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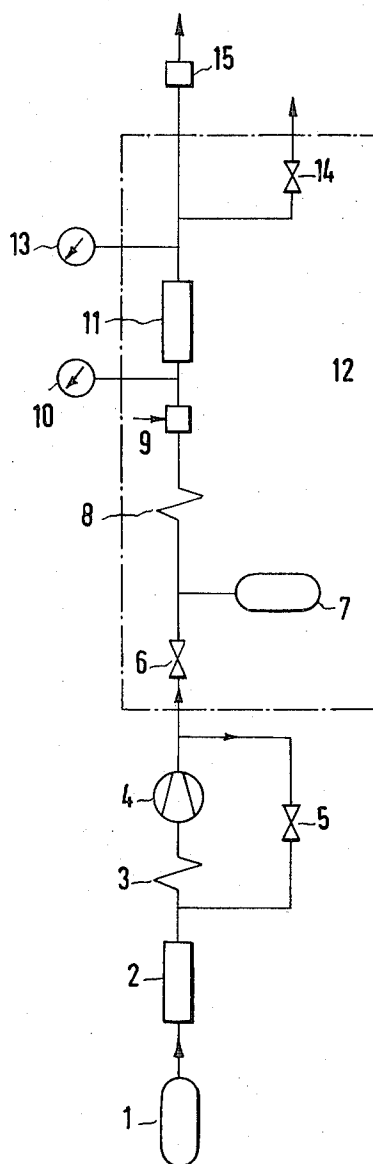
O. VITZTHUM ET AL
FLAME IONIZATION DETECTOR FOR SUPERCRITICAL
FLUID CHROMATOGRAPHY

3,827,859

Filed Nov. 28, 1972

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FIG. 1



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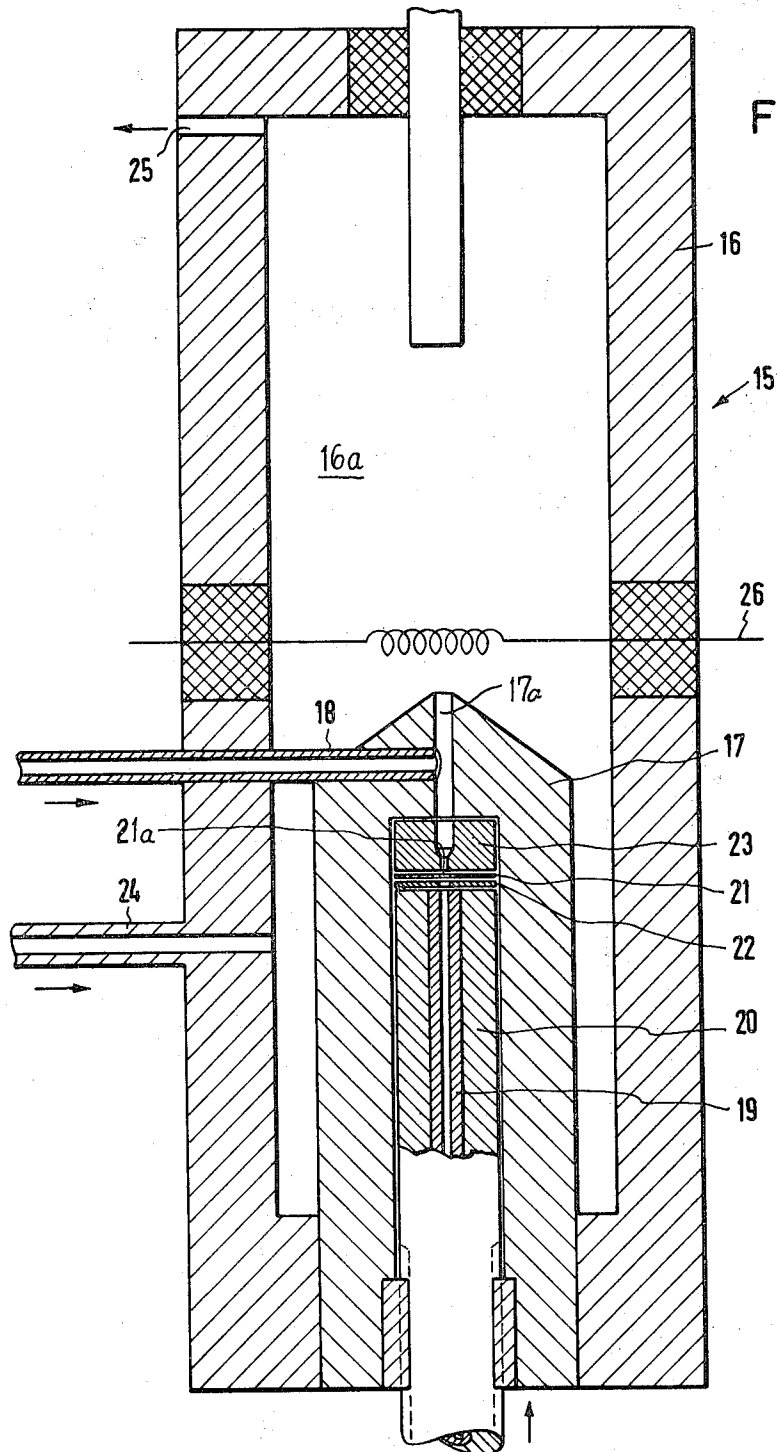


