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(54) **MASS SPECTROMETER WITH MODULATED MOLECULAR BEAM.**

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Description

The invention relates to a mass spectrometer with modulated molecular beam.

Mass spectrometers with molecular beams are used when reactive systems in a gas phase are studied with regard to the presence of non-stable substances. In such a mass spectrometer the number of collisions to which the gas constituents are exposed on their way to the ion source of the mass spectrometer is reduced to a minimum. Since a background pressure develops in a vacuum system to which gas is constantly supplied, it is an advantage to modulate the molecular beam before it reaches the ion source. The substances in the molecular beam can then be better separated from the substances in the background by phase-sensitive detection. The principle of modulated molecular beams is also an advantage in the rapid measurement of small concentrations of stable gas constituents. This applies in particular to substances which are easily adsorbed on or desorbed from the walls of the vacuum system, which is the case with water vapour for example.

The signal-to-noise ratio in a mass spectrometer with a modulated molecular beam is determined inter alia by the background pressure which exists at the ion source. The object of the invention is to produce a higher signal-to-noise ratio by lowering the background pressure in the ion source of the mass spectrometer without the background signal being modulated in phase with the molecular beam; modulation of the background signal in fact cannot be separated from the modulation of the molecular beam.

For the purpose mentioned above, in a mass spectrometer with modulated molecular beam according to the invention, the arrangement defined in claim 1 has been provided.

According to US—A—3 801 788 a mass spectrometer is previously known wherein there is provided a chopper in the modulation chamber in front of the inlet opening of the ionizing chamber the modulation chamber is bounded by a wall in front of the inlet opening and has a skimmer for the passage of the molecular beam.

A mass spectrometer arranged in this manner according to the present invention provides an exceptionally good signal-to-noise ratio which is not restricted by the finite dynamic range of the detector-signal amplifiers.

To illustrate the invention, one embodiment of the mass spectrometer arranged according to the invention will be described in more detail below with reference to the accompanying drawings in which

FIG. 1 is a front view of the mass spectrometer,

FIG. 2 is a cross sectional view on the line II—II in FIG. 1, and

FIG. 3 is a cross sectional view on the line III—III in FIG. 2.

The mass spectrometer comprises a first vacuum chamber 10 with a flange 11 for connection of a vacuum pump and with a flange 13 for connection of a pipe 12 through which the gas to be studied is supplied in conventional manner. To form a molecular beam, the chamber has a conical nozzle 14 communicating with the pipe 12 and having an inlet in the tip of the cone in the usual manner. The diameter of the opening depends on what pressure is present at the outside of the nozzle, but the size thereof is generally of the order of 0.1 mm. For the creation of a molecular beam it is necessary for the vacuum pump connected to the flange 11 to maintain a pressure in the chamber of about 13×10^{-3} Pascal or lower.

Another vacuum chamber 15 is defined inside the vacuum chamber 10 with which it communicates through a conical so-called skimmer 16 which is disposed coaxially with the nozzle 13. The size of the opening in the tip of the cone on the skimmer is of the order of 1 mm. A flange 18 is provided on the vacuum chamber 15 for the connection of a vacuum pump, and in this chamber a pressure of 13×10^{-5} to 13×10^{-7} Pascal is maintained.

The first and second vacuum chambers 10 and 15, respectively, together form a molecular beam but in certain cases, namely if the gas which is to be studied has a sufficiently low pressure or is a fairly inactive gas, the first vacuum chamber 10 could be omitted, provided, however, that a sufficiently small opening can be formed in the tip of the cone of the skimmer 16. Thus, the vacuum chamber 10 can be regarded as an ante-chamber and the vacuum chamber 15 as the actual beam-forming chamber.

