Part of BS 4359, the following definitions, together with those given in BS 2955 apply.

2.1 adsorbate. The adsorbed gas.

2.2 adsorbed amount (n^s). The number of moles of the gas adsorbed at a given pressure p .

2.3 adsorbent. The powder on which adsorption occurs.

2.4 adsorptive. The gas to be adsorbed.

2.5 equilibrium adsorption pressure (p). The pressure of the gas in equilibrium with the adsorbate.

2.6 isotherm. A curve obtained by plotting the adsorbed amount against the equilibrium pressure or relative pressure.

2.7 molecular cross-sectional area (a_m). The average area occupied by the adsorbate molecule in the monolayer.

2.8 monolayer amount (n_m^s). The number of moles of the adsorbate that forms a monomolecular layer over the surface of the adsorbent.

2.9 relative pressure (x). The ratio of the equilibrium adsorption pressure, p , to the saturation vapour pressure, p° .

2.10 saturation vapour pressure (p°). The vapour pressure of the bulk liquefied adsorbate at the temperature of adsorption.

2.11 specific surface area (S). The surface area per unit mass (S_m) or volume (S_v) of the powder usually expressed in $\text{m}^2 \cdot \text{g}^{-1}$ or $\text{m}^2 \cdot \text{m}^{-3}$ respectively.

3 Symbols

For the purposes of this Part of BS 4359 the following symbols apply.

Symbol	Quantity	Unit or value
a_n	molecular cross-sectional area	nm^2
A_c	area under calibration peak P_c (see figure 10)	
A_d	area under desorption peak P_d (see figure 10)	
F_a	flow rate of adsorptive gas stream in continuous flow method	
F_c	flow rate of carrier gas stream in continuous flow method	
F_t	flow rate of total gas stream in continuous flow method	
H	initial pressure of helium in gas burette	Pa or mmHg
H'	pressure of helium in gas burette and sample bulb at temperature T (only used in a full correction procedure)	Pa or mmHg
H''	pressure of helium in gas burette and sample bulb at liquid nitrogen temperature	Pa or mmHg
m	mass of outgassed sample	g
n^s	adsorbed amount	mol
n_m^s	monolayer amount	mol
n_c	amount of adsorptive introduced into gas stream in continuous flow method	mol
n_d	amount of adsorbate desorbed	mol
n_i	amount of nitrogen introduced	mol
N_A	Avogadro number	$6.022 \times 10^{23} \text{ mol}^{-1}$
p	equilibrium adsorption pressure	Pa or mmHg
p°	saturation vapour pressure	Pa or mmHg
p_1	initial pressure of nitrogen in gas burette	Pa or mmHg
p_b	barometric pressure	Pa or mmHg
p'	equilibrium pressure of nitrogen in burette and sample bulb	Pa or mmHg

Symbol	Quantity	Unit or value
Q	dead space factor	mol·Pa
R	universal gas constant	8.31 J/(K·mol)
S	specific surface area per unit mass (S_m) or per unit volume (S_v)	m ² ·g ⁻¹ or m ² ·m ⁻³
T	burette temperature	K
V_n	total volume of burette and tubing above fiducial mark n (determined when the apparatus is being set up)	cm ³
x	relative pressure	dimensionless

4 Principles

4.1 General

The principle of the BET method was described by S. Brunauer, P. H. Emmett and E. Teller [1] *. A more recent review has been given by S. J. Gregg and K. S. W. Sing [2].

Gas adsorption methods depend upon the determination of the amount of a gas (the adsorptive) that, when adsorbed on the surface of the powder, would cover the surface with a single layer of gas molecules. This quantity has a statistical value calculated from the experimental data using the BET adsorption model. In principle, any gas may be used provided that its behaviour in contact with the powder under investigation may be represented by the BET model.

4.2 Choice of methods

4.2.1 The required experimental data may be obtained by either volumetric, or gravimetric or continuous flow methods.

4.2.2 In volumetric methods, a known amount of a gas is admitted to a sample bulb containing the powder, usually maintained at the normal liquid boiling point of the gas. Adsorption of the gas on to the powder occurs and the pressure in the confined volume falls until the adsorbate and the adsorptive are in equilibrium. Thus the amount of adsorbate at the equilibrium pressure is the difference between the amount of gas admitted and the amount of gas in the free space at the equilibrium pressure. These quantities are readily determined by conventional volumetric techniques (i.e. gas burette and manometer). The volumes of the gas burette bulbs are found by pre-calibration with mercury. The remaining volumes are found by gas expansion using helium. When calculating these volumes, corrections have to be made to allow for the different temperatures and pressures in appropriate parts of the system. In the simplified procedure described in this standard, corrections for non-ideality have been ignored since the consequent errors will be less than errors due to experimental uncertainties. The measurements necessary for full correction are included for use if desired.

