

MEDOR™ SPECIFICATIONS

Gas analysis - Determination of sulphur compounds in natural gas or air

Gas chromatographic method using an electrochemical detector for the determination of odoriferous sulphur compounds.

0 INTRODUCTION

The first MEDOR (Licence Gaz de France) was product two analyses THT (MEDOR "M") in 1970.

1 SCOPE AND FIELD OF APPLICATION

ISO 6326/2 or DIN 51855/7 specifies a gas chromatographic method for the qualitative and quantitative analysis of odoriferous sulphur compounds in natural gas.

Sulphur compounds may occur naturally in natural gas and remain as traces after treatment, or they may have been injected deliberately to allow subsequent olfactory detection.

The method is applicable to the following compounds :

- hydrogen sulphide ;
- methanethiol or methyl mercaptan and homologues up to butanethiols ;
- thiacyclopentane or THT.

It is not applicable for the determination of carbonyl sulphide (see MEDOR COS).

Under normal conditions of application, this method can be used to determine the content of each compound within a concentration range from 0,1 to 100 mg (concentration expressed in milligrams of sulphur) per cubic metre of gas at standard pressure and temperature, standard instrument for better sensitivity (see energyMEDOR).

The detector used is not sensitive to the major components of natural gases.

NOTES

1 The chromatographic conditions described enable hydrogen sulphide and methanethiol to be determined if the ratio of the concentration of the former to the concentration of the latter is less than 10.

The same applies for two thiols eluted consecutively. The resolution of the chromatographic column can be improved to increase this ratio (energyMEDOR column 1.6mm).

2 The method can also be used to determine the contents of

- the same sulphur compounds in air. If such an application is contemplated, it is appropriate, however, to take account of possible interferences from gases or vapours which can be detected by the electrochemical cell, and which could contaminate the atmosphere under consideration ;

- organic sulphides and disulphides ; the conditions of analysis are however different and are in specific application DMS / MES / DES / DMDS.

2 APPARATUS

The apparatus operates at room temperature (see 3.4.2) and consists essentially of four parts (option : regulated temperature for column) in standard with energyMEDOR.

2.1 Device for sample injection

To avoid adsorption and desorption phenomena, the use of metal in this part of the apparatus shall be restricted.

2.1.1 Manual injection

The sample is taken using a gas syringe, and immediately injected through a PTFE septum at the top of the column.
No manual injection in energyMEDOR.

2.1.2 Automatic injection

A programmer controls the injection line valves for the gas to be analysed. The non-metallic parts of the injector are of polyamide (loops) or PTFE (seats of electromagnetic valves).

2.2 Column

2.2.1 Tube

Material : glass or PTFE
Internal diameter : 4 mm or 1.6 mm
Length : 40 cm or 120 cm.

2.2.2 Packing

2.2.2.1 Support

Nature : Chromosorb W
Particle size : 150 to 180 µm (80 to 100 mesh, Tyler series).

2.2.2.2 Stationary phase

Column "S" or "M". Different % for "S" or "M".

2.3 Electrochemical (see the figure)

This consists of a glass container. The electrodes, two pieces of platinum gauze (diameter 50 mm, 3 600 wires per cm²), are welded 22 mm apart in a borosilicate glass tube and separately connected to the amplifier or to the recorder by a platinum wire.

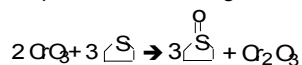
The electrolyte, a 10 % solution of chromic oxide in distilled water, is contained in a vessel into which the tube with the electrodes dips such that the solution is retained by capillarity within the tube at

the level of the upper grid, the level in the vessel itself being mi-way between the two grids.

The gas flow from the chromatographic column is discharged through a nylon tube of 2 mm internal diameter, 5 mm above the upper grid centre (MEDOR "S").

As soon as elution of a sulphur compounds occurs, a redox-reaction occurs on the surface electrode creating a potential difference between the two electrodes, thus causing a current which is observed in a low resistance measuring circuit. For example,

thiacyclopentane is oxidised to tetramethylene sulphoxide according to the reaction.



2.4 Recorder or integrator

2.4.1 Recorder

Type : potentiometric
Sensitivity : 1 mV full scale
Response time : of the recorder of 1 s.

NOTE - If the detector is fitted with an amplifier, a 1V full scale recorder may be used.

2.4.2 Integrator

- integrator and programmable calculator (computer) energyMEDOR.

The advantage of the last two devices is that they allow both the identification and determination of sulphur compounds contents.

3 PROCEDURE

3.1 Preparation of the apparatus

3.1.1 Carrier gas

Nature : nitrogen or air
Pressure : approximately 2 bar
Flow rate : 100 ml / min at 20°C.

