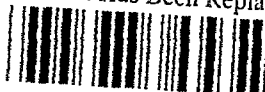


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Inventor: Mr. W. Hilscher

File: D

Gas mixture for flame ionization detectors

5 The invention relates to a flame ionization detector operated with an oxygen gas mixture, to a method for operating the flame ionization detector and to the use of oxygen-containing gas mixtures for flame ionization detectors.

10 Flame ionization detectors (FID) are detectors which are used in gas chromatography. The principle of measurement by flame ionization detector is based on the combustion of organic compounds in a hydrogen-air flame, an ion current being measured in the process. Flame
15 ionization detectors are described in "C.F. Poole and S.K. Poole, Chromatography today, published by Elsevier, Amsterdam 1991, pp. 260-264".

 Surprisingly, it was found that the measuring sensitivity of flame ionization detectors can be considerably increased by the use of a gas mixture which
20 comprises an oxygen content in the range of from 25 to 50 percent by volume, in particular from 40 to 45 percent by volume, instead of the air which is used customarily.

 The invention therefore relates to a flame
25 ionization detector whose operation involves the use of a gas mixture which comprises from 25 to 50 percent by volume of oxygen.

 The invention further relates to a method for operating flame ionization detectors, wherein a gas
30 mixture is used which comprises from 25 to 50 percent by volume of oxygen.

 The invention additionally relates to the use of a gas mixture which comprises from 25 to 50 percent by volume of oxygen, for operating flame ionization
35 detectors.

 The gas mixture used for flame ionization detec-

tors generally comprises oxygen and nitrogen, i.e. from 25 to 50 percent by volume of oxygen and from 75 to 50 percent by volume of nitrogen. Alternatively, instead of nitrogen, other inert gases such as noble gases or mixtures of inert gases can be used. Examples of suitable noble gases include helium, argon, krypton and xenon. One or more noble gases may also be present, mixed with nitrogen, in the gas mixture.

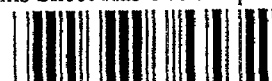
As the oxygen content of the gas mixture increases, so does the sensitivity of flame ionization detectors. An oxygen content of more than 50 percent by volume in the gas mixture causes damage to the measuring electrodes and is therefore not recommended.

The greatest sensitivity increase in flame ionization detectors is achieved with gas mixtures having an oxygen content in the range of from 35 to 45 percent by volume of oxygen. Particularly suitable for operating flame ionization detectors, therefore, are gas mixtures having an oxygen content in the range of from 35 to 45 percent by volume of oxygen.

The gas mixtures can be used particularly advantageously with aliphatic or aromatic hydrocarbons such as alkanes (e.g. propane, butane, pentane, hexane, heptane, octane, nonane or decane) or mononuclear aromatic compounds (e.g. benzene, toluene, xylene) as the sample.

The use of the gas mixtures increases the detection limit of flame ionization detectors for organic compounds. Thus, for example, the detection of aromatic compounds such as benzene, toluene or xylene in the range of from 20 to 1000 ppb (for each component in nitrogen; ppb indicates the concentration by volume, i.e. ppb = $1:10^9$ parts by volume) is possible without an enrichment system in gas chromatography analysis.

The sensitivity increase of the flame ionization detectors when employing the gas mixtures is generally in a range of from 30 to 100%, based on the sensitivity when employing air or synthetic air. The detection sensitivity (detection limit) of the flame ionization detector is increased accordingly.



Examples

In the following Examples 1 to 3, the measuring sensitivity of the flame ionization detector is compared using the following samples when separated by gas chromatography:

- Example 1) 5.0 ppm of propane in nitrogen,
Example 2) 1.5 ppm of propane in nitrogen,
Example 3) 270 ppb of benzene; 270 ppb of toluene;
270 ppb of xylene; in nitrogen.

10 Example 1

Separations by gas chromatography of one type of sample (5 ppm of propane in nitrogen) are carried out using different FID gas mixtures under otherwise identical conditions. The signal of the flame ionization detector of the tests is compared. The detector signal when synthetic air is used as the gas mixture is defined as 100 percent. Concentration by volume of the samples is specified in the units ppm ($1:10^6$ parts by volume) or ppb ($1:10^9$ parts by volume).

