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(54) **ION SOURCE**

(57) The object of the present invention is an ionic source, preferably the ionic source of a mass spectrometer the inner walls of which are coated with a high density graphite material.

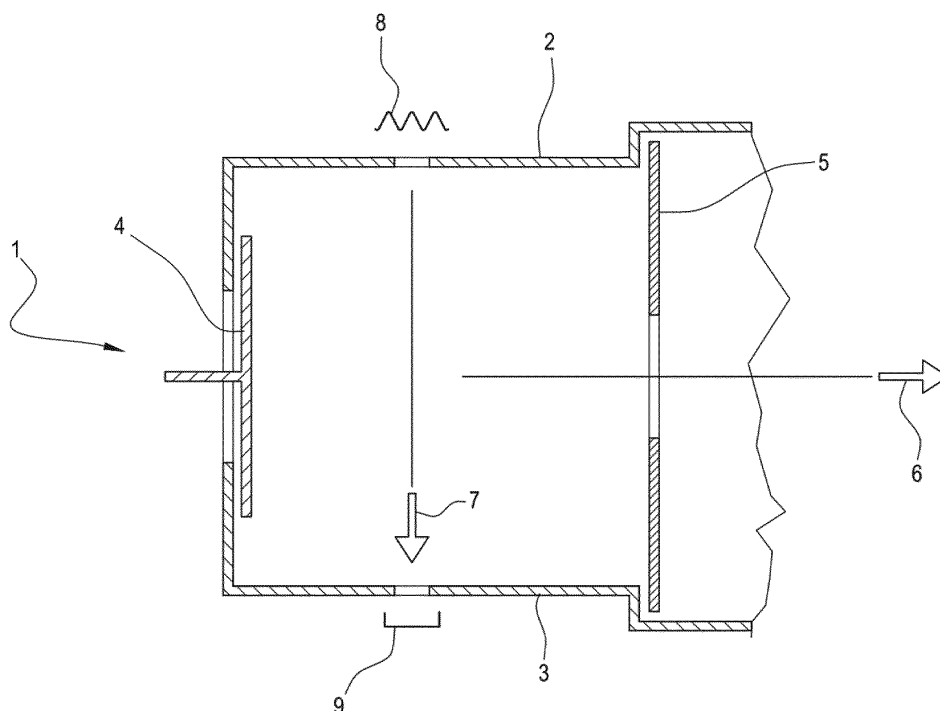


FIG.1

Description

[0001] The object of the present invention is an ionic source the inner walls of which are coated with a high density graphite material.

PRIOR ART

[0002] Mass spectrometry is a technique that is widely used for qualitative and quantitative analysis of substances and mixtures of substances, even complex mixtures of substances. Mass spectrometers are often used as detectors coupled with a gas chromatograph (GC-MS system). In one mass spectrometer, the ionic source has the function of receiving the substances to be analyzed, ionizing and sending the substances to be analyzed - after they have been ionized and fragmented - to the other components of the spectrometer that select the ions according to the mass-load ratio thereof.

[0003] An ionic source is made up of an ionization chamber, inside which a beam of electrons emitted by a heated filament flows through a sample to be ionized and then impinges on a collector, and by a system for acceleration of the ions produced in the chamber. The ion sources most used are electronic ionization (EI) or chemical ionization (CI) sources. In an electronic ionization (EI) ionic source, a beam of electrons (emitted by an incandescent metal filament) passes through the chamber, colliding with the substance to be analyzed contained in the same chamber, bringing about the ionization and fragmentation thereof. In a chemical ionization ionic source on the other hand, ionization of the substance to be analyzed is mediated by the presence of a reagent gas.

[0004] The walls of the ionization chambers of both the electronic ionization and chemical ionization ionic sources are generally made of electrically and thermally conductive materials such as for example stainless steel. These materials meet given requirements, including: stability at operating temperatures, chemical inertia, electrical and thermal conductivity.

[0005] In the industry, it is known to make or coat the inner walls of the ionization chambers with different materials to limit the surface contamination thereof and maintain high instrument performance.

[0006] For example, US patent application 2013/0299691 discloses a mass spectrometer in which the ionic source is coated with various materials, for example metallic carbides and borides, ceramic materials or DLC, an amorphous carbon material, for the purpose of preventing or limiting contamination of the surfaces of the chamber.

[0007] It is further known that in certain operating conditions, the inner walls of the ionization chamber can lead to undesired reactions that significantly alter the spectra of the analyzed substances.

[0008] Patent application WO2016/083964 discloses an ionic source in which the inner walls of the ionization chamber are coated with at least one layer of graphene. This ionic source enables the spectral distortions to be minimized that are due to the interaction between the walls of the ionization chamber and the samples of substances to be analyzed when the mass spectrometer is used as a detector in a GC-MS system that uses hydrogen as a carrier gas and in addition enables the response of the GC-MS instrument to certain substances to be improved, improving the shape and height of the peaks associated therewith.

[0009] This solution is effective for attenuating the spectral alterations of a large number of organic substances; nevertheless, certain classes of particularly reactive substances, such as the nitro compounds, can have an alteration of the mass spectrum also through the use of the ionization chambers disclosed in WO2016/083964; and further, also using the ionic source disclosed in WO2016/083964, the response and the sensitivity of the GC-MS system can be reduced in relation to high-boiling organic substances that contain medium-long chain hydrocarbons in the molecular structure.