4.2.3 Gravimetric methods are similar to volumetric

methods in principle and in the apparatus employed but the amount of gas adsorbed is determined by noting the increase in mass of the sample. This simplifies the procedure as there is no need to measure the dead space but the apparatus is more fragile, a sensitive balance is required and it may be necessary to apply buoyancy corrections.

4.2.4 Continuous flow methods are based on gas chromatography, in which the adsorption and desorption of the adsorptive in an inert carrier gas are measured. The surface area of the powder is usually calculated from the data obtained during desorption. The apparatus is robust and no dead space correction or high vacuum system is required.

4.2.5 Single point methods may be used for routine or series measurements but only after a full BET plot has been shown to be linear at least up to the relative pressure value of the single point chosen (see appendix B).

4.3 Calculation

In all of these methods, a series of adsorption measurements are made on a sample of the solid by admitting successively larger amounts of the gas to the volume containing the sample, and the amounts adsorbed are plotted against relative pressure, and an adsorption isotherm is obtained. Part of a typical nitrogen isotherm as determined for BET analysis is shown in figure 3.

The specific surface area per unit mass, S_m , of the powder is calculated from n_m^s , the uptake of gas corresponding to monomolecular coverage of the solid surface, by assessing a value a_m for the average area occupied by each molecule (see appendix A). The following equation relates these quantities

$$S_m = \frac{n_m^s a_m N_A}{m} \quad (1)$$

For nitrogen, for which $a_m = 0.162 \text{ nm}^2$, equation (1) becomes

$$S_m = 9.76 \times 10^4 \frac{n_m^s}{m} \quad (2)$$

The monolayer amount, n_m^s , is obtained by determining the adsorbed amount, n^s , at a series of relative pressures, x , and interpreting the data by means of the BET equation in the form

$$\frac{x}{n^s(1-x)} = \frac{1}{n_m^s C} + \frac{(C-1)x}{n_m^s C} \quad (3)$$

where C is a constant.

The plot of $x/\{n^s(1-x)\}$ against x should be a straight line as in the example shown in figure 4 of slope $(C-1)/(n_m^s C)$ and intercept $1/(n_m^s C)$ from which

$$n_m^s = \frac{1}{(\text{slope} + \text{intercept})}$$

and

$$C = \frac{\text{slope}}{\text{intercept}} + 1$$

* The numbers in square brackets used throughout the text of this standard refer to the bibliographic references given in appendix G.