3.1.2 Check for absence of leaks

3.1.3 Check of the electrolyte level

3.1.4 Adjustment of the recorder zero setting

3.1.5 Automatic injection

Adjust the flow rates of the gas to be analysed and the calibration gas mixture to 150 ml/min to purge the injection loop.

3.2 Analysis

Inject 20 ml or 10 ml of the sample, irrespective of the injection device used.

This is the maximum volume and can be reduced when the concentration of sulphur compounds is high. If the operation is automatic, the duration of the analysis cycle. Including the injection and elution stages, is 35 min - Medor "S". Only THT - Medor "M" (10 minutes).

3.3 Examination of the chromatogram

3.3.1 Qualitative analysis

The order and elution time for various constituents at 20°C for a flow rate of 100 ml/min N₂ MEDOR "S" is :

MEDOR "S"	energyMEDOR	
hydrogen sulphide (for manual operation only)		30 s
40 s		
methanethiol	60 s	66 s
ethanethiol	80 s	150 s
D.M.S		200 s
propane-2-thiol	160 s	240 s
2-methylpropane-2-thiol	240 s	342 s
M.E.S		390 s
propane-1-thiol	290 s	426 s
butane-2-thiol	560 s	
thiacyclopentane ou THT	2100 s	720 s

Duration of analysis : 45 min for MEDOR "S" and 15 min for energyMEDOR

NOTE - In order to reduce the total time of the analysis, the column described in Medor "M", for the determination of thiacyclopentane, may be used in parallel with the column described in 2.2 (see RS2).

The elution of thiacyclopentane may also be accelerated either by increasing the flow rate of the carrier gas, after the elution of butane-2-thiol, from 100 to 500 ml/min by means of an automatic device, or by using only approximately the first third of the column described in 2.2 for the elution of thiacyclopentane, by means of a commutation valve placed on the column at this distance. In these last two cases, the total time of analysis is only 15 min whilst still using only a single injection.

3.2) Quantitative analysis

3.1) Calibration

Carry out external calibration.

Because the physical and chemical characteristics of the compounds analysed are very different, several types of calibration mixture have to be considered.

a) Calibration gas mixtures prepared by a variant of the manometric method. It is easy to prepare a mixture for calibration under pressure where the component is thiacyclopentane and the complementary gas is nitrogen.

Such a mixture is stable when stored in a light alloy cylinder.

b) Calibration gas mixtures prepared by the permeation method on a gas flowing at a know rate. This is the technique recommended for preparing mixtures of components such as hydrogen sulphide and methanethiol.

c) Liquid calibration mixtures. This is the case with ethanethiol, its higher homologues and thiacyclopentane. Mixtures of such products in cyclohexane are stable. They should, however, be kept in a refrigerator if they are to be used over a long period.

d) Calibration mixtures for deferred injection. Under automatic conditions using an integrating calculator, it is useful to inject a calibration mixture containing only one component at a point in the cycle such that the elution of the latter occurs clear of the gas being analysed. Knowledge of the relative response factors with respect to this compound enables the concentration of the sulphur compounds to be determined in the gas being analysed. The component of this calibration mixture prepared by the manometric method may be one of the compounds to be analysed (thiacyclopentane) or a different substance (methyl ethyl sulphide).

3.2) Calculation of concentration

Use the following formula :

$$X_i = E_1 \frac{A_i}{A_E}$$

where

X_i is the content of substance *i* in the sample ;

E_i is the content of compound i in the calibration mixture ;

A_i is the measurement of peak i on the sample chromatogram ;

A_E is the measurement of peak i on the chromatogram for calibration mixture ;

3.4) Precautions to be taken to obtain satisfactory quantitative results

3.1) Sampling

To minimise adsorption phenomena in the transfer line, the following conditions shall be observed :

- The gas to be analysed shall be taken from a stream directly connected to the main stream. Taking a sample from a dead space would give erroneous results.
- The only materials that can be used for the transfer line are PTFE and polyamide. However, in the case of high gas flow rates, stainless steel can be used. Copper and its alloys are specifically to be avoided as well as pressure reducing valves containing rubber parts.
- Analysis is representative only if the gas is taken from a pipe in which the gas flow is sufficiently high.
- When gases having different sulphur compounds contents are analysed consecutively, care shall be taken that the line is purged until stable conditions are achieved.

3.2) Detector

The detector is sensitive to sudden temperature changes. It shall therefore be placed in surroundings with a constant temperature, or, better, in a temperature-controlled environment, or energyMEDOR.

The relationship between detector response and concentration is not strictly linear. A calibration mixture shall, therefore, be used in which the concentration of the same component in the natural gas to be analysed. This obviously limits the application of automatic methods for gases with large variations in composition.

3.5) Handling precautions

All sulphur compounds present a fairly high toxic hazard. Their odour, even at low concentration levels, is extremely disagreeable. All safety precautions concerning sample handling and gas mixture preparation shall, therefore, be observed. Care shall also be taken that the lines are gas-tight.