[0010] In this context, there is the need to have at one's disposal an ionic source for a mass spectrometer that minimizes the alterations of the spectrum of the analyzed organic substances due to the interaction of the inner walls of the ionic source with said substances.

[0011] In particular, the need is felt to dispose of an ionic source that minimizes alterations to the spectrum and the response of specific organic substances, such as nitro compounds and the high-boiling organic substances containing hydrocarbons, in particular medium-long chain hydrocarbons.

[0012] Further, in the industry, the need is felt to dispose of an ionic source that is able to solve the problem indicated above when the analyses are conducted on a gaseous sample comprising not only hydrogen but also further gases normally used as carrier gases for the GC-MS analysis, such as for example nitrogen and the noble gases.

SUMMARY OF THE INVENTION

[0013] A first aspect of the present invention accordingly relates to an ionic source comprising:

- (i) an ionization chamber;

- (ii) at least one repeller electrode; and
- (iii) an outlet wall,

characterized in that the inner surface of at least one of the elements (i) - (iii) comprises at least one graphite material having a density of 1.65 - 2.26 g/cm³.

[0014] The present invention further relates to a mass spectrometry method comprising:

- (a) ionizing in the ionic source as disclosed above a sample, which is preferably gaseous, comprising at least one organic substance, producing ions; and
- (b) analyzing the ions produced in the ionic source according to the mass - load ratio thereof.

[0015] The present invention further relates to a gas chromatography-mass spectrometry method comprising:

- (A) setting up a first gaseous sample comprising at least one analyte and at least one carrier gas chosen from hydrogen, nitrogen, at least one noble gas and mixtures thereof;
- (B) setting up a separation column comprising at least one stationary phase that is able to selectively adsorb said at least one analyte;
- (C) introducing the first sample at one end of the separation column and allowing the sample to flow through the column, thus obtaining at least one second gaseous sample;
- (D) ionizing said at least one second gaseous sample in one mass spectrometer comprising an ionic source as disclosed above, producing ions; and
- (E) analyzing the ions produced according to the mass-load ratio thereof.

DESCRIPTION OF THE FIGURES

[0016]

Figure 1 is a diagram of an ionic source according to a preferred embodiment of the present invention.

Figure 2 shows some chromatograms of the isopropyl myristate acquired by using different ionic sources: in Figures 2B and 2C the chromatograms are shown that were acquired using ionic sources according to the invention, as disclosed in Example 2 and in Example 3, respectively.

Figure 2A shows the chromatogram of the isopropyl myristate acquired using an ionic source modified with low-density graphite, not according to the invention, as disclosed in Example 1 by way of comparison.

Figure 3 shows some spectra of the 1-tert-butyl-2-methoxy-4-methyl-3,5-dinitrobenzene: in Figure 3A the spectrum acquired in the conditions disclosed in Example 4 is shown, in Figure 3B the spectrum acquired in the conditions disclosed in Example 5 is shown.

Figure 4 shows the chromatograms obtained following the GC-MS analysis of certain phthalates, recorded as shown in Examples 6 and 7.

DETAILED DESCRIPTION OF THE INVENTION

[0017] In the context of the present invention, the term "graphite material" refers to a material consisting essentially of graphite carbon (apart from the impurities that are inevitably present), i.e. a material in which the carbon is in graphite allotropic form regardless of the presence of possible structural defects. The graphite material used to implement the present invention is a material characterized by a long-range crystalline structure, preferably in the three dimensions, that is determinable by a diffractometry analysis.

[0018] In the context of the present invention, the term "density" refers to the apparent density of the graphite material, determined as indicated above.

[0019] The term "inner surface" refers in the present description and in the attached claims to the surface of an element, in particular of at least one of the elements (i)-(iii), which is in contact with the sample subjected to ionization in the ionic source.

[0020] In the context of the present invention, the term "high-boiling organic substance" relates to an organic substance with a boiling point greater than or equal to 250°C, preferably greater than or equal to 300°C, measured at a pressure of about 0.1 MPa.

[0021] In the context of the present invention, the term "medium-long chain hydrocarbon" refers to a saturated or unsaturated cyclic or acyclic linear or branched hydrocarbon containing at least 6, preferably at least 8 carbon atoms.

[0022] In the context of the present invention, the term "nitro compound" refers to an organic compound comprising at least one NO₂ group linked to a carbon atom.

[0023] A first aspect of the present invention relates to an ionic source, in particular to an ionic source for a mass spectrometer, comprising:

- (i) an ionization chamber;
- (ii) at least one repeller electrode (also called "repeller"); and
- (iii) an outlet wall,

characterized in that the inner surface of at least one of the elements (i) - (iii) comprises at least one graphite material having a density of 1.65 - 2.26 g/cm³.

[0024] Preferably, the graphite material that is useful for implementing the present invention does not comprise amorphous carbon, in particular the graphite material useful for implementing the present invention does not comprise DLC (diamond-like carbon).

[0025] Preferably, the graphite material can have a density of about 1.80-2.26 g/cm³, preferably 1.80-2.25 g/cm³.

[0026] The inner surface of at least one of the elements (i) - (iii) can consist of at least one graphite material as disclosed above.