Disposed centrally in the mass spectrometer is a cylindrical third vacuum chamber 19 which constitutes the ionizing chamber of the mass spectrometer and which is mainly surrounded by the vacuum chamber 15 but also to minor extent by the vacuum chamber 10. The third vacuum chamber has a flange 20, FIG. 3, for the connection of a vacuum pump, and in this chamber a pressure of 13×10^{-7} to 13×10^{-9} Pascal should be maintained which should be compared with the pressure of 13×10^{-5} Pascal which is obtained in today's typical mass spectrometers with only two vacuum chambers. Inside the chamber 19 there is the ion source 21 of the mass spectrometer, which is preferably mounted so as to be rotated as well as displaced. In the present case it is assumed that the ion source is adapted for photoionization with laser beams, and for this purpose there is connected to the chamber 19 a tube 22 with a window 23 to direct a laser beam into the ion source. Other forms of ionization may, however, be provided in the mass spectrometer according to the invention. The chamber 19 is in communication with the chamber 15 through two diametrically opposite diaphragms, a "front one" 24 and a "back one" 25, and these diaphragms are adjustable so that the aperture can be adjusted. As can be seen from FIG. 2, the molecular beam, which is indicated by dot and dash lines 26, passes through the third vacuum chamber 19 and through the ion source 21 situ-

ated therein. The diaphragms are movable perpendicular to the molecular beam and have an aperture diameter of about 2 mm, but the aperture diameter of the front diaphragm 24 can be made somewhat smaller than that of the back one since the diameter of the molecular beam increases. Deflection grids, mass filters, detectors and multipliers can be mounted in the chamber 19 by means of a flange 27 or be mounted in the chamber in another manner but these elements, which may be of conventional construction, have not been shown in the drawings and will not be described in detail because they are immaterial to the invention. It will be pointed out, however, that if the mass filter is located at right angles to the molecular beam, the mass detector and the multiplier will be protected from the emitted substance in known manner. Moreover, the aperture diameter of the back diaphragm 25 can be kept down.

Disposed in the chamber 15, the second vacuum chamber of the mass spectrometer, is a motor-driven chopper 28 of any type for modulation of the molecular beam before it passes into the third chamber 19 through the front diaphragm 24. Thus, the molecular beam always is terminated in the chamber 15, as a result of which the background pressure in the chamber 15, which is determined by the molecular beam and the effusive flow from the first vacuum chamber 10, is roughly constant. With a purely effusive molecular beam, the background pressure is of the order of magnitude of 13×10^{-7} Pascal, whereas with so-called "free-jet" expansion, the pressure in the molecular beam may rise by two orders of magnitude which means that the background pressure in the chamber 15 is close to 13×10^{-5} Pascal.

Disposed in the path of the molecular beam in the chamber 15, after the back diaphragm 25, is a reflector 29 which is constructed in the form of a pivotal wing which is adjustable at any angle. This reflector can be utilized to adjust the effusive inflow into the chamber 19 from the chamber 15 in the best manner. The reflector compensates for the modulation of the background pressure which may occur as a result of diffuse molecule dispersion from the chopper 28 and related effusive inflow through the front diaphragm 24. The molecules scattered diffusely from the reflector and the effusive inflow through the back diaphragm 25 are phase-shifted by 180° in relation to those which are scattered from the chopper. Thus, the inflow variation as a result of the different termination points of the molecular beam before or after the chamber 19 and the varying size of the diaphragms 24 and 25 can be reduced to a minimum by suitable selection of chopper frequency and reflector angle.

Disposed immediately in front of the back diaphragm 25 in the chamber 15 is a window 30 for ruling. Furthermore, flanges 31 are provided for the connection of pressure gauges to the three chambers as well as flanges 32 for the connection of manipulators by means of which the diaphragms 24 and 25 and the reflector 29 can be adjusted.

It is clear from the above description that no molecules are held up in the third vacuum chamber 19 as a result of which the background signal is prevented from being modulated with the chopper frequency which in turn means that this signal is not measured. In other words, balanced molecule conditions are obtained in the chamber 19. Compared with present-day typical mass spectrometers with only two vacuum chambers, an improvement in the signal-to-noise ratio and hence in the measuring sensitivity of the order of 10—100 times is achieved by the arrangement according to the invention depending on the background pressure at the mass number being examined and the possibility for stray ions to reach the mass detector.