FIG. 2

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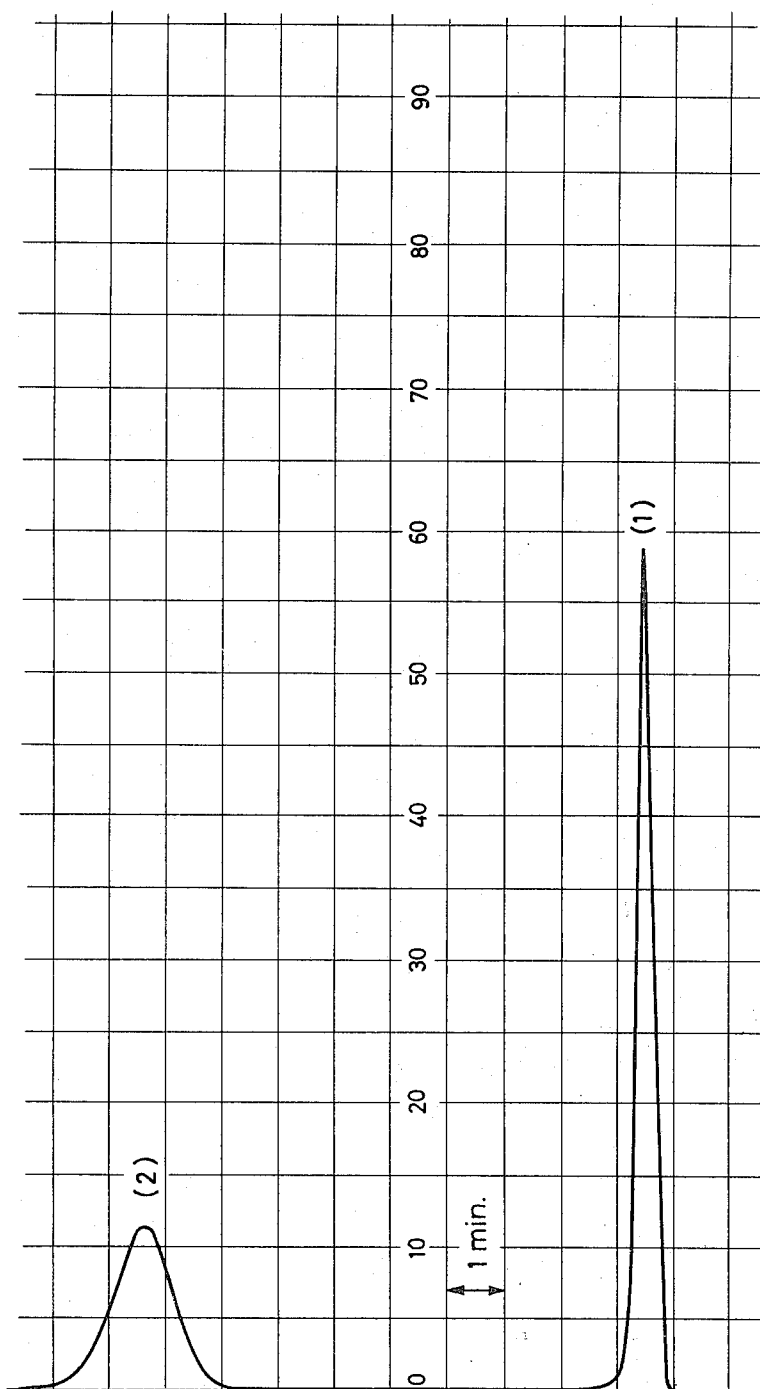
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FIG. 3