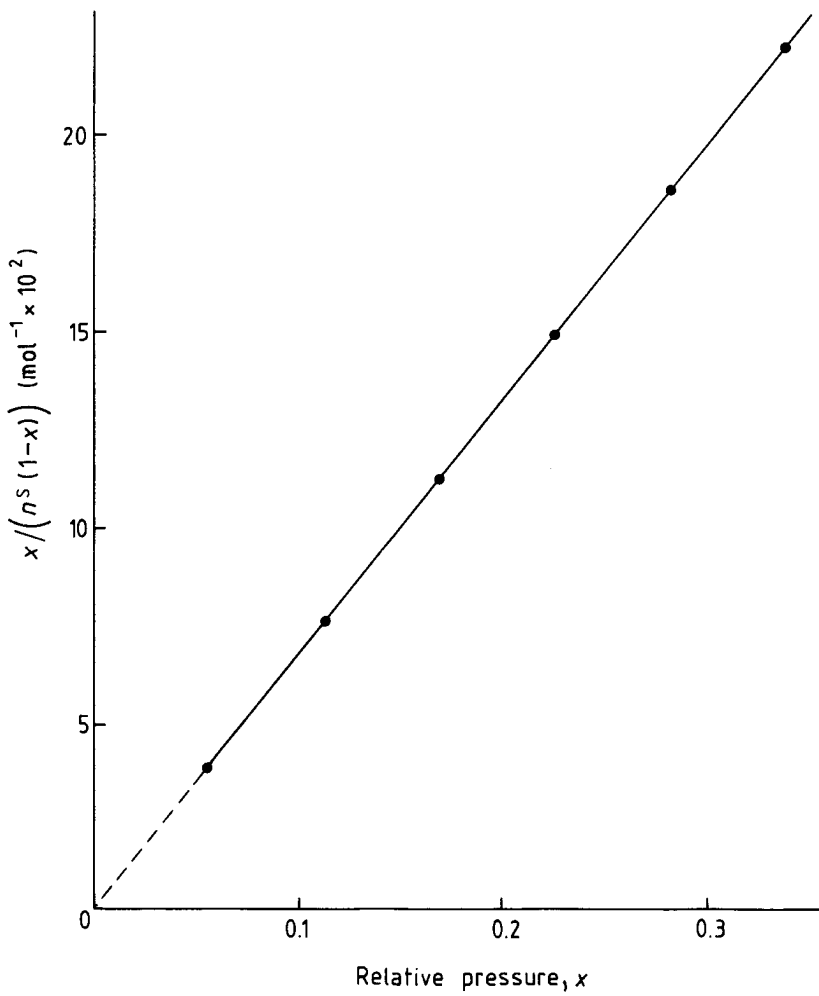


Figure 4. BET plot corresponding to adsorption isotherm of figure 3

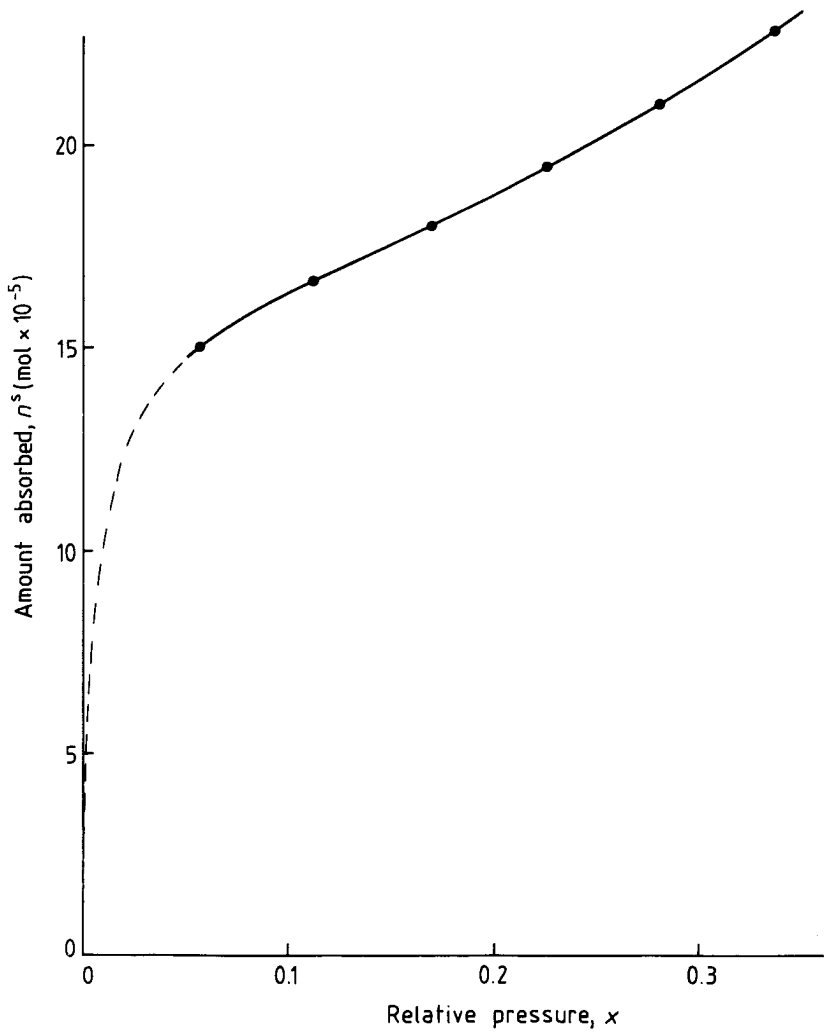


Figure 3. Part of adsorption isotherm showing experimental points

The plot is usually linear within the relative pressure range 0.05 to 0.35 but may deviate from linearity at either end. Such points which deviate should be omitted from the calculation of n_m^s . The range of linearity may be shifted to lower relative pressures in some cases.

The value of C should be calculated.

BET methods are not applicable in cases where the value of C is less than 10; in cases where the value of C is between 10 and 100 there may be unacceptable errors; in all cases where the value of C is greater than 100 the methods are applicable.