4 ACCURACY for MEDOR « S »

The repeatability of the method is better than 5 %.

The method enables the concentration of each compound to be determined with an accuracy of about 10 %.

5 TEST REPORT

The test report shall contain the following information :

a) Sampling conditions :

pressure ;
temperature ;
date.

b) Results of the analysis :

The concentrations, expressed in milligrams of sulphur per cubic metre of gas (under standard conditions of the pressure and temperature).

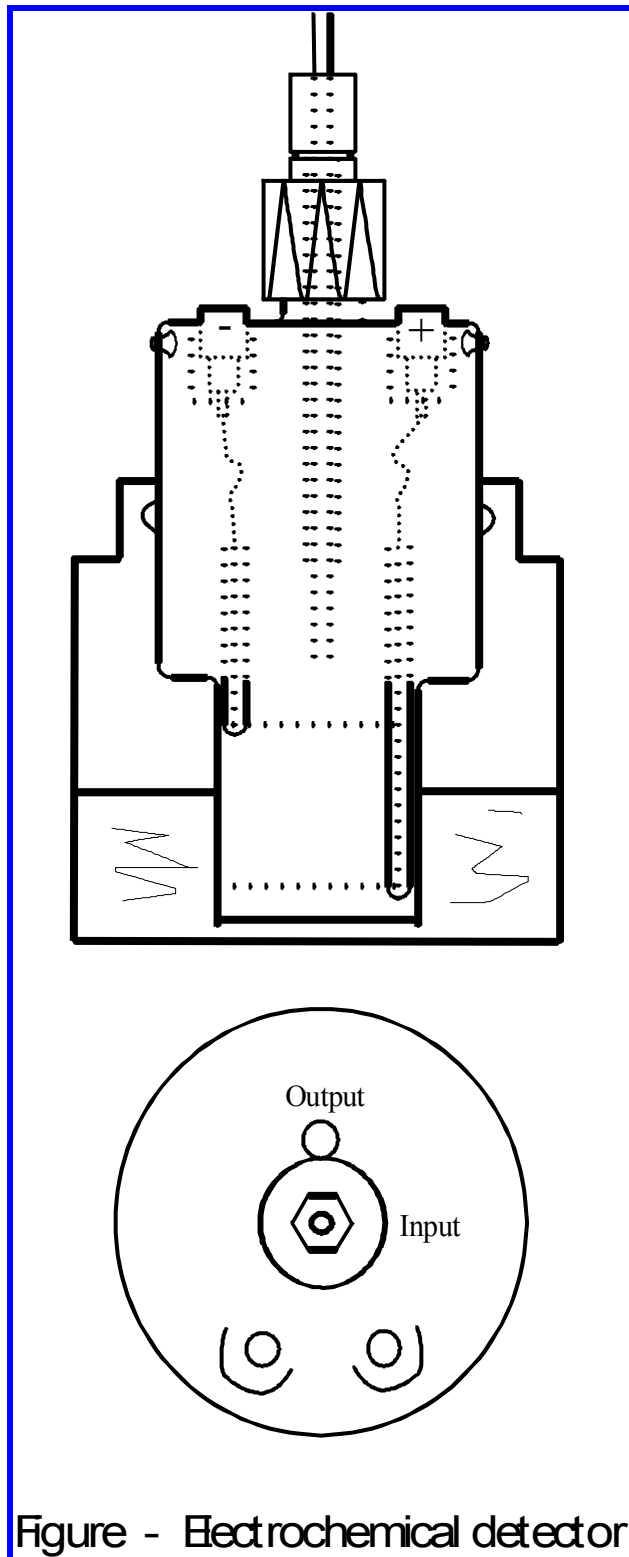


Figure - Electrochemical detector

	MEDOR	energyMEDOR	POSITIVE EFFECTS
Electrometer	No	Yes	Sensitivity
Column DI (mm)	4	1.6	Resolution R.T. (THT)
Length (mm)	400	1200	
Commutation	No	Yes	
Detector mm	30 x 25	5 x 20	Sensitivity and resolution
Carrier gas	N2 or air	He	Better chromatography
Temperature control	No	Yes	Accuracy
Flow control	No	Yes	Accuracy
Soft for automatic cycle / control / restart / calculation / communication	No	Yes	Accuracy
Injector dead volume	Yes	No	Resolution and accuracy
Loop (ml)	10	0,25	To use μ detector and column 1.6

MEDOR "M" : 10 % accuracy and 5 % repeatability for THT.

MEDOR "S" : depend of Methanol and composition of the mix sulphur.

EnergyMEDOR : - relative standard deviation<5% on concentration over 48H
 - relative standard deviation<0,6% on retention time over 48H.