

Analysis of fuel gases —

Part 11: Methods for non-manufactured gases —

Section 11.4 Determination of sulfur compounds in natural gas —

Subsection 11.4.4 Hydrogen sulfide, carbonyl sulfide, and sulfur-containing odorants by gas chromatography using a flame photometric detector

Committees responsible for this British Standard

The preparation of this British Standard was entrusted to Technical Committee PTI/15, Natural gas and gas analysis upon which the following bodies were represented:

- AEA Technology
- British Coal Corporation
- British Compressed Gases Association
- British Gas plc
- British Glass Manufacturers' Confederation
- Chemical Industries Association
- Department of Trade and Industry (Gas and Oil Measurement Branch)
- Department of Trade and Industry (National Physical Laboratory)
- Institute of Petroleum
- Institution of Gas Engineers
- Sira Limited
- Society of Chemical Industry
- Society of Glass Technology

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National foreword

This Subsection of BS 3156 has been prepared by Technical Committee PTI/15, Natural gas and gas analysis. It is identical with ISO 6326-4:1994 *Natural gas — Determination of sulfur compounds — Part 4: Gas chromatographic method using a flame photometric detector for the determination of hydrogen sulfide, carbonyl sulfide and sulfur-containing odorants*, published by the International Organization for Standardization (ISO). ISO 6326-4 was prepared by Subcommittee 1, Analysis of natural gas, of Technical Committee 193, Natural gas, in which the United Kingdom participated.

This British Standard forms part of a series, each Subsection of Section 11.4 is identical with the corresponding Part of ISO 6326 and Section 11.4 of BS 3156 will consist of the following Subsections:

- *Subsection 11.4.1: Introduction;*
- *Subsection 11.4.2: Odoriferous sulfur compounds by gas chromatography using an electrochemical detector;*
- *Subsection 11.4.3: Hydrogen sulfide, mercaptan sulfur, and carbonyl sulfide sulfur by potentiometry;*
- *Subsection 11.4.4: Hydrogen sulfide, carbonyl sulfide and sulfur-containing odorants by gas chromatography using a flame photometric detector;*
- *Subsection 11.4.5: Lingener combustion method.*

In the United Kingdom the preferred method is that given in this Subsection of BS 3156. The flame photometric detector is available from most manufacturers of chromatographs, both laboratory and process units, and is applicable to any sulfur compound. By contrast, the electrochemical detector is available from a single supplier and is operated under completely different conditions in order to measure carbonyl sulfide to those used for all other sulfur compounds.

Cross-reference

International Standard	Corresponding British Standard
ISO 6143:1981	BS 4559 <i>Methods for preparation of calibration gas mixtures</i> Section 9.1:1988 <i>Determination of composition by comparison methods</i> (Identical)

The reference to ISO 4260 is for information only. A British Standard related to ISO 4260 is BS 5379, which is identical to EN 41, and is in course of being replaced by the adoption by CEN of ISO 4260.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

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

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 8, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

Introduction

The standardization of several methods for the determination of sulfur compounds in natural gas is necessary in view of the diversity of these compounds [hydrogen sulfide, carbonyl sulfide, thiols (mercaptans), tetrahydrothiophene (THT), etc.] and the purposes of the determinations (required accuracy, measurement at the drilling head or in the transmission pipes, etc.).

In order to enable the user to choose the method most appropriate to his needs and to perform the measurements under the best conditions, ISO 6326 has been prepared in several parts.

ISO 6326-1 gives a rapid comparison of standardized methods and therefore provides information for the choice of the method.

The other parts of ISO 6326, including this part, describe in detail the various standardized methods.

The determination of total sulfur is specified in ISO 4260:1987, *Petroleum products and hydrocarbons — Determination of sulfur content — Wickbold combustion method*.

1 Scope

This part of ISO 6326 specifies a precise and accurate method for the analysis of sulfur compounds in natural gas.

This method is applicable to the determination of hydrogen sulfide, carbonyl sulfide, C1-C4 thiols and sulfides and tetrahydrothiophene (THT), generally in the range 0,5 µmol/mol to 50 µmol/mol. It is also applicable to the quantitative determination of sulfur compounds other than hydrogen sulfide, when hydrogen sulfide is present at concentrations up to 5 000 µmol/mol.

The method uses a single temperature-programmed column, and a sulfur-selective flame photometric detector (FPD).

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this part of ISO 6326. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this part of ISO 6326 are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 6143:1981, *Gas analysis — Determination of composition of calibration gas mixtures — Comparison methods*.

3 Principle

The components are separated using a temperature-programmed oven and a column of styrene/divinylbenzene porous polymer beads and measured with a sulfur-selective flame photometric detector. Potentially interfering hydrocarbons are also separated from the sulfur compounds. Some sulfur compounds are not completely resolved from others. Identification can be aided by selective scrubbing of the sample to remove different types of sulfur compound (see 7.4.2).

4 Materials

4.1 Gases

4.1.1 Carrier gas, nitrogen, helium or argon, [purity > 99,9 % (m/m)], free from oxygen and moisture.

4.1.2 Auxiliary gases, hydrogen and oxygen or air, [purity > 99,9 % (m/m)].

4.2 Reference materials, individual thiols and sulfides in the range C1 to C4, tetrahydrothiophene, hydrogen sulfide and carbonyl sulfide.

5 Apparatus

5.1 Gas chromatograph, capable of temperature programming and fitted with an FPD.

NOTE 1 The FPD is insensitive to hydrocarbons, and therefore may not register the presence of a hydrocarbon which co-elutes with and, consequently, may quench the response of a sulfur compound. The conditions quoted in this method should avoid such interference for the majority of natural gas compositions. If required, the column effluent can be split between the FPD and a parallel flame ionization detector (FID). The FID will clearly show potential hydrocarbon interference.

5.1.1 Column oven, with a temperature range of 50 °C to 250 °C, capable of being maintained at within ± 0,5 °C at any temperature in the range during an analysis.

5.1.2 Temperature control. The oven shall be provided with a linear programmer suitable for providing a rate of temperature change of 10 °C/min over the specified range.

5.1.3 Flow controller, to supply a suitable carrier gas flowrate.

5.1.4 Pressure controllers and restrictors, to supply suitable auxiliary gas flowrates.

5.2 Injection device, comprising either

— a gas-tight syringe, of capacity 5 ml, constructed of glass and polytetrafluoroethylene (PTFE), or

— a bypass injector, capable of injecting samples from 0,5 ml to 5 ml.