5 Outgassing

Before adsorption measurements are made, it is necessary to remove physisorbed material from the surface of the adsorbent by 'outgassing'. The essential objective of this process is to enable reproducible adsorption data to be obtained while avoiding irreversible changes to the adsorbent surface. The outgassing technique should be selected according to the adsorption system under study and the conditions should be controlled so that the objectives are achieved.

Several outgassing techniques are available. The commonest is exposure of the surface to high vacuum, usually at elevated temperature. This is generally used with the volumetric and gravimetric methods of measurement. In some cases it is adequate to flush the adsorbent with an inert gas (which may be the adsorptive), at elevated temperature. The continuous flow method generally employs this technique. With some microporous materials, one or more cycles of flushing with an inert gas followed by heating in vacuum may be necessary before reproducible adsorption data can be obtained. Whatever technique is used, it is sometimes possible to reduce the outgassing time, especially for very damp materials, by a preliminary drying of the sample in an oven at a suitable temperature.

When vacuum conditions are used, outgassing to a residual pressure of about 10^{-4} mmHg is usually sufficient; more severe vacuum conditions (e.g. 10^{-8} mmHg) may cause surface changes with some adsorbents. A suitable vacuum system would include a rotary pump and diffusion pump (oil or mercury), a cold trap (liquid nitrogen or solid carbon dioxide) and a continuous reading vacuum gauge. As the rate of outgassing is strongly temperature dependent, whether vacuum or flushing conditions are used, the temperature should be the maximum compatible with minimizing outgassing time but avoiding changes to the adsorbent (sintering, decomposition, etc.). The outgassing temperature is best selected from a thermal gravimetry curve obtained in vacuum; a temperature within the lowest range over which the curve has a zero or a minimum slope should be used. If this information is not available, selection of the temperature should be guided by experience and a general knowledge of the properties of the adsorbent, and trials conducted if necessary. For many inorganic and industrial materials an outgassing temperature of between 110 °C to

140 °C is suitable. An upper limit of about 400 °C is set by the use of glass sample bulbs.

The progress of outgassing should be followed by monitoring a suitable variable. This may be the pressure in the system (commonly used for the vacuum technique), the mass of the adsorbent (applicable to the gravimetric method), the composition of the residual gas (suitable for the vacuum technique), the composition of the flushing gas (applicable to the continuous flow method), or any convenient combination of these. When the observed variable has reached a steady value, which may require from 0.25 h to many hours depending on the sample, the completeness of outgassing should be checked. With the vacuum technique, this can be done by isolating the heated sample from the pumps and trap and checking that the pressure over the sample does not rise significantly over a period of about 0.25 h to 0.5 h.

In all cases, the outgassing conditions (temperature, duration, residual pressure, partial pressures, etc.) should be recorded.

6 Volumetric method

6.1 Apparatus and materials

6.1.1 General. A simple volumetric apparatus of all-glass construction is described in 6.1.2 to 6.1.6. This form of apparatus was chosen as it is simple and cheap to construct and, using the design conditions given in this standard, will give ideal points equally spaced on the BET plot.

Other forms of apparatus constructed of metal and using designs based on two pressure-measuring devices or piston-based volume measurement may be used.

The apparatus consists essentially of the following units:

- (a) vacuum manifold;
- (b) sample bulbs;
- (c) manometer, calibrated in divisions of 0.2 mmHg;
- (d) gas burette;
- (e) nitrogen and helium reservoirs.

A recommended arrangement is shown in figure 5; alternative forms of the sample bulbs are shown in figure 6; and the gas burette is shown in figure 7. The dimensions given in figure 6 are approximate only. The volumes of the gas burette bulbs have been chosen [3] so that six evenly spaced points can be obtained on the BET plot within the relative pressure range of 0.05 to 0.35.

6.1.2 Sample bulb. The choice of size of the sample bulb depends upon the bulk density of the powder and its anticipated total surface area (see 6.3.1). The volume of the sample bulb should be chosen so that the selected size of sample occupies two-thirds of the volume of the bulb. Free space above the powder is necessary to reduce powder entrainment during evacuation of the sample volume. To minimize errors the free space above the powder should be kept as small as possible. For low surface area powders ($< 1.0 \text{ m}^2 \cdot \text{g}^{-1}$) it may be necessary to fill the bulb completely and reduce the dead space still further with a solid glass rod.