The mass spectrometer according to the invention, like the mass spectrometers now common with two vacuum chambers, can be used for the study of both non-stable substances and stable substances. A particularly interesting application is as a detector in a gas chromatograph, in which case a more sensitive system can be obtained by correct adaptation between chromatograph and spectrometer. Particularly in the diagnosis of combustion and emission, the mass spectrometer according to the invention may be expected to provide the possibility of improved mapping out of the complex reaction stages.

Claims

1. A mass spectrometer with a modulated molecular beam, comprising a modulation chamber (15) with a gas inlet (16) and a connection (18) to a vacuum pump for producing a molecular beam (26), an ionization chamber (19) containing the ion source (21) of the mass spectrometer and having a connection (20) to a vacuum pump to produce a lower pressure in the ionization chamber (19) than in the modulation chamber (15), and a chopper (28) in the modulation chamber for modulating the molecular beam supplied to the ionization chamber, characterized in that the ionization chamber (19) is at least partially surrounded by the modulation chamber (15) and communicates directly with the surrounding portion of the modulation chamber through front and back openings (24, 25) in the path of the molecular beam (26), which openings have the minimum possible conductance but are sufficiently large to permit passage of the molecular beam, the chopper (28) being disposed in front of the front opening (24) for the entry of the molecular beam into the ionization chamber.

2. A mass spectrometer as claimed in claim 1, characterized in that disposed in the modulation chamber (15) in front of the back opening (25) is a reflector (29) which can be adjusted to various angular positions, for the molecular beam (26) emerging from the ionization chamber (19) to balance out periodic variations in the background

pressure at the ion source, caused by the chopper (28).

3. A mass spectrometer as claimed in claim 1 or 2, characterized in that the openings (24, 25) consist of adjustable diaphragms disposed at right angles to the molecular beam (26).

4. A mass spectrometer as claimed in one of the claims 1 to 3, characterized in that the modulation chamber (15) communicates through a skimmer (16) with an ante-chamber (10) with a gas inlet (14) and a connecton (11) to a vacuum pump.

Revendications

1. Spectromètre de masse comportant un faisceau moléculaire modulé, comprenant une chambre de modulation (15) avec une entrée de gaz (16) et un raccordement (18) avec une pompe à vide pour produire un faisceau moléculaire (26), une chambre d'ionisation (19) contenant la source d'ions (21) du spectromètre de masse et ayant un raccordement (20) avec une pompe à vide pour produire, dans la chambre d'ionisation (19), une pression inférieure à celle de la chambre de modulation (15), et un obturateur périodique (28) dans la chambre de modulation destiné à moduler le faisceau moléculaire envoyé dans la chambre d'ionisation, caractérisé en ce que la chambre d'ionisation (19) est, au moins partiellement, entourée par la chambre de modulation (15) et communique directement avec la portion de la chambre de modulation qui l'entoure par des ouvertures antérieure et postérieure (24, 25) situées sur le trajet du faisceau moléculaire (26), ouvertures qui présentent la conductance minimale possible, mais sont suffisamment grandes pour permettre le passage du faisceau moléculaire, l'obturateur (28) étant disposé en face de l'ouverture antérieure (24) permettant l'entrée du faisceau moléculaire dans la chambre d'ionisation.

2. Spectromètre de masse selon la revendication 1, caractérisé en ce qu'il comprend, disposé dans la chambre de modulation (15) en face de l'ouverture postérieure (25), un réflecteur (29) qui peut être ajusté sur différentes positions angulaires, pour que le faisceau moléculaire (26) sortant de la chambre d'ionisation (19) compense les variations périodiques de la pression de base régnant au niveau de la source d'ions, dues à l'obturateur périodique (28).