[0027] The graphite material having a density of 1.65 - 2.26 g/cm³ can be chosen from polycrystalline graphite, preferably isotropic polycrystalline graphite, and pyrolytic graphite, preferably highly oriented pyrolytic graphite.

[0028] Polycrystalline graphite is a graphite material with consistent crystallographic domains (crystalline grains) of limited size. Polycrystalline graphite can be obtained by graphitization at high temperature of a carbon material. Preferably, the polycrystalline graphite can be isotropic, i.e. it is possible for it not to have a preferential crystallographic orientation of the microstructure and thus have the same chemical-physical properties in all directions. The isotropic polycrystalline graphite can be obtained by pressing in a uniform manner (isostatic pressing) the carbon material during the graphitization process. Polycrystalline graphite and isotropic polycrystalline graphite are commercially available graphite materials. Polycrystalline graphite, optionally isotropic polycrystalline graphite, is easy to work and enables layers of graphite material to be made that also have complex geometries.

[0029] Pyrolytic graphite is a graphite material with a high degree of crystallographic orientation along the axis that is perpendicular to the surface of the material. Pyrolytic graphite can be obtained by graphitization of the pyrolytic carbon or by CVD (Chemical Vapour Deposition) at temperatures above about 2,500°K (about 2,227°C). The highly oriented pyrolytic graphite can be obtained by chemical vapour deposition at temperatures of about 3,300°K (about 3,027°C), with suitable hot pressing processes to develop the orientation of the planes. The CVD processes for obtaining the pyrolytic graphite and the highly oriented pyrolytic graphite are *per se* known in the prior art.

[0030] Pyrolytic graphite, which is optionally highly oriented, generally has a higher density than polycrystalline graphite. It is further characterized by very low surface porosity.

[0031] The graphite materials can have extremely variable density, depending on the process conditions in which they are obtained; for example polycrystalline graphites are commercially available with density of 1.30 g/cm³. Nevertheless, it has been observed experimentally that only graphite materials having densities in the ranges indicated above can be used to reduce the spectrum alterations and/or to increase the sensitivity of the mass spectrometers in relation to nitro compounds and organic compounds containing medium-long chain hydrocarbons.

[0032] In one embodiment, the graphite material can be polycrystalline graphite having a density of about 1.65-2.00 g/cm³, preferably about 1.80-2.00 g/cm³.

[0033] In one embodiment, the graphite material can be pyrolytic graphite having a density of about 2.00 - 2.26 g/cm³, preferably about 2.00 - 2.25 g/cm³, preferably about 2.15 - 2.23 g/cm³.

[0034] In one embodiment, the graphite material can be polycrystalline graphite, preferably isotropic polycrystalline graphite, the inner surface of which can be at least partially coated by pyrolytic graphite, optionally by highly oriented pyrolytic graphite. Preferably, the inner surface of the polycrystalline graphite can be completely coated by pyrolytic graphite. The Applicant has surprisingly observed that when the graphite material has the features disclosed above, the ionic source according to the invention can be used for mass spectrometry of organic substances that are reactive to materials constituting conventional ionic sources.

[0035] In particular, the ionic source as disclosed above can be advantageously used for ionization of high-boiling organic substances containing medium-long chain hydrocarbons, nitro compounds and mixtures thereof, minimizing the alteration of the mass spectrum and/or the loss of sensitivity of the instrument for the analyzed substances due to the interaction of the substances with the inner surfaces of the ionic source.

[0036] The ionic source according to the invention comprises:

- (i) an ionization chamber; and/or
- (ii) at least one repeller electrode; and/or
- (iii) an outlet wall

in which

- at least one of the elements (i)-(iii) can be made entirely of graphite material, or consist of graphite material; and/or
- the inner surface of at least one of the elements (i)-(iii) can be at least partially coated by at least one layer comprising the (or consisting of the) graphite material.

[0037] In one embodiment, the at least one repeller electrode (ii) can be made entirely of a graphite material as disclosed above.

[0038] In one embodiment, the at least one repeller electrode (ii) and the outlet wall (iii) can be made entirely of a graphite material as disclosed above. According to one embodiment, all the elements (i)-(iii) can be made entirely of a graphite material as disclosed above.

[0039] At least one of the elements (i)-(iii) can be made entirely of or consist of, a graphite material chosen from polycrystalline graphite, pyrolytic graphite and polycrystalline graphite the inner surface of which is at least partially coated with at least one layer comprising pyrolytic graphite.

[0040] Preferably, the graphite material can be isotropic polycrystalline graphite, optionally at least partially, preferably completely, coated with at least one layer comprising pyrolytic graphite, optionally highly oriented pyrolytic graphite.

[0041] Alternatively, at least one of the elements (i)-(iii) can be made entirely of or consist of, pyrolytic graphite (bulk), the inner surface of which can be optionally at least partially, preferably completely, coated with at least one layer comprising pyrolytic graphite, in which said at least one layer can be preferably, but not exclusively, obtained by chemical vapour deposition (CVD) .

[0042] In these embodiments, the at least one layer of optionally highly oriented pyrolytic graphite can be obtained by depositing a gaseous precursor of graphite carbon on the graphite material by CVD (Chemical Vapour Deposition) and subsequently graphitizing.

[0043] According to this embodiment, the elements (i)-(iii) of the ionic source can be made with shapes and dimensions that are *per se* known in the industry, that are optionally configured to replace identical elements of ionic sources found on the market.