6.1.3 Vacuum manifold. The vacuum manifold consists of a rotary pump followed by a two-stage oil or mercury diffusion pump, connected through cold traps cooled with solid carbon dioxide or liquid nitrogen to a main manifold of bore about 20 mm. A McLeod or preferably a continuous-reading gauge covering the pressure range of 10^{-5} mmHg to 10^{-2} mmHg should be attached to this manifold for initial testing for leaks and outgassing.

6.1.4 Sample bulbs. Sample bulbs of various sizes are required, depending on the expected surface area of the powder and its bulk density. The bulbs in common use have a volume of 10 cm^3 ; two forms are shown in figure 6. The narrow tube connecting the bottom of the bulb to the main stem in figure 6(b) serves to aid the removal of the adsorbed gas from the powder during outgassing by reducing the tendency of the powder to become entrained. Glass spurs should be used on the sample bulb and duplicated on the sample port for spring loading.

6.1.5 Manometer. The bore of the manometer should be between 7 mm and 8 mm. The mercury manometer is connected at the lower end to a mercury reservoir. A controlled leak may be fitted to the reservoir. In the arrangement shown in figure 5, the manometer is integral with the gas burette. If the total height of the mercury column exceeds about 760 mm the mercury reservoir will require pressurizing.

6.1.6 Gas burette. The design of the gas burette is shown in figure 7. The gas burette has five bulbs with fiducial marks on the connecting tubing. This tubing should be of the same bore (7 mm to 8 mm) as the manometer. The capacities of the bulbs are approximately 10, 15, 25, 50 and 150 cm^3 . The volume of the tubing between taps C and E and above fiducial mark 6 should be not more than 3 cm^3 such that the cumulative volumes are approximately 3, 13, 28, 53, 103 and 253 cm^3 .