3. Spectromètre de masse selon la revendication 1 ou 2, caractérisé en ce que les ouvertures (24, 25) consistent en des diaphragmes ajustables disposés perpendiculairement au faisceau moléculaire (26).

4. Spectromètre de masse selon l'une des revendications 1 à 3, caractérisé en ce que la chambre de modulation (15) communique par un calibreur (16), avec une anti-chambre (10) comportant une entrée de gaz (14) et un raccordement (11) avec une pompe à vide.

Patentansprüche

1. Massenspektrometer mit einem modulierten Molekularstrahl, der eine Modulationskammer (15) mit einem Gaseinlaß (16) und einer Verbindung (18) zu einer Vakuumpumpe zur Erzeugung eines Molekularstrahls (26), eine Ionisationskammer (19), die die Ionenquelle (21) des Massenspektrometers enthält und eine Verbindung (20) zu einer Vakuumpumpe zur Erzeugung eines geeknüber dem Druck in der Modulationskammer (15) geringeren Druckes in der Ionisationskammer (19) hat, und einen Zerhacker (28) in der Modulationskammer zur Modulation des in die ionisationskammer eingeführten Molekularstrahls aufweist, dadurch gekennzeichnet, daß die Ionisationskammer (19) zumindest teilweise durch die Modulationskammer (15) umgeben ist und direkt mit dem umgebenden Teil der Modulationskammer über Vorder- und Hinteröffnungen (24, 25) im Strahlengang des Molekularstrahls (26) in Verbindung steht, wobei die Öffnungen den geringstmöglichen Leitwert haben, aber hinreichend groß sind, um den Durchgang des Molekularstrahls zu erlauben, und daß der Zerhacker (28) vor der Vorderöffnung (24) für den Eintritt des Molekularstrahls in die Ionisationskammer angeordnet ist.

2. Massenspektrometer nach Anspruch 1, dadurch gekennzeichnet, daß innerhalb der Modulationskammer (15) vor der Hinteröffnung (25) ein in verschiedenen Winkelstellungen einstellbarer Reflektor (29) für den aus der Ionisationskammer (19) austretenden Molekularstrahl (26) zum Ausgleich von durch den Zerhakker (28) verursachten, periodischen Änderungen im Hintergrunddruck der Ionenquelle angeordnet ist.

3. Massenspektrometer nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Öffnungen (24, 25) aus verstellbaren Membranen bestehen, die im rechten Winkel zum Molekularstrahl (26) angeordnet sind.

4. Massenspektrometer nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Modulationskammer (15) über einen Abstreifer (16) mit einer Vorkammer (10) in Verbindung steht, die einen Gaseinlaß (14) und eine Verbindung (11) zu einer Vakuumpumpe aufweist.