[0044] In one embodiment, the inner surface of at least one of the elements (i)-(iii) can be at least partially coated by at least one layer comprising the (or consisting of the) graphite material as disclosed above.

[0045] Preferably, the inner surface of the ionization chamber (i) can be at least partially coated with at least one layer comprising the graphite material; more preferably the inner surface of the ionization chamber (i) and of the at least one repeller electrode (ii) can be at least partially coated by at least one layer comprising the graphite material; still more preferably the inner surface of all the elements (i)-(iii) can be at least partially coated with at least one layer comprising the graphite material.

[0046] The inner surface of at least one of the elements (i)-(iii) can be completely coated with at least one layer comprising the graphite material as disclosed above. Preferably, the inner surface of the ionization chamber (i) can be completely coated by at least one layer comprising the graphite material; more preferably, the inner surface of the ionization chamber (i) and at least one repeller electrode (ii) can be completely coated by at least one layer comprising the graphite material; still more preferably, the inner surface of all the elements (i)-(iii) can be completely coated by at least one layer comprising the graphite material.

[0047] The at least one layer comprising the (or consisting of the) graphite material can be chosen from polycrystalline graphite, preferably isotropic polycrystalline graphite; polycrystalline graphite, the inner surface of which is at least partially, preferably completely, coated with pyrolytic graphite and preferably highly oriented pyrolytic graphite.

[0048] In one embodiment, the layer of graphite material can have a total thickness of less than or equal to about 2.5 mm, preferably comprised between about 50 micron and about 2.5 mm.

[0049] In one embodiment, the graphite material can be a layer comprising polycrystalline graphite, preferably isotropic polycrystalline graphite having a thickness of less than or equal to about 2.5 mm, preferably about 0.4 - 1.5 mm.

[0050] In one embodiment, the graphite material can be a layer comprising pyrolytic graphite having a thickness less than or equal to about 2.5 mm, preferably about 0.4 - 1.5 mm.

[0051] In one embodiment, the graphite material can be a layer of pyrolytic graphite, preferably high density, having a thickness that is less than or equal to about 500 micron, preferably less than or equal to about 300 micron, more preferably about 50-100 micron. In this embodiment the pyrolytic graphite can be deposited as a thin layer by CVD onto polycrystalline graphite or onto a further layer of non graphite material having the function of a support as disclosed below.

[0052] The layer comprising graphite material can be an insert, having a first surface and a second surface opposite the first, in which said first surface (inner surface) comprises the (or consists of the) graphite material as disclosed above. Preferably, the insert can have a total thickness of about 0.4-2.5 mm, and be configured (having a suitable shape and dimensions) to coat at least partially, preferably completely, at least one of the elements (i)-(iii).

[0053] The layer of graphite material can optionally comprise an outer, preferably metallic, support layer, more preferably made of stainless steel, having the function of being a structural support for the at least one graphite material. In

one insert, the outer support layer can be coupled with graphite material on the second (outer) surface of said insert.

[0054] Alternatively, and preferably, the layer of graphite material can consist of at least one graphite material as disclosed above.

[0055] The embodiment that provides for coating at least one of the elements (i)-(iii) with at least one layer of graphite material is particularly advantageous because it enables a commercially available ionic source that is optionally already operational to be modified simply, optionally also on-site.

[0056] The different embodiments disclosed above can be further advantageously combined with one another. Thus, for example, the at least one repeller electrode (ii) and the outlet wall (iii) can be made entirely of the graphite material disclosed above and the ionization chamber (i) can be totally covered with at least one layer of graphite material as disclosed above.

[0057] The ionization chamber of the ionic source of the invention can be chosen from an electronic ionization chamber (EI) and a chemical ionization chamber (CI), it can be preferably an electronic ionization chamber. Figure 1 shows the diagram of a preferred embodiment of the invention, in which the ionic source was indicated overall by 1. Said ionic source 1 comprises:

a housing 2 configured to form the electronic ionization chamber 3;
a repeller electrode 4; and
an outlet wall 5 configured to allow the passage of the ions 6 generated in the ionization chamber 3 through collision of the electrons 7 with the sample to be analyzed (not shown).

[0058] The ionic source 1 is configured to generate the ions 6 through collision of the sample to be analyzed with the electrons 7, in which the electrons 7 are emitted by a filament 8 and gathered by a collector 9. The ions 6 generated by the collision are accelerated by the repeller 4 to the outlet wall 5, exiting the ionic source. After leaving the ionic source, the ions 6 can be separated by an analyzer that is *per se* known in the art, according to the mass-load ratio thereof.

[0059] According to this embodiment, the inner surface of the ionization chamber 3, and the outlet wall 5 can be completely covered by a layer comprising the graphite material as disclosed above; preferably, they can be completely coated by a layer comprising polycrystalline graphite, preferably isotropic polycrystalline graphite (insert), or pyrolytic graphite, preferably highly oriented pyrolytic graphite; more preferably, they can be completely covered by a layer comprising polycrystalline graphite, preferably isotropic polycrystalline graphite, the inner surface of which is completely coated with pyrolytic graphite, preferably highly oriented pyrolytic graphite.

[0060] The repeller electrode 4 can be completely covered by a layer comprising the graphite material as disclosed above or made entirely of graphite material.