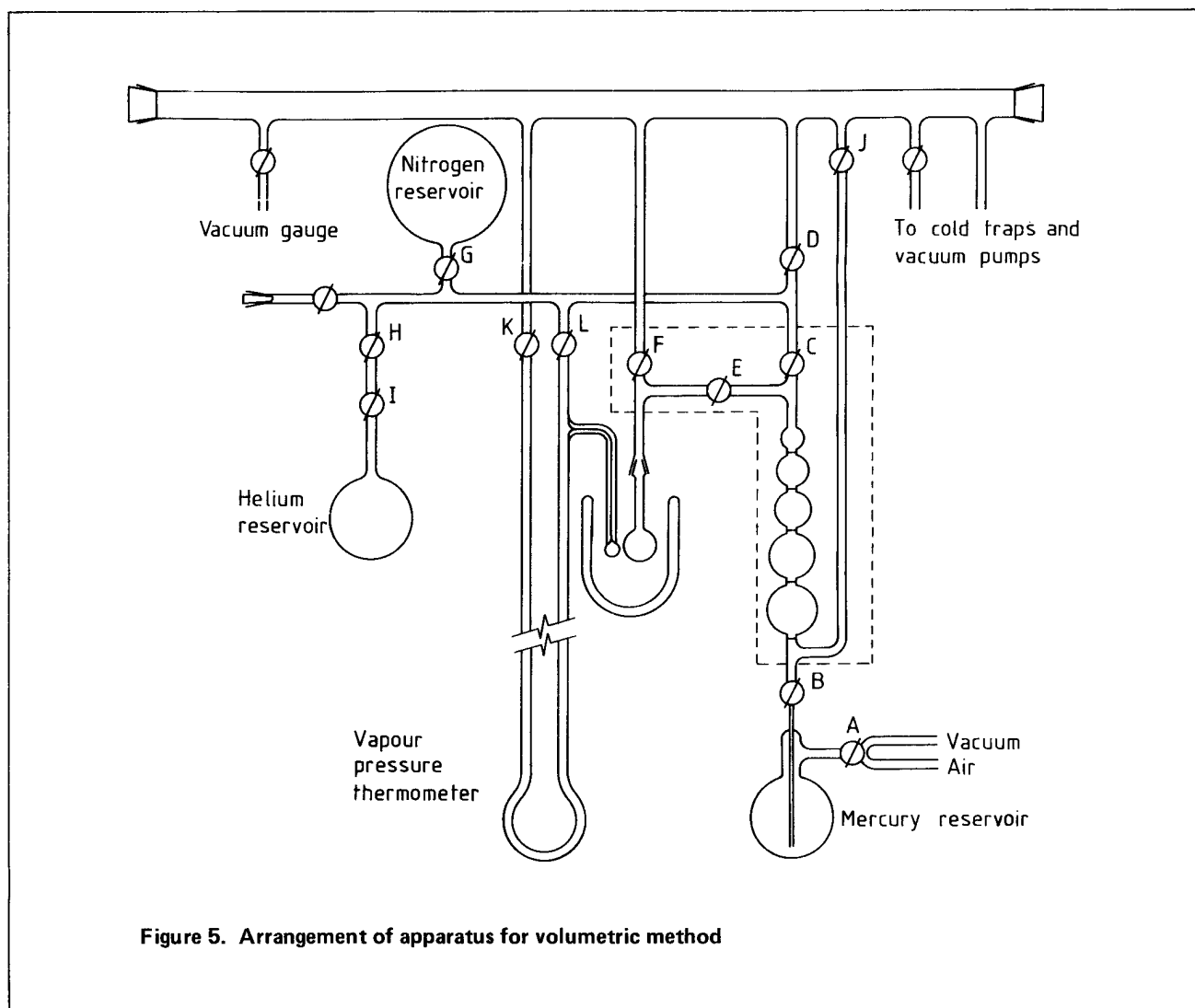
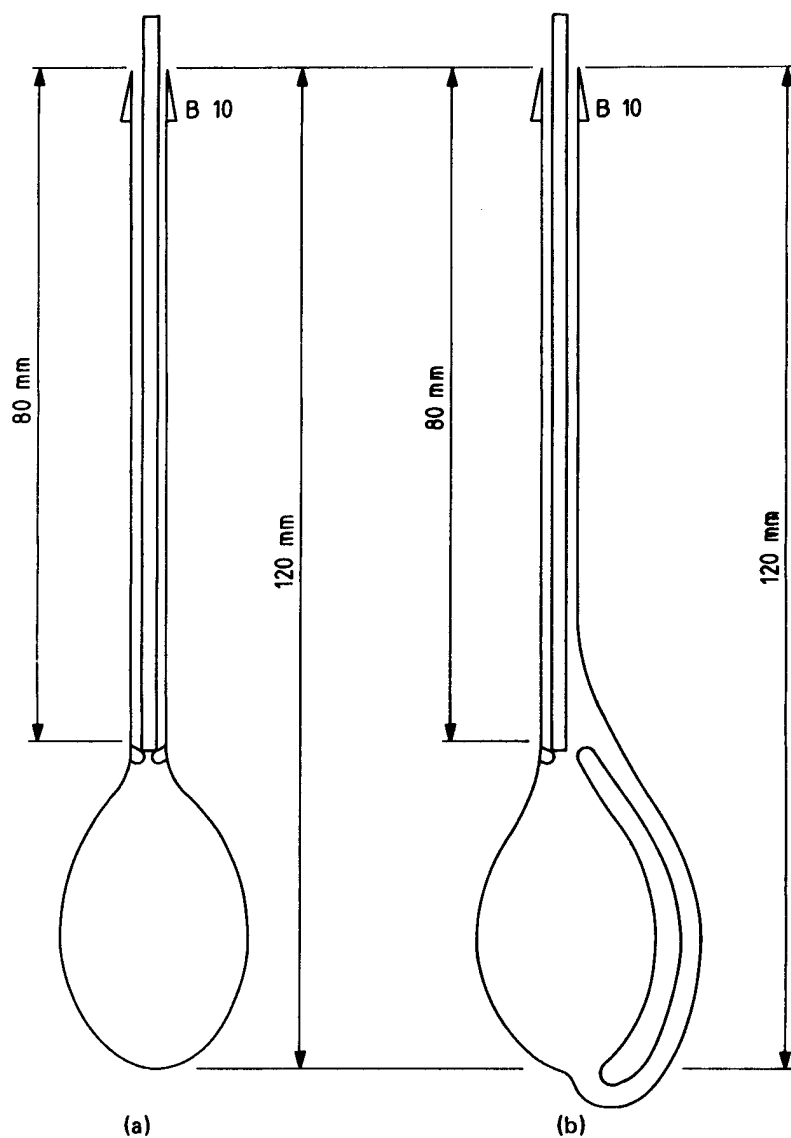


Figure 5. Arrangement of apparatus for volumetric method



NOTE. Dimensions are approximate only.

Figure 6. Sample bulbs of 10 cm³ volume