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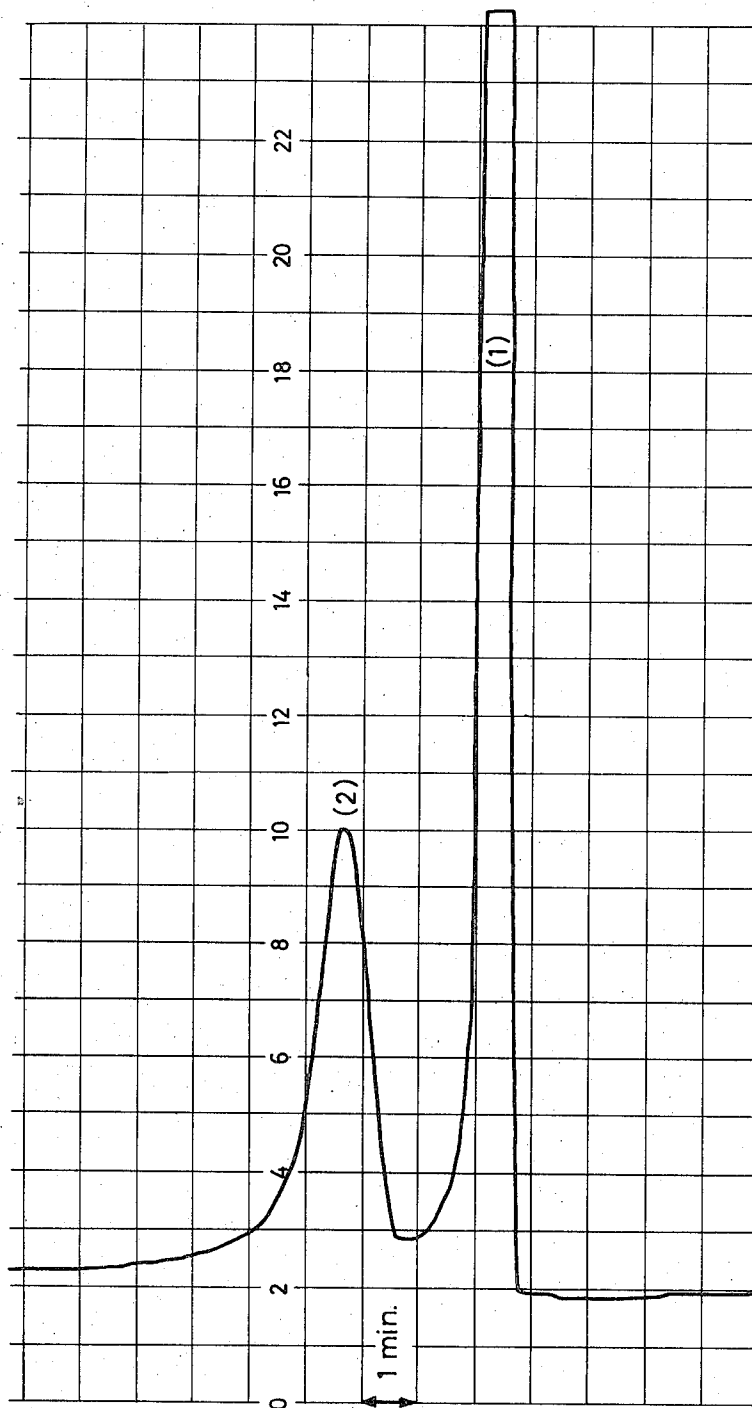
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FIG. 4