[0061] A further aspect of the present invention refers to a method for modifying an ionic source comprising:

- (i) an ionization chamber;
- (ii) at least one repeller electrode; and
- (iii) an outlet wall,

comprising

- coating at least partially the inner surface of at least one of the elements (i)-(iii) with at least one layer comprising the graphite material as disclosed above; and/or
- replacing at least one of the elements (i)-(iii) with a graphite material as disclosed above.

[0062] The modifying method for modifying an ionic source according to the invention can comprise at least one coating step of coating at least partially, preferably completely, the inner surface of at least one of the elements (i)-(iii), preferably all the elements (i)-(iii) with at least one layer chosen from polycrystalline graphite and pyrolytic graphite, preferably with a layer comprising polycrystalline graphite, the inner surface of which is at least partially, preferably totally, coated with pyrolytic graphite.

[0063] The method for modifying an ionic source according to the invention can comprise at least one step of replacing at least one of the elements (i)-(iii) with a graphite material chosen from polycrystalline graphite, preferably isotropic polycrystalline graphite, optionally at least partially, preferably completely, coated with pyrolytic graphite, preferably of highly oriented pyrolytic graphite, and pyrolytic graphite.

[0064] The modifying method for modifying the ionic source enables alterations in the mass spectra of specific organic substances to be minimized by reduction or elimination, in particular high-boiling organic substances containing medium-long chain hydrocarbons, nitro compounds and mixtures thereof.

[0065] The ionic source according to the invention can be used in a mass spectrometer reducing or eliminating the alterations in the mass spectra and in the chromatograms of the organic substances. This advantage is clearer for certain

types of chemicals such as for example the high-boiling organic substances containing hydrocarbons, preferably medium-long chain saturated aliphatic hydrocarbons, nitro compounds and mixtures thereof.

[0066] In particular, the Applicant observed that by using the ionic source according to the present invention, the alterations of the spectra of the nitro compounds due to the interaction of the nitro groups with the inner surfaces of the ionic source can be significantly reduced or cancelled. Further, by using the ionic source according to the present invention, the response (sensitivity) of the instrument to the high-boiling organic substances containing hydrocarbons, preferably medium-long chain hydrocarbons, can be advantageously improved.

[0067] A further aspect of the present invention relates to the use of an ionic source as disclosed above to minimize the alterations of the mass spectrum and/or increase the analytical sensitivity of a mass spectrometer in the analysis of at least one organic compound chosen from nitro compounds, high-boiling organic compounds containing at least one medium-long chain hydrocarbon and mixtures thereof.

[0068] Preferably, the nitro compounds can be aromatic nitro compounds. Preferably, the high-boiling organic substances containing a medium-long chain hydrocarbon can be esters or ethers containing medium-long chain hydrocarbons.

[0069] A further aspect of the present invention relates to a mass spectrometer comprising the ionic source as disclosed above.

[0070] This mass spectrometer has the advantage of being a more precise, accurate and sensitive detector when used in a GC-MS system.

[0071] In a further aspect, the present invention relates to a mass spectrometry method comprising:

- (a) ionizing in the ionic source as disclosed above a sample, which is preferably gaseous, comprising at least one organic substance, thereby producing ions; and
- (b) analyzing the ions produced in the ionic source according to the mass - load ratio thereof.

[0072] The method can be actuated by one in a mass spectrometer comprising the ionic source according to the invention.

[0073] As indicated previously, the mass spectrometry method according to the invention has the advantage of greater accuracy, precision and/or sensitivity in detecting the mass spectra of certain organic substances, disclosed below.

[0074] Preferably, the sample can further comprise at least one gas chosen from hydrogen, nitrogen, a noble gas and mixtures thereof. According to one embodiment, the noble gas can be selected from helium, argon and mixtures thereof.

[0075] Some chemical substances, such as for example nitro compounds, are particularly reactive both against materials constituting inner surfaces of the ionic sources, and some carrier gases, such as for example hydrogen, used in the GC-MS analyses. The spectra of these substances can thus undergo alterations by interacting with both the carrier gas and with the inner surfaces of the ionic source.

[0076] The high-boiling organic substances containing hydrocarbons, preferably medium-long chain hydrocarbons, such as for example esters containing medium-long chain hydrocarbons, can be adsorbed onto the inner surface of the components of the ionic sources, giving rise to a lowering of the height of the peaks and the appearance of tails that compromise the quantitative and qualitative analysis of the compounds.

[0077] These problems can be resolved or minimized using a mass spectrometer comprising an ionic source according to the invention.

[0078] Preferably, when the at least one analyte is a high-boiling organic substance with a boiling temperature comprised between 250°C and 300°C, the graphite material can be advantageously polycrystalline graphite, preferably isotropic polycrystalline graphite.

[0079] Preferably, when the at least one analyte is a high-boiling organic substance with boiling temperature T_b greater than 300°C and/or a nitro compound, the graphite material can be advantageously pyrolytic graphite, preferably highly oriented pyrolytic graphite.

[0080] The mass spectrometers can be used as a detector for identifying substances in combination with various chromatographic techniques, such as for example gas chromatography and high performance liquid chromatography (HPLC). The mass spectrometer comprising the ionization chamber according to the invention is particularly adapted to be used as detector in a GC-MS system.