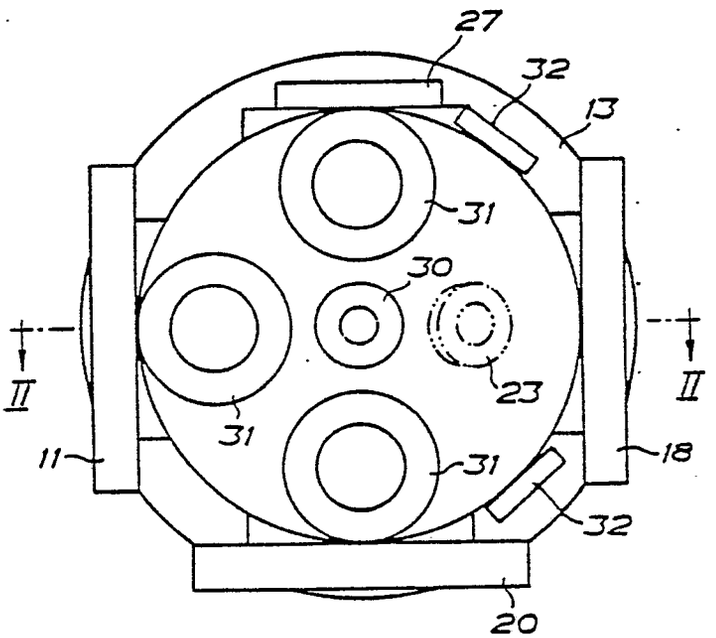
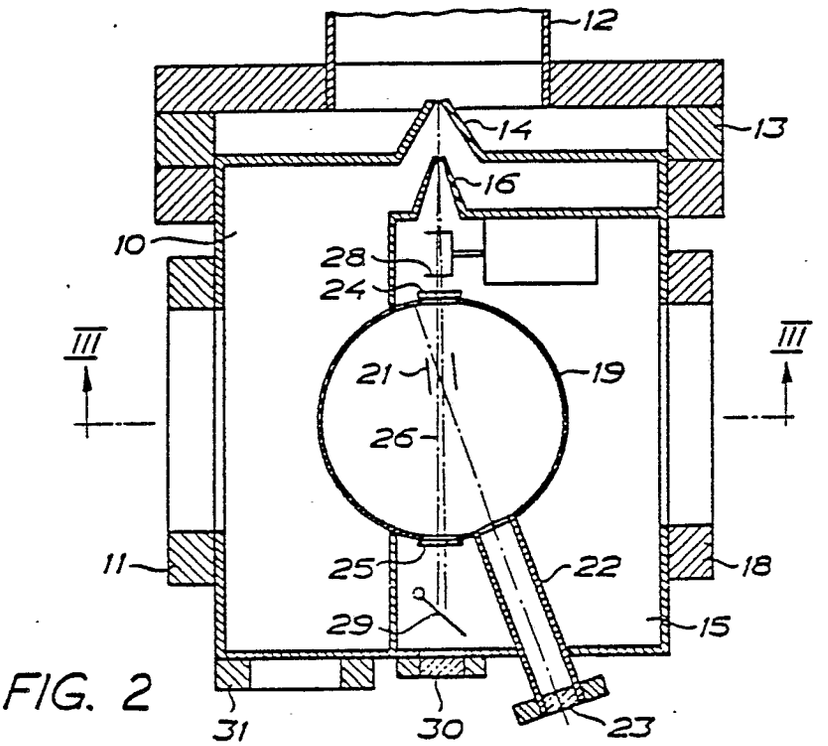


FIG. 1


12
13
14
16
10
28
24
III
III
21
19
26
11
25
22
18
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31
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23

FIG. 2

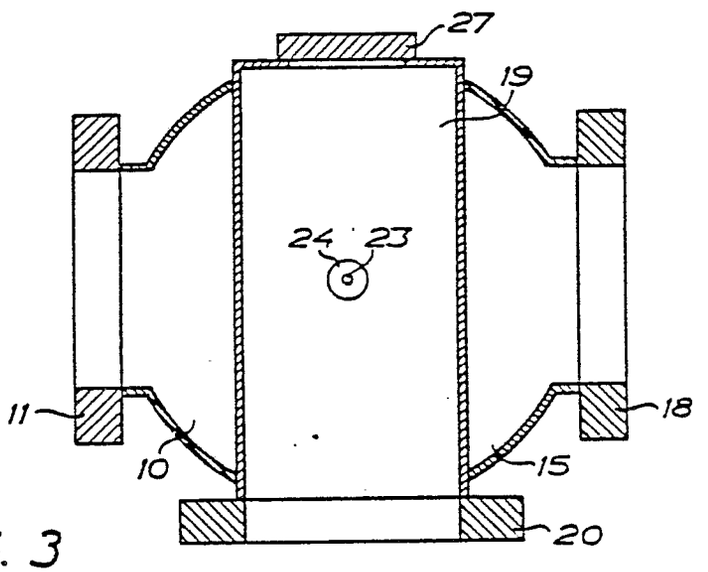
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FIG. 3