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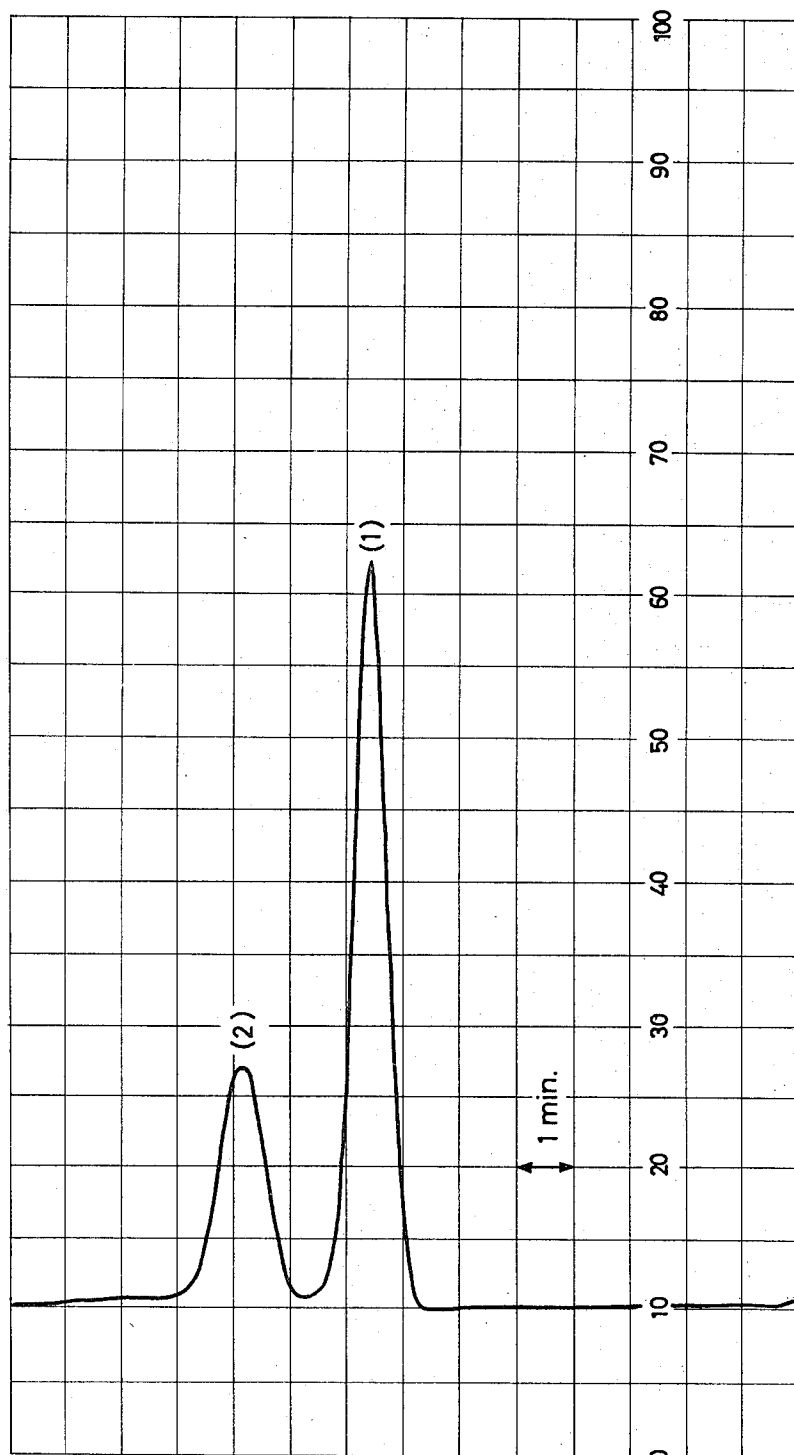
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FIG. 5



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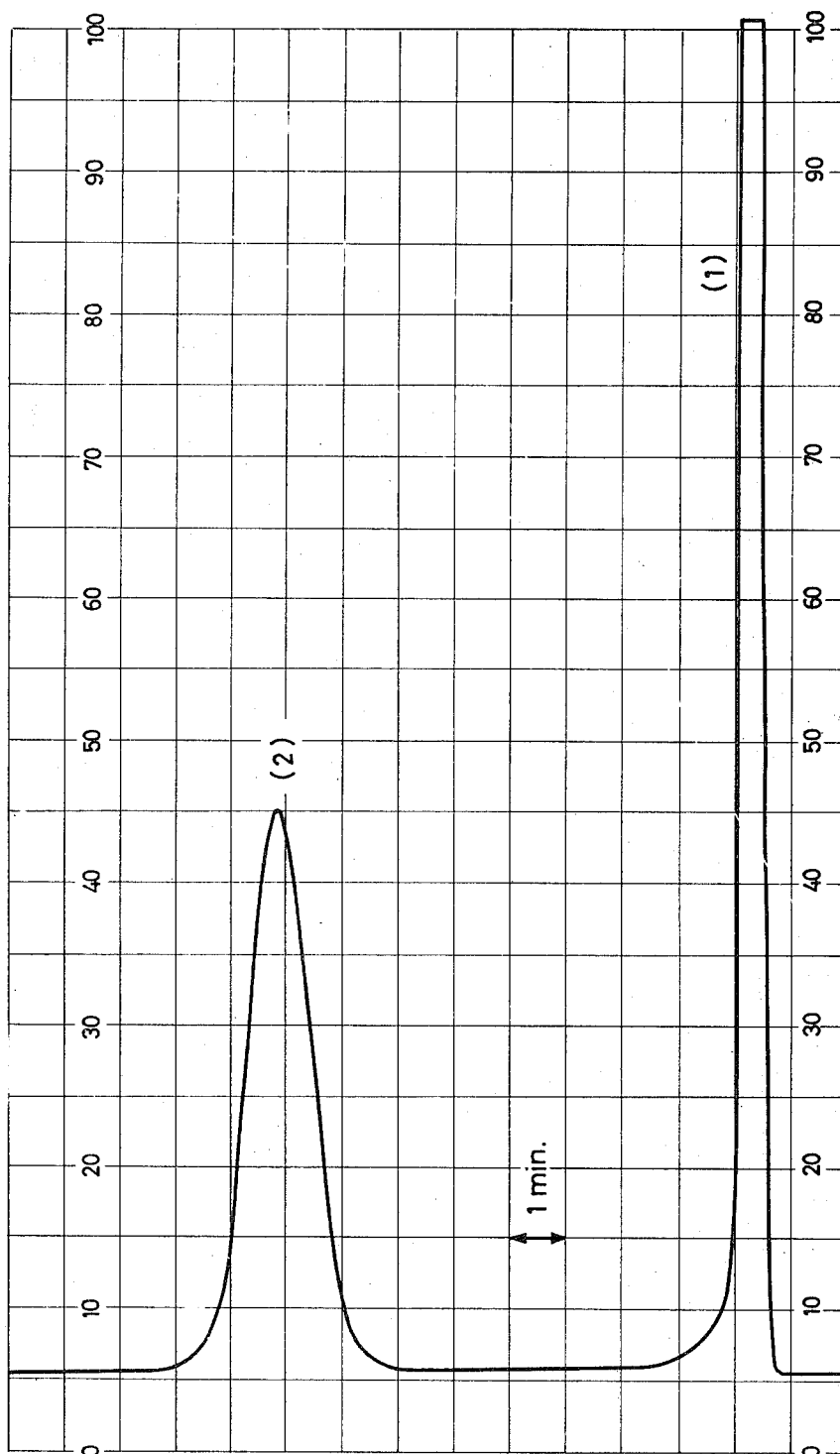
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FIG. 6