[0081] In an additional aspect, the present invention relates to a gas chromatography-mass spectrometry method ("GC-MS method") comprising:

- (A) setting up a first gaseous sample comprising at least one analyte and at least one carrier gas chosen from among hydrogen, nitrogen, a noble gas and mixtures thereof;
- (B) setting up a separation column comprising at least one stationary phase capable of selectively adsorbing said at least one analyte;
- (C) introducing the first sample at one end of the separation column and allowing the sample to flow through the

column, thereby obtaining at least one second gaseous sample;

(D) ionizing said at least one second gaseous sample in one mass spectrometer comprising an ionic source as disclosed above, thereby producing ions; and

(E) analyzing the ions produced according to the mass-load ratio thereof. In one embodiment, the noble gas can be selected from helium, argon and mixtures thereof.

[0082] In one embodiment, the first gaseous sample can comprise a plurality of analytes and step (C) can be conducted by separating the plurality of analytes according to the affinity thereof for the stationary step.

[0083] The mass spectrometry methods or gas chromatography-spectrometry methods disclosed above, can be particularly adapted to the analysis of samples comprising at least one analyte chosen from:

- high-boiling organic substances containing medium-long chain hydrocarbons, preferably esters or ethers of long chain hydrocarbons;
- nitro compounds, preferably aromatic nitro compounds, more preferably benzene nitro compounds;
- and
- mixtures thereof.

[0084] The Applicant has surprisingly observed that in the MS or GC-MS analysis of the substances indicated above the spectral alterations caused by the reactions can occur inside the ionic source, whether it be a stainless steel ionic source or an ionic source coated with a layer of graphite having different features from those shown, they can be attenuated or eliminated by the use of an ionic source according to the invention.

[0085] The present invention will be disclosed further below by means of some examples that have a non-limiting illustrative purpose.

Measurement methods

[0086] Density: the density of the graphite material is calculated by determining the weight of the graphite material with an analytical balance and the volume of the graphite material through immersion of the material in a graduated cylinder that is partially filled with distilled water.

Comparison Example 1

[0087] In one mass spectrometer found on the market, the ionic source has been modified as follows. The stainless steel inner surface of the ionization chamber (i) having the following features:

- cylindrical shape;
- inner diameter of 13.5 mm;
- length of 14 mm

was entirely covered with a layer that is about 1.0 mm thick consisting of graphite having density of about 1.58 g/cm³.

[0088] The graphite material (insert) layer had the shape of a hollow cylinder and was inserted inside the ionization chamber so as to coat completely the metal walls. The hollow cylinder also comprised an outlet wall (iii) consisting of graphite having density of about 1.58 g/cm³ and having the same shape and dimensions as the original outlet wall.

[0089] The repeller originally present in the ionic source was replaced with a repeller (ii) consisting of isotropic polycrystalline graphite having density of about 1.58 g/cm³, having the same shape and dimensions as the original repeller.

[0090] The outlet wall originally present in the ionic source was replaced with the outlet wall (iii) comprised in the hollow cylinder.

[0091] The spectrometer was used to acquire the mass spectrum of the isopropyl myristate, the tetradecanoic acid isopropyl ester (CAS No:110-27-0).

[0092] An isopropyl myristate solution in a 750 ppm weight/weight concentration in diethyl ether was introduced into a gas chromatographic column and eluted, and using hydrogen as a carrier gas, in the following conditions:

Carrier	H ₂
Injection vol.	1.0 µl
Injector	split 1:40 (260°C)

(continued)

Carrier	H ₂
Column	WAX stationary phase, film thickness 0.25 µm inner diameter 0.25 mm; length 60 m
Thermal ramp	start 80 °C, hold 3.5 min. 7.5°C/min to 150°C, hold 3 min, 7.5°C/min to 210°C, hold 0 min, 9°C/min to 250°C, hold 13 min
Flow H ₂	1 ml/min., constant flow
mass spectrometer	Spectrometer with single quadropole with high-vacuum oil-distribution pump ionic source at 230 °C Quadrupole at 150 °C

[0093] The gas chromatogram of the compound is shown in Figure 2A.

Example 2

[0094] The stainless steel inner surface of the ionization chamber (i) of the ionic source of Example 1 was covered entirely with a layer about 1.0 mm thick consisting of isotropic polycrystalline graphite having a density of 1.86 g/cm³.

[0095] The graphite material (insert) layer had the shape of a hollow cylinder and was inserted inside the ionization chamber so as to coat completely the metal walls. The hollow cylinder also comprised an outlet wall (iii) consisting of isotropic polycrystalline graphite having density of about 1.86 g/cm³ and having the same shape and dimensions as the original outlet wall.

[0096] The repeller originally present in the ionic source was replaced with a repeller (ii) consisting of isotropic polycrystalline graphite having a density of 1.86 g/cm³, having the same shape and dimensions as the original repeller.

[0097] The outlet wall originally present in the ionic source was replaced with the outlet wall (iii) comprised in the hollow cylinder.

[0098] The gas chromatogram of the isopropyl myristate shown in Figure 2B was acquired in the same conditions as disclosed in Example 1

[0099] Comparing the graphic of Figures 2A and 2B, the significant increase in height is observed, which is indicative of an improvement in the sensitivity of the instrument. The peak of Figure 2B is further more symmetrical, having a much less pronounced tail.

Example 3

[0100] The inner surface of the graphite material used for the components (i)-(iii) of Example 2 was entirely covered with a layer of pyrolytic graphite, depositing by CVD an organic precursor on the surface of the graphite material and subsequent graphitization.

