

METHODS FOR THE ANALYSIS OF FUEL GASES

Part 1. General analysis

BS 3156 : Part 1 : 1968



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The Institution desires to call attention to the fact that this British Standard does not purport to include all the necessary provisions of a contract.

In order to keep abreast of progress in the industries concerned, British Standards are subject to periodical review. Suggestions for improvements will be recorded and in due course brought to the notice of the committees charged with the revision of the standards to which they refer.

A complete list of British Standards, numbering over 4000, fully indexed and with a note of the contents of each, will be found in the British Standards Yearbook, price 15s. The BS Yearbook may be consulted in many public libraries and similar institutions.

This standard makes reference to the following British Standards:

BS 410. Test sieves.

BS 1041. Code for temperature measurement.

BS 1752. Laboratory sintered or fritted filters.

BS 1756. Methods for the sampling and analysis of flue gases.

Part 2. Analysis by the Orsat apparatus.

Part 3. Analysis by the Haldane apparatus.

BS 2069. Gas sampling tubes.

British standards are revised, when necessary, by the issue either of amendment slips or of revised editions. It is important that users of British Standards should ascertain that they are in possession of the latest amendments or editions.

The following BSI references relate to the work on this standard:
Committee references SFE/17, SFE/17/4
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CONTENTS

	Page
Co-operating organizations	4
Foreword	5

METHODS

1. Introduction	6
2. The constant volume method	6
3. The ' Metro ' method for nitrogen	21

APPENDIX

A. Approximate conversion factors	25
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TABLES

1. Reagent volumes and times for various gases	8
2. Correction of pressure for temperature variation	16
3. Example of results of a gas analysis	19
4. Determination of carbon density of unsaturated hydrocarbons on another sample of the same gas	20

FIGURES

1. Diagram of a constant volume gas analysis apparatus	10
2. ' Metro ' apparatus	23

CO-OPERATING ORGANIZATIONS

The Solid Fuel Industry Standards Committee, under whose supervision this British Standard was prepared, consists of representatives from the following Government departments and scientific and industrial organizations:

- Association of Boiler Setters, Chimney and Furnace Constructors
- Association of Consulting Engineers
- British Cast Iron Research Association
- *British Coal Utilisation Research Association
- *British Coke Research Association
- British Electrical and Allied Manufacturers' Association
- *British Iron and Steel Federation
- British Ironfounders' Association
- British Mechanical Engineering Federation
- Chamber of Coal Traders
- *Chemical Industries Association
- Coal Utilisation Council
- Coke Oven Managers' Association
- Combustion Engineering Association
- Confederation of British Industry
- Council of Ironfoundry Associations
- *Electricity Council, the Central Electricity Generating Board and Area Boards in England and Wales
- *Gas Council
- Heating and Ventilating Contractors Association
- Imperial Chemical Industries Limited
- Institute of British Foundrymen
- *Institute of Fuel
- *Institution of Gas Engineers
- Institution of Heating and Ventilating Engineers
- Institution of Mechanical Engineers
- Iron and Steel Institute
- Low Temperature Coal Distillers' Association of Great Britain Ltd.
- *Ministry of Housing and Local Government
- *Ministry of Power
- Ministry of Public Building and Works
- *National Coal Board
- *Society of British Gas Industries
- *Water-tube Boilermakers' Association
- Women's Advisory Council on Solid Fuel

The Government departments and scientific and industrial organizations marked with an asterisk in the above list, together with the following, were directly represented on the committee entrusted with the preparation of this British Standard:

- British Ceramic Research Association
- British Laboratory Ware Association
- Institute of Petroleum
- Institute of Sewage Purification
- Institution of Chemical Engineers
- Institution of Civil Engineers
- Institution of Electrical Engineers
- Royal Institute of Chemistry
- Scientific Instrument Manufacturers' Association
- Society of Chemical Industry
- Society of Glass Technology

BRITISH STANDARD METHODS FOR THE ANALYSIS OF FUEL GASES

Part 1. General analysis

FOREWORD

The edition of BS 3156 published in 1959 under the authority of the Solid Fuel Industry Standards Committee provided standard methods for the sampling and analysis of fuel gases and was the second of a series of BS Methods for the sampling and analysis of gases, of which the first, BS 1756 : 1952, dealt with the sampling and analyses of flue gases. The latter standard has now been revised and issued in separate parts, of which Part 1 deals with sampling; the sampling of gases is also dealt with in BS . . . *. It is therefore not considered necessary to deal with sampling in the present revision of BS 3156. The contents of this standard still cover well-established methods and do not deal with many specialized methods, several of which, such as those using paramagnetic and infra-red analyses, are already being studied separately and may be the subject of other standards.