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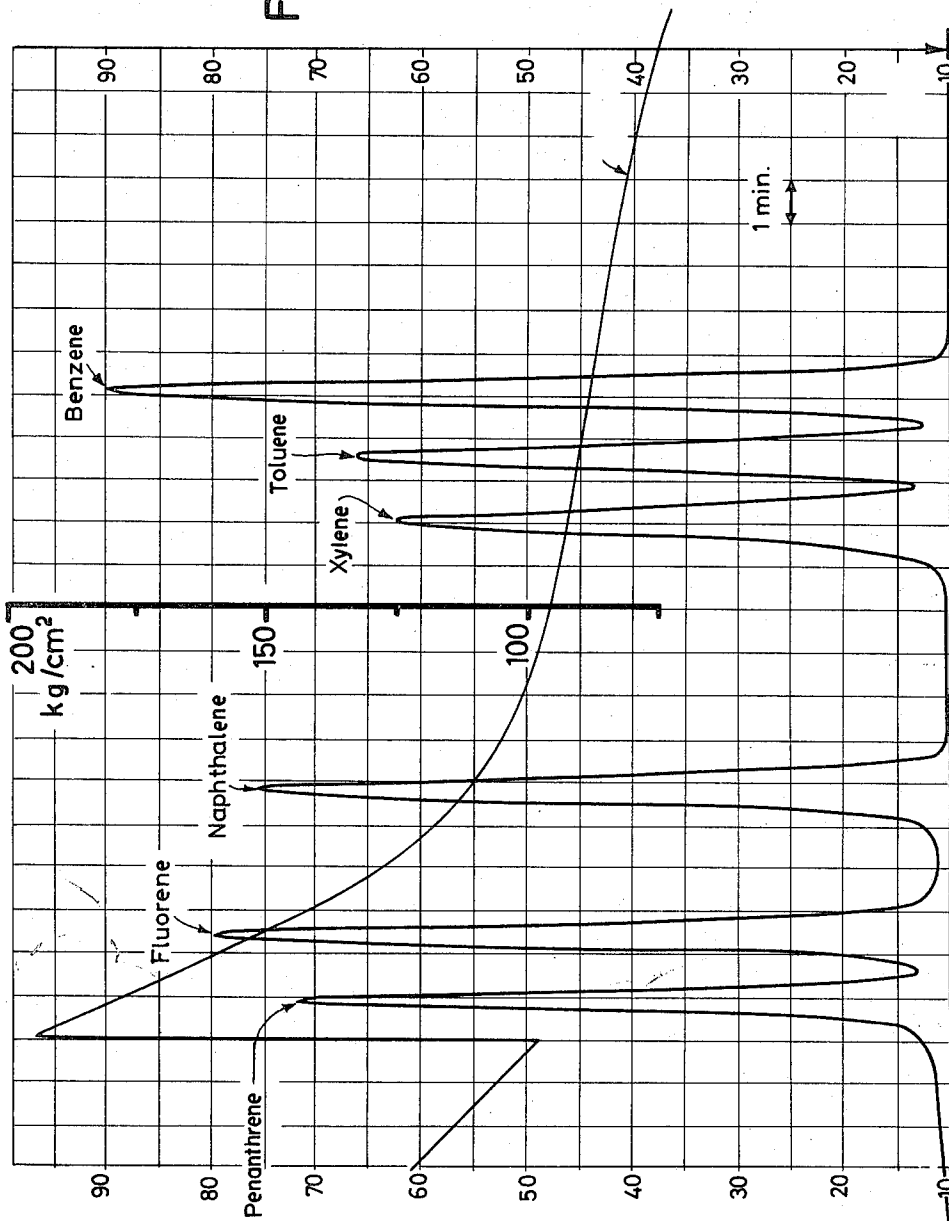
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FIG. 7