20 Test conditions:

Flame ionization detector: Siemens

FID settings: 32×10^{-12} A

Gas chromatograph: Sicromat® II, Siemens

Separation column: 50 m $\text{Al}_2\text{O}_3 \cdot \text{KCl}$; internal diameter:
25 0.53 mm;

Carrier gas: nitrogen 6.0

Separation conditions: 80°C isothermal

Sample: 5 ppm of propane in nitrogen (amount of sample: 250 μl)

30 FID combustion gas: 30 ml/min of hydrogen (100%)

FID gas mixture (oxidant): 450 ml/min of oxygen/nitrogen mixture

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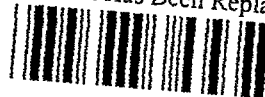


Table 1: Results of Example 1

Gas mixture (composition in vol%)	Relative sensitivity
Synthetic air (20% O ₂ , 80% N ₂)	100
25% O ₂ , 75% N ₂	132
35% O ₂ , 65% N ₂	165
40% O ₂ , 60% N ₂	194

Example 2

Test conditions:

Flame ionization detector: Siemens

10 FID settings: 8×10^{-12} A

Gas chromatograph: Sicromat® II, Siemens

Separation column: 50 m Al₂O₃*KCl; internal diameter:
0.53 mm;

Carrier gas: nitrogen 6.0

15 Separation conditions: 80°C isothermal

Sample: 1.5 ppm of propane in nitrogen (amount of sample:
250 µl)FID combustion gas: 30 ml/min of hydrogen,
40 vol%/helium, 60 vol%20 FID gas mixture (oxidant): 450 ml/min of oxygen/nitrogen
mixture

Table 2: Results of Example 2

Gas mixture (composition in vol%)	Relative sensitivity
Synthetic air (20% O ₂ , 80% N ₂)	100
40% O ₂ , 60% N ₂	128

Example 3

Test conditions:

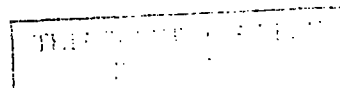
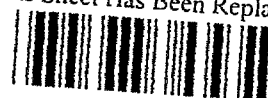
Flame ionization detector: Siemens

FID settings: 4×10^{-12} A

30 Gas chromatograph: Sicromat® II, Siemens

Separation column: 50 m DB 624, film thickness 3 µm;

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internal diam.: 0.53 mm;
Carrier gas: nitrogen 6.0
Separation conditions: 80°C isothermal
Sample: 270 ppb of benzene, 270 ppb of toluene and
5 270 ppb of xylene in nitrogen
Amount of sample: 250 μ l
FID combustion gas: 30 ml/min of hydrogen (100%)
FID gas mixture (oxidant): 450 ml/min of oxygen/nitrogen
mixture

10 Table 3: Results of Example 3

Gas mixture (composition in vol%)	Relative sensitivity
Synthetic air (20% O ₂ , 80% N ₂)	Benzene: 100 Toluene: 100 Xylene: 100
40% O ₂ , 60% N ₂	Benzene: 200 Toluene: 192 Xylene: 178

Example 4

15 Measurements with flame ionization detector without gas
chromatograph

Test conditions:

Flame ionization detector: Total Hydrocarbon Analyser

FID settings: Range 6

20 measuring instrument: Total Hydrocarbon Analyser,
model 521, fluid systems

Separation column: none

Conditions: 85°C cabinet temp.

Recorder: Kompensograph II (Siemens); 0-10 V DC

25 Sample: 845 ppb of saturated hydrocarbons (C₁-C₄) in
nitrogen

FID combustion gas: hydrogen (100%)

FID gas mixture (oxidant): oxygen/nitrogen mixture



Table 4: Results of Example 4

Gas mixture (composition in vol%)	Relative sensitivity
Synthetic air (20% O ₂ , 80% N ₂)	100
40% O ₂ , 60% N ₂	137

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Claims

1. A flame ionization detector whose operation involves the use of a gas mixture which comprises from 25 to 50 percent by volume of oxygen.
- 5 2. The flame ionization detector as claimed in claim 1, wherein the gas mixture comprises from 35 to 45 percent by volume of oxygen.
3. A method for operating flame ionization detectors, wherein a gas mixture is used which comprises from
10 25 to 50 percent by volume of oxygen.
4. The method as claimed in claim 3, wherein the gas mixture comprises from 35 to 45 percent by volume of oxygen.
5. The use of a gas mixture which comprises from 25
15 to 50 percent by volume of oxygen, for operating flame ionization detectors.
6. The use as claimed in claim 5, wherein the gas mixture comprises from 35 to 45 percent by volume of oxygen.
- 20 7. The use as claimed in claim 5, wherein the gas mixture comprises at least one inert gas.
8. The use as claimed in claim 5, wherein the gas mixture comprises nitrogen and/or one or more noble gases.
- 25 9. The use as claimed in claim 5, wherein the gas mixture comprises from 35 to 45 percent by volume of oxygen and from 65 to 55 percent by volume of an inert gas.
- 30 10. The use as claimed in claim 5, wherein the gas mixture comprises from 35 to 45 percent by volume of oxygen and from 65 to 55 percent by volume of nitrogen.



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