

METHODS FOR THE ANALYSIS OF FUEL GASES

Part 4. Gas chromatographic analysis

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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.

A complete list of British Standards, numbering over 5000, fully indexed and with a note of the contents of each, will be found in the British Standards Yearbook, 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 458. Xylenes.

BS 507. Ethanol.

BS 805. Toluenes.

BS 1756. Methods for the sampling and analysis of flue gases.
Part 1. Methods of sampling.

BS 2461. Gas washing bottles.

BS 3282. Glossary of terms relating to gas chromatography.

BS*Methods of sampling chemical products.
Part 2. Sampling of gases.

BS*The preparation of gaseous mixtures.

* In course of preparation.

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
Draft for comment 68/814

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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 Ironfounders' Association

British Mechanical Engineering Federation

*British Steel Industry

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

Domestic Solid Fuel Appliances Approval Council

*Electricity Council, the Central Electricity Generating Board and the 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 4. Gas chromatographic 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 British Standard methods for the sampling and analysis of gases, of which the first, BS 1756 : 1952 dealt with the sampling and analysis 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 analysers, 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. Gas chromatographic analysis.
- Part 5. Techniques for high pressure gases.

NOTE. Metric (SI) units have been used throughout this standard. Conversions may be achieved by reference to BS 350, 'Conversion factors and tables'.

* BS 1756, 'Methods for the sampling and analysis of flue gases', Part 1, 'Methods of sampling'.

† BS, 'Methods of sampling chemical products', Part 2, 'Sampling of gases' (in course of preparation).

METHODS

1. SCOPE

This British Standard deals with the analysis by gas chromatography of mixtures containing the following:

- (1) 'Permanent' gases: hydrogen, oxygen, nitrogen, methane, carbon monoxide, carbon dioxide, ethylene, ethane.
- (2) Light hydrocarbon gases: propane, propylene, *isobutane*, acetylene, butane.
- (3) Other constituents: benzene, toluene, naphthalene, methanol.

2. INTRODUCTION

Gas chromatography is a process of separation of a mixture of compounds, achieved by means of a partition between a stationary phase and a gaseous mobile phase. The sample to be analysed is introduced into the mobile phase (the carrier gas) and is carried by it through a long, narrow column containing a stationary phase, which may be a granular sorbent (gas-solid chromatography) or a liquid of minimal volatility held on an inert porous solid (gas-liquid chromatography). The components of the sample distribute themselves between the two phases, in proportions depending on their sorptions (in the case of gas-solid chromatography) or their solubilities (in the case of gas-liquid chromatography). Since the sorptions or the solubilities generally differ from one component to another, each one is carried along the column at a different rate.

The components are eluted by the carrier gas and enter the detector at intervals of time characteristic for a particular column and conditions, so that each component can be identified from its retention time.

On passing the gas stream through a suitable detecting system, the signal from which is transmitted to a recorder, a chart record chromatogram is obtained on which the size of the peak is a measure of the quantity of a given component.

Unlike the classical methods of analysis, such as the constant volume apparatus, most gas chromatographs do not give an absolute measurement of any constituent. As with other physical methods, these require calibration and therefore it is not necessary to define the apparatus used in great detail. Many variations in apparatus are capable of giving the required performance. In this standard the procedure has been adopted of defining the characteristics of the apparatus necessary to achieve an adequate reproducibility. Even when the fundamental principles of operation are sufficiently understood, there are various factors which can occasionally cause inaccuracies and guidance is, therefore, given on the means of eliminating the major sources of error. A British Standard is in course of preparation which will cover this matter in detail.

3. DEFINITIONS

Reference should be made to BS 3282* for definitions of the terms used in this Part of this standard.

4. GENERAL

4.1 Assembly. This clause describes briefly the general principles of a typical apparatus. A block diagram is shown in Fig. 1. Basically, the gas chromatograph assembly comprises carrier gas supply with flow control unit, sample injector, column, detector and recorder. The column and detector are normally in a constant temperature enclosure.

4.2 Carrier gas. The chromatogram represents the changes in composition of the gas stream leaving the column as the various components are eluted. In theory, any gas could be used as carrier gas, but in practice the choice will normally be limited, by the requirements of the detector and the need to avoid interference with the constituents of the sample, to helium, argon, nitrogen or hydrogen. Within the above limitations, the purity of commercial grade gases is adequate provided that the supply unit is not changed between calibration and sample runs.

Occasionally it may be necessary to specify the carrier gas to obtain adequate sensitivity of detection, or to obscure an unresolved component (e.g. argon and oxygen). Hydrogen may be preferred to helium as carrier because of the difference in cost, but it must be remembered that leakage of hydrogen, particularly into the oven, may produce a fire or explosion hazard.

4.3 Carrier gas control. It is necessary to control the carrier gas flow rate or inlet pressure. The exact values do not matter, but variations greater than about $\pm 1\%$ may noticeably affect the separation obtained from the column and the response of the detector. A nominal value will usually be specified for the flow rate.

4.4 Sample introduction. The volume of sample introduced should be accurately reproducible. This may be achieved using a sample loop and bypass such as shown in Fig. 2. Such a system may be readily constructed from glass tubing and taps, or a commercial bypass injector may be used. The volume of sample is not critical, though a nominal value is usually recommended. It is simplest to introduce the sample at ambient temperature and pressure, but for highest precision the same temperature and pressure should be used for the sample and the calibration check. The rate of flow may be indicated by passing gas from the outlet of the sample loop through a tube extending just below the surface of a container of liquid. The flow of sample through the sample loop is stopped

* BS 3282, 'Glossary of terms relating to gas chromatography'.

before the sample is introduced into the carrier gas stream. In some determinations, a liquid sample is introduced into a heated vaporizer or else directly on to the column packing by means of a hypodermic syringe.

It should be noted that the range of a particular determination can often be varied by a change in the volume of sample introduced.

4.5 Column. The length and diameter of the column and the particle size of the packing may be recommended, though alternatives can usually be tolerated. These may necessitate compensatory adjustments in flow rate. The material of construction shall be such that it does not react with any of the constituents. The nature of the column packing is always specified and frequently also the pre-treatment and conditioning. The end of the column should be plugged with suitable porous material to prevent carry over of packing. The column temperature should remain constant to within about ± 0.1 degC; fluctuations greater than this are likely to cause detectable changes in retention times. The configuration of the column, e.g. straight or coiled, is immaterial.

4.6 Detector and control unit. In this standard, two forms of detectors are specified, thermal conductivity and flame ionization, but other detectors may be used where appropriate.

The thermal conductivity detector usually consists of two or four hot-wire filaments* supported in cavities in a metal block. A wide range of size, shape and material of construction may be used, but it should be noted that the filaments may react with constituents of the samples. The temperature should remain constant to within ± 0.1 degC, otherwise the stability and sensitivity will be affected.

The power supply to the filaments should be controlled within close limits. The detector should give a sensibly straight base line with carrier gas flowing through the column while set at adequate sensitivity for the minimum constituents it is required to determine.

In the flame ionization detector the effluent from the column is burned in a hydrogen flame and the ions formed are detected by changes in electrical conductivity. The geometry and materials of construction may vary widely. The hydrogen and air flow rates affect the response; they should be selected for maximum sensitivity consistent with the requirement that variations have the minimum effect upon sensitivity. The air supply should be free from impurities which would be detected in the flame.

The control unit for either detector should include provision for attenuating the signal from the detector, preferably in binary steps, so that all major peaks can be adjusted to fall between half and full scale. It is not generally advisable to alter the attenuation setting while a component is being eluted.

* Or thermistors.