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FLAME IONIZATION DETECTOR FOR SUPERCRITICAL FLUID CHROMATOGRAPHY

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U.S. Cl. 23—254 EF

5 Claims

ABSTRACT OF THE DISCLOSURE

A flame ionization detector for use with supercritical fluid chromatography apparatus wherein the reducing valve which transforms the test gas coming from the separating column under supercritical conditions to subcritical conditions before burning at the burner nozzle, is in the form of one or more diaphragms disposed immediately upstream of the burner nozzle outlet and having central bores whose diameters are in the range from 2 to 10 microns.

BACKGROUND OF THE INVENTION

The present invention relates to a flame ionization detector for use in supercritical fluid chromatography.

It is known to use flame ionization detectors for the highly sensitive detection of substances which issue from the separating column of a gas chromatograph. This is accomplished by adding hydrogen to the carrier gas mixed with the chromatographically separated substances and burning the mixture in a burner nozzle with access to oxygen. Ions are formed by the combustion of the carbonaceous substances contained in the carrier gas so that the electrical conductivity of the flame issuing from the burner nozzle is greatly increased. By arranging two electrodes in the vicinity of the flame, one of which may be the burner nozzle, and applying a DC voltage across the electrodes, the ionic current is measured.

Difficultly volatile substances, such as particularly macromolecular substances cannot be separated, however, with the conventional method of gas chromatography. But since such substances are soluble in gases which are present in the supercritical phase, that is, above their critical temperature and pressure, they may be separated by gas chromatography, even though under high pressure, if such highly condensed supercritical gases are used as a mobile phase. This is described more fully in J. Org. Chem., 27 (1962), pp. 700-701. In this high pressure chromatography, which may be referred to as supercritical fluid chromatography, operating pressures of up to 2000 atm. are used in the separating column. In order to be able to use the flame ionization detector in this situation, the pressure and the temperature of the supercritical carrier gas, which contains the high molecular substances in dissolved form, are generally reduced by means of a reducing valve, usually in the form of a needle valve, to subcritical conditions through expansion. This is described more fully in chemie-Ingenieur-Technik, 42 (1970), p. 703, FIG. 1.

This procedure has the disadvantage that the solution of the substances in the carrier gas becomes unstable by the expansion and the substances conglomerate to flocules or other aggregates, which can become so large that a visible veil appears, and with higher substance concentrations, condensation appears additionally on the reducing valve and clogging of the adjoining pipes may result (see Science, 162 (1968), pp. 67 to 73, particularly p. 70). The importance of this disadvantage with respect

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to detecting the substances in the flame ionization detector is that the peaks recorded in the recorder are distorted by jagged spikes. These distortions are attributable to the bursting of the previously flocculated substance particles in the flame. They render the reproduction of the measurement difficult or may even make it impossible.

In order to overcome these difficulties, it is possible to operate the flame ionization detector at the pressure of the separating column, but this is not practical because the control of the fuel gases and of the flame is much too complicated in such a situation. This is the reason why this principle was only suggested for underpressures or for higher pressures up to a maximum of about 150 atm. (see J. of Chromatographic Science, 8 (1970), pp. 226-228).

It is therefore desirable to reduce the pressure in the separating column for very high operating pressures e.g. up to 2000 atm., before the carrier gas is introduced into the flame ionization detector. However, flocculation of the substances must be avoided during this necessary pressure reduction, because this flocculation is the cause of the distortions of the chromatogram, so that the single-phase system of the carrier gas issuing from the separating column should be maintained at least until the carrier gas is introduced with the molecular substance into the flame.

These conditions are accomplished with the apparatus of the present invention.

SUMMARY OF THE INVENTION

According to the present invention, the supercritical carrier gas is expanded to subcritical conditions directly upstream of the burner nozzle of the flame ionization detector by reducing the pressure with a diaphragm arrangement provided with a fine central bore positioned a short distance upstream of the burner nozzle. This has the effect that a chromatogram recorded by a potentiometric recorder indicates the substance peaks without spike distortions so that the accuracy of the recording and selectivity of the system are substantially improved.

The diameter of the central bore of a suitable diaphragm in accordance with the present invention may be in the range from 2 to 10 microns, e.g. 2.5 μ , 5 μ , or 10 μ . Such bores can be produced, for example, with a power laser. One or several such diaphragms may be installed, depending upon the operating pressure used in the separating column of the fluid chromatographic system. By way of example, using two diaphragms with 10 μ bores, the outflow velocity of CO₂ with an inlet pressure of 250 atm. is limited to 70 ml./min., an amount which does not overload the flame ionization detector. To achieve a similar reduction of the outflow velocity with an inlet pressure of 1000 atm., four diaphragms of 0.2 mm. thickness with 5 μ bores should be installed. Generally the diaphragms may be of a thickness of about 0.1 mm. or 0.2 mm. and consist preferably of platinum-iridium. The flame ionization detector is constantly heated with a 50 watt heater.

While pressure reduction by means of diaphragms instead of reducing valves is known in itself and has been suggested, for example in the field of mass spectroscopy (see Int. J. Mass Spectrum, Ion Phys. 4 (1970), pp. 9-20), it is not known to have been suggested for the purpose of feeding high-molecular substances in the nonagglomerated state to the burner nozzle of a flame ionization detector. Particularly in view of the extraordinary thermodynamic instability of nonvolatile isolated macromolecules in diluted gases, where an immediate agglomeration of the macromolecules can be expected (see Science, 162 (1968), p. 69), it is very surprising that the molecules remain distributed in the arrangement according to the invention obviously in a

metastable state, even in the expanded carrier gas, without agglomeration until they enter the burner nozzle.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic showing of a supercritical fluid chromatography system.

FIG. 2 is a sectional view of a flame ionization detector in accordance with the present invention.

FIGS. 3-7 are chromatograms obtained in the tests described in examples 1-5, respectively.

DETAILED DESCRIPTION OF THE INVENTION

A supercritical fluid chromatographic system with which the present invention may be used is shown in FIG. 1. Pressure bottle 1 contains a supply of CO₂ carrier gas and feeds this gas through a cleaning column 2, a heat-exchanger 3 for heating the CO₂, and a two-stage diaphragm compressor 4. The latter two components are bridged by a bypass valve 5 and feed the carrier gas into a temperable waterbath 12 containing the separating column system. This system contains a throttle valve 6, a buffer autoclave 7, a heat exchanger 8 and an injection block 9. The separating column itself, 11, has manometers 10 and 13 disposed at either side to indicate the pressure in the inlet line and the outlet line respectively. The outlet line is connected to a flame ionization detector 15 and also to a split valve 14.

A flame ionization detector 15 in accordance with the present invention is shown in detail in FIG. 2. In a detector housing 16 is inserted a heated burner nozzle 17 which may be made of a thick walled 4571-VA steel. Hydrogen is supplied through a capillary tube 18 into the nozzle duct 17a while a fuel gas such as synthetic air, is fed through tube 24 into the burner chamber 16a. An ignition electrode 26 is provided for initiating burning and the waste gases issued from the chamber 16a through opening 25 in the housing 16 wall.

The carrier gas issuing from the separating column 11 of the chromatographic system under high pressure conditions is fed together with the dissolved substances to the flame ionization detector 15 through a pipe element 20 containing capillary tube 19. At the transition point between the pipe 20 and the nozzle duct 17a is disposed the diaphragm arrangement of the present invention.

The arrangement comprises a thin diaphragm 21 supported just upstream of the nozzle duct 17a by a stiffening piece 23 and with a gold packing 22 on its upstream side for sealing the high-pressure chamber within pipe 20. The high pressure gas is expanded through bore 21a in diaphragm 21 to normal pressure upon entering the nozzle duct 17a. The arrangement may be adapted for various pressure gradients by varying the size of the bore 21a in the diaphragm 21 which as previously stated may be in the range from 2 to 10 microns, and/or by using a stack of several diaphragms 21, each with an interposed packing 22.

The effectiveness of operation of a flame ionization detector according to the present invention for detecting and separating various substances was tested and demonstrated in the following examples.

EXAMPLE 1

The flame ionization detector was used in the detection of 2,4-dimethyl phenol. For the test 1 μ l. (microliter) of a mixture of 50% 2,4-dimethyl phenol (2) and 50% benzene (1) was used.

Diameter of separating column: 2 mm.

Length of separating column: 3 m.

Filling of separating column: Durapak/Carbowax 400/ Porasil C, 100/120 mesh

Working conditions:

Carrier gas: CO₂

Pressure in the separating column: 155 kg./cm.²

Temperature in the separating column: 40° C.

Outflow velocity from the separating column: 2 l./min.

The flow ratio for the FID is 1:10, so that about 200 ml./min. pass through the FID.

The chromatogram obtained in this test is shown in FIG. 3.

EXAMPLE 2

Detection of di-N-decylphthalate

For the test were used 2 μ l. (microliter) of a mixture of 10% di-N-decylphthalate (2) and 90% benzene (1).

Diameter of separating column: 2 mm.

Length of separating column: 3 m.

Filling of separating column: Durapak/Carbowax 400/ Porasil C, 100/120 mesh

Working conditions:

Carrier gas: CO₂

Pressure in separating column: 300 kg./cm.²

Temperature in separating column: 60° C.

Outflow velocity for separating column: 4 l./min.

The flow ratio for the FID is 1:20, so that about 200 ml./min. pass through the FID.

The chromatogram obtained in this test is shown in FIG. 4.

EXAMPLE 3

Detection of sebacic-bis-2-ethylhexyl ester

For the test was used a benzene solution (1) containing 1 μ l. (microliter), 0.5 mg. sebacic-bis-2-ethylhexyl ester (2).

Diameter of separating column: 2 mm.

Length of separating column: 3 m.

Filling of separating column: Durapak/Carbowax 400/ Porasil C, 100/120 mesh

Working conditions:

Carrier gas: CO₂

Pressure in separating column: 244 kg./cm.²

Temperature in separating column: 40° C.

Outflow velocity from separating column: 1 l./min.

The flow ratio for the FID is 1:10, so that about 100 ml./min. pass through the FID.

The chromatogram obtained in this test is shown in FIG. 5.

EXAMPLE 4

Detection of DL-alpha-tocopherol (vitamin E)

For the test were used 2.5 μ l. (microliter) of a mixture of 25% DL-alpha-tocopherol (vitamin E) (2) and 75% acetone (1).

Diameter of separating column: 2 mm.

Length of separating column: 3 m.

Filling of separating column: Durapak/Carbowax 400/ Porasil C, 100/120 mesh

Working conditions:

Carrier gas: CO₂

Pressure in separating column: 212 kg./cm.²

Temperature in separating column: 40° C.

Outflow velocity from separating column: 4 l./min.

Outflow velocity for the FID is 1:20, so that about 200 ml./min. pass through the FID.

The chromatogram obtained in this test is shown in FIG. 6.

EXAMPLE 5

Separation of a mixture of aromatic substances: For the test is used 1 μ l. (microliter) of a mixture of benzene, toluene, xylene, naphthalene, fluorene and phenanthrene.

Dimension of separating column: 3 m. x 1/4" x 7/64"

Filling of separating column: Porasil C, Carbowax 400, 100/120 mesh

Working conditions:

Carrier gas: CO₂
 Pressure in separating column: 75-200 kg./cm.²
 Temperature in separating column: 40° C.
 Diameter of aperture in the FID-diaphragm: 10 μ
 Flow velocity through the FID-diaphragm: 40-100 ml./min.
 Volume velocity H₂: 64 ml./min.
 Volume velocity air: 340 ml./min.
 Paper feed: 1 cm./min.

The chromatogram obtained in this test is shown in FIG. 7.

Referring again to FIG. 2, it is preferred that the diaphragm 21 be disposed upstream of the burner nozzle a distance of less than 10 mm. and preferably within the range from 4 to 6 mm. from the nozzle exit.

What is claimed is:

1. Flame ionization detector, particularly for use in supercritical fluid chromatography apparatus of the type having:

- (a) a separating column for containing a test gas at supercritical conditions;
- (b) a burner nozzle having an outlet duct;
- (c) means for conducting test gas from said separating column to said burner nozzle outlet duct; and
- (d) means in said conducting means for reducing the

test gas to subcritical conditions before entering said burner nozzle outlet duct;
 the improvement wherein said reducing means comprises:
 (e) at least one diaphragm disposed upstream of said burner nozzle outlet duct and having a bore through which test gas passes, whose diameter is in the range from 2 to 10 microns.
 2. A detector as in claim 1 wherein the diameter of the bore is 5 microns.
 3. A detector as in claim 1 wherein the diaphragm is of platinum-iridium.
 4. A detector as in claim 1 wherein the diaphragm is disposed upstream a distance of less than 10 mm. from the burner nozzle outlet duct exit.
 5. A detector as in claim 4 wherein the diaphragm is disposed upstream a distance within the range from 4 to 6 mm. from the burner nozzle outlet duct exit.

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ROBERT M. REESE, Primary Examiner

U.S. Cl. X.R.

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