The term 'fuel gas' can be applied to any gas which burns. The methods described in this standard are, in general, applicable to most fuel gases, although some minor changes in procedure may be required for the exceptional gases. These changes are indicated for the gases about which relevant information is available.

Fuel gases in the British Isles are derived chiefly from coal, coke, oil or natural gas, and this standard deals principally with such gases. It is a statutory requirement that town gas shall be substantially free from hydrogen sulphide; the term 'purified gas' refers to such gas, while the term 'crude gas' refers to gas containing hydrogen sulphide and other substances such as tar fog and naphthalene.

This standard is divided into five main parts, viz:

- Part 1. General analysis.
- Part 2. Special determinations.
- Part 3. Combustion characteristics.
- Part 4. Chromatographic analysis.
- Part 5. Techniques for high pressure gases.

NOTE. Metric (SI) units have been used throughout this standard. Where appropriate, approximate British equivalents, based on current practice, have been given. More accurate conversions may be achieved by using the factors in Appendix A or by reference to BS 350, 'Conversion factors and tables'.

* In course of preparation.

METHODS

1. INTRODUCTION

1.1 Constituents. The determination of the following constituents is considered in Part 1: Carbon dioxide, oxygen, unsaturated hydrocarbons, hydrogen, carbon monoxide, saturated hydrocarbons and nitrogen.

1.2 Types of apparatus. Almost every type of apparatus for gas analysis has, at some time, been adapted for the analysis of fuel gases. This British Standard, however, recommends only the constant-volume apparatus for general analysis and the 'Metro' apparatus when the determination of nitrogen alone is required.

For the determination of combustible constituents in fuel gases the use of techniques involving explosion, or combustion over hot wires, with added air or oxygen, is unsatisfactory, for the following reasons:

- (1) Eudiometer wires or combustion spirals may become contaminated with grease and mercury, either of which may be oxidized.
- (2) The results of the combustion of a fuel gas containing hydrogen, methane and other saturated hydrocarbons cannot be adequately interpreted.
- (3) The addition of oxygen or air for combustion necessitates a reduction in volume of the gas sample taken, with a consequent loss of accuracy.

Because of these considerations, several types of gas analysis apparatus working at constant pressure, such as the Orsat and the Haldane apparatus (see BS 1756*) and modifications of them, which are very useful for the determination of some constituents of fuel gases and even for the approximate determination of combustible constituents, cannot be recommended for the general analysis of fuel gases. Other methods are, however, available†.

* BS 1756, 'Methods for the sampling and analysis of flue gases', Part 2, 'Analysis by the Orsat apparatus', Part 3, 'Analysis by the Haldane apparatus'.

† See Foreword.

2. THE CONSTANT VOLUME METHOD

2.1 Introduction. Many variations and modifications have been proposed since the original designs of Bone* and Bone and Wheeler†. Some of these have been made to increase the speed and accuracy of operation, others to widen the scope of the apparatus or to standardize the components for ease of manufacture and assembly. In general there is little evidence regarding the accuracy and repeatability of the results which may be obtained with a particular apparatus, and where investigations have been carried out they have usually been concerned with repeatability rather than with accuracy.

Three forms of the constant volume gas analysis apparatus which have been widely used are those described by Gooderham‡, by Edgcombe§, and by Flint, Horspool and Mendoza||. These three forms of the apparatus were used in extensive collaborative work, carried out in connection with the production of this standard, to assess the accuracy and repeatability of the constant volume method of gas analysis. A gas mixture was prepared from accurately measured volumes of gases of known purity and samples were sent to all the laboratories concerned. The results obtained using the three forms of apparatus, in conjunction with the reagents and general procedure described below, were in close agreement with each other and with the actual composition of the gas sample. The various forms of apparatus differ somewhat and the details and dimensions of the components may be obtained by reference to the original publications.