[0101] The gas chromatogram of the isopropyl myristate shown in Figure 2C was acquired in the same conditions as disclosed in Example 1

[0102] It can be observed that the peak of Figure 2C has a greater height, greater symmetry and a smaller tail with respect to the peak of Figure 2A and of Figure 2B.

Example 4

[0103] The mass spectrometer equipped with the modified ionic source as in Example 2 has been used for detecting the mass spectrum of the 1-tert-butyl-2-methoxy-4-methyl-3,5-dinitrobenzene (CAS No. 83-66-9, known also as "artificial musk ambrette") in the operating conditions disclosed in Example 1. The solution injected into the column had a concentration of 750 ppm in diethyl ether.

[0104] The mass spectrum of the substance (at the top of the peak) is shown in Figure 3A.

Example 5

[0105] The mass spectrometer equipped with the modified ionic source as in Example 3 was used for detecting the

mass spectrum of the 1-tert-butyl-2-methoxy-4-methyl-3,5-dinitrobenzene (CAS No. 83-66-9). The spectrum was recorded in the same conditions as Example 4. The solution injected into the column had a concentration of 750 ppm in diethyl ether.

[0106] The mass spectrum of the substance (at the top of the peak) is shown in Figure 3B.

[0107] As can be noted by the comparison between the two spectra of Figures 3A and 3B and the reference spectrum of 1-tert-butyl-2-methoxy-4-methyl-3,5-dinitrobenzene available on specialized data banks (see for example the NIST data bank available on-line <http://webbook.nist.gov/cgi/cbook.cgi?ID=C83669&Mask=200#Mass-Spec>), the spectrum obtained by ionizing the sample in an ionic source modified according to what is disclosed in Example 5 approaches more closely the reference spectrum, in which the main peaks for this substance are values of $m/z=253$ and $m/z=268$. In the detected spectrum, using the ionic source modified as shown in Example 4, the intensity of the 253 and 268 peaks is less, whereas the intensity of the peaks at $m/z=193$ and $m/z=208$ increase, each of which is 60 a.m.u. away from a reference peak.

Example 6

[0108] In one mass spectrometer found on the market, the ionic source has been modified in the manner described in Example 2. A methanol solution containing bis(2-ethylhexyl) phthalate, benzyl butyl phthalate and di-n-octyl phthalate, each in a 200 ppm concentration, was subjected to GC-MS analysis in the conditions set out below.

Carrier	H ₂
Injection vol.	0.5 µl
Injector	split 1:50 (300°C)
Column	WAX stationary phase, film thickness 0.25 µm inner diameter 0.25 mm; length 60 m
Thermal ramp	start 100°C, hold 3.0 min. 10.0°C/min to 250°C, hold 20 min. 2,°C/min to 255°C, hold 5 min.
Flow H ₂	1.1 cc/min for 18 min, then 1.2 cc/min for 15 min, then 1.3 cc/min until the end
mass spectrometer	Spectrometer with single quadrupole with high-vacuum oil-distribution pump ionic source at 230 °C Quadrupole at 150 °C

[0109] Figure 4A shows the chromatogram of the ion at $m/z=149$, which is typical of the phthalates. In Figure 4, the peaks are indicated by numbers (1) to (3) in which:

- (1) = bis(2-ethylhexyl) phthalate
- (2) = benzyl butyl phthalate
- (3) = di-n-octyl phthalate

Example 7

[0110] In one mass spectrometer found on the market, the ionic source has been modified in the manner described in Example 3. A methanol solution containing bis(2-ethylhexyl) phthalate, benzyl butyl phthalate and di-n-octyl phthalate, each in a 200 ppm concentration, was subjected to GC-MS analysis in the conditions of Example 6. The chromatogram is shown in Figure 4B.

Claims

1. An ionic source comprising:

- (i) an ionization chamber;
- (ii) at least one repeller electrode; and
- (iii) an outlet wall,

characterized in that the inner surface of at least one of the elements (i) - (iii) comprises at least one graphite material having a density of 1.65-2.26 g/cm³.

2. The ionic source according to claim 1, wherein the graphite material has a density of 1.80 - 2.26 g/cm³, preferably 1.80 - 2.25 g/cm³.

3. The ionic source according to claim 1 or 2, wherein the graphite material is chosen from polycrystalline graphite, preferably isotropic polycrystalline graphite, and pyrolytic graphite, preferably highly oriented pyrolytic graphite.

4. The ionic source according to claim 3, wherein the graphite material is polycrystalline graphite having a density of 1.65 - 2.00 g/cm³, preferably 1.80 - 2.00 g/cm³.

5. The ionic source according to claim 3, wherein the graphite material is pyrolytic graphite having a density of 2.00 - 2.26 g/cm³, preferably 2.00 - 2.25 g/cm³, more preferably 2.15-2.23 g/cm³.

6. The ionic source according to any one of claims 1 to 5, wherein at least one of the elements (i)-(iii) is made entirely of graphite material and/or the inner surface of at least one of the elements (i)-(iii) is coated at least partially with at least one layer comprising the graphite material.

7. The ionic source according to any one of claims 1-6, wherein at least one of the elements (i)-(iii) is made entirely of pyrolytic graphite, the inner surface of which is optionally at least partially, preferably completely, coated with at least one layer comprising pyrolytic graphite, wherein said at least one layer is preferably obtained by chemical vapour deposition.

8. The ionic source according to any one of claims 1-6, wherein the at least one of the elements (i)-(iii) is entirely made of polycrystalline graphite, the inner surface of which is at least partially coated with at least one layer comprising pyrolytic graphite.

9. The ionic source according to any one of claims 1-6, at least one of the elements (i)-(iii) is entirely made of pyrolytic graphite, at least partially, preferably completely coated with at least one layer comprising highly oriented pyrolytic graphite.

10. The ionic source according to any one of claims 1-9, wherein the ionization chamber of the ionic source is chosen from an electronic ionization chamber and a chemical ionization chamber, preferably it is an electronic ionization chamber.

11. The ionic source according to any one of claims 1-10, wherein the at least one repeller electrode (ii) and the outlet wall (iii) are made entirely of graphite material and the ionization chamber (i) is totally coated with at least one layer of graphite material.

12. A mass spectrometry method comprising:

- (a) ionizing in an ionic source according any one of claims 1-11 a sample, preferably gaseous, comprising at least one analyte, thereby producing ions; and
- (b) analyzing the ions produced in the ionic source according to the mass-load ratio thereof.

13. A mass gas chromatography-spectrometry method comprising:

- (A) setting up a first gaseous sample comprising at least one analyte and at least one carrier gas chosen from hydrogen, nitrogen, a noble gas and mixes thereof;
- (B) setting up a separating column comprising at least one stationary phase capable of adsorbing selectively at least one analyte;
- (C) introducing the first sample to an end of the separating column and enabling the sample to flow through the column, thereby obtaining at least one second gaseous sample;

(D) ionizing said at least one second gaseous sample in a mass spectrometer comprising an ionic source according to any one of claims 1-11, thereby producing ions; and
(E) analyzing the ions produced according to the mass-load ratio thereof.

5 **14.** A method according to claim 12 or 13, wherein the at least one analyte is chosen from:

- high-boiling organic substances containing medium-long chain hydrocarbons, preferably esters or long-chain hydrocarbon ethers;
- nitro compounds, preferably aromatic nitro compounds, more preferably benzene nitro compounds;
- 10 and
- mixtures thereof.

15 **15.** A use of an ionic source as disclosed in any one of claims 1 to 11 to minimize alterations of the mass spectrum and/or increase the analytic sensitivity of a mass spectrometer in the analysis of at least one organic compound chosen from nitro compounds, high-boiling organic compounds containing at least one medium-long chain hydro-
carbon and mixtures thereof.

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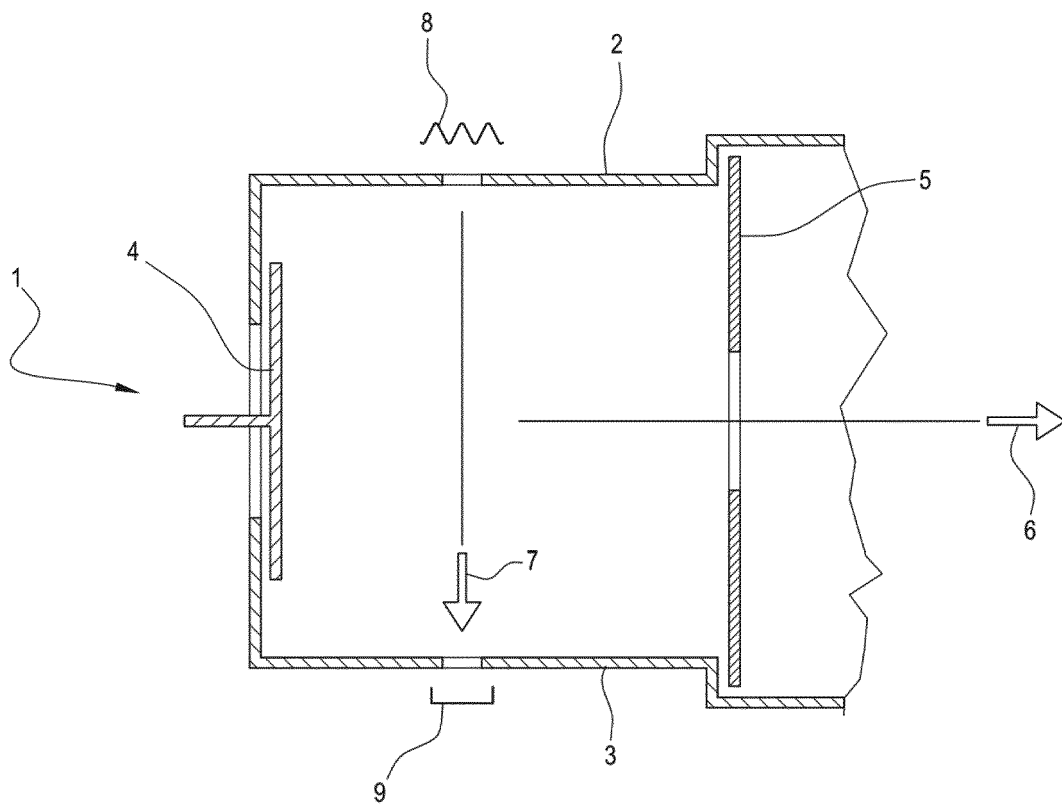