In this standard only one form of the constant volume gas analysis apparatus is described in detail, but the use of this apparatus is not mandatory. The other forms of the apparatus used in the collaborative work mentioned are considered to be equally satisfactory, but for detailed instructions users are referred to the original papers. *It cannot, however, be too strongly emphasized that modifications of apparatus or technique other than those referred to in this standard should not be used unless they have been proved to be satisfactory as regards both accuracy and reproducibility by the analysis of gas mixtures of known composition.*

While the apparatus and techniques described are suitable for the analysis of all types of common fuel gases, the volumes of the various reagents used and the time the gas is in contact with the reagent may have to be varied to suit the type of gas being analysed. The procedure described below is for town gas, but the volumes of the reagents and the contact times required for some other fuel gases are given in Table 1.

* W. A. Bone, *Proc. Chem. Soc.*, 1898, 154.

† W. A. Bone and R. V. Wheeler, *J. Soc. Chem. Ind.*, 1908, 27, 10.

‡ W. J. Gooderham, *J. Soc. Chem. Ind.*, 1938, 57, 388T.

§ L. J. Edgcombe, *Fuel*, 1946, 25, 163 and unpublished work.

|| D. Flint, J. M. Horspool and M. P. Mendoza, *B.C.U.R.A. Members' Information Circular*, No. 80, 1953.

TABLE 1. REAGENT VOLUMES AND TIMES FOR VARIOUS GASES

Gas	KOH (carbon dioxide)		$H_2SO_4 + Ag_2SO_4$ ($C_{12}H_{10}$)		CrCl ₃ or alkaline pyrogallol (oxygen)		CuO 260–280°C (hydrogen)		KOH (carbon monoxide)		Amel-type reagent 600–650°C ($C_{12}H_{10} + 2$)		KOH (nitrogen left)	
	ml	min	ml	min	ml	min	ml	min	ml	min	ml	min	ml	min
Coal gas from high temperature carbonization	1	3	2	4	1	2	20	20	2	twice* 3	20	20	2	twice* 3
Blue water gas from coke	1	3	none		2	2	20	20	2	twice* 3	20	20	1	3
Carburetted water gas of calorific value less than 15 MJ/m ³ (400 Btu/ft ³)	1	3	2	4	1	2	20	20	2	twice* 3	20	20	2	twice* 3
Carburetted water gas of calorific value greater than 15 MJ/m ³ (400 Btu/ft ³)	1	3	2	twice* 4	1	2	20	20	2	twice* 3	20	20	2	twice* 3
Producer gas (from coke)	1	3	none		2	2	20	20	2	twice* 3	20	20	1	3
Producer gas (from coal)	1	3	2	4	2	2	20	20	2	twice* 3	20	20	1	3
Methane	1	3	none		1	2	none	none	none		20	20	2	twice* 3

* The word 'twice' indicates that two consecutive washes should be given, with fresh reagents.

In general the constant volume gas analysis apparatus has the following advantages over the constant pressure type:

- (1) The use of fresh liquid reagents facilitates complete absorption and the small quantities used minimize solubility errors.
- (2) The use of mercury eliminates solubility errors which would arise with any other confining liquid.
- (3) The effect of dead spaces is eliminated.
- (4) Errors of calibration are minimized, as graduations are made by length and not by volume.
- (5) Errors arising from the adsorption of gases on hot, solid reagents are minimized because the combustion tubes are evacuated.
- (6) Errors due to deviation from Boyle's Law are reduced, as all pressures measured are lower than atmospheric.
- (7) The apparatus can be used to analyse any fuel gas or mixture of fuel gases specified in the Foreword.

The following disadvantages should, however, be recognized:

- (1) Being a difference method it cannot determine constituents present in small concentrations (say 1 %) to a high order of accuracy.
- (2) It cannot separate hydrocarbons except into saturated and unsaturated types.
- (3) Very careful control of conditions is necessary in the combustion technique for the determination of hydrogen.
- (4) The constant volume technique requires an operator with considerable practice to obtain reliable results.

2.2 Principle. In the constant volume method of gas analysis the initial pressure of the sample, occupying a selected reference volume in a burette, is measured with a mercury manometer. The composition of the sample is calculated from the changes of pressure which occur on the selective removal of various constituents by washing with liquid reagents or by reaction with hot solid reagents, all pressure measurements being made with the residual gas occupying the reference volume. Corrections are applied to the pressure readings for change of temperature of the gas in the burette.

2.3 Apparatus. The essential components of the apparatus are:

- (1) *A combined burette and manometer* immersed in a water jacket
- (2) *An absorption pipette* in which constituents may be selectively removed by washing with liquid reagents
- (3) *Two combustion tubes*, in one of which hydrogen and carbon monoxide, and in the other methane and other saturated hydrocarbons, are oxidized to water and carbon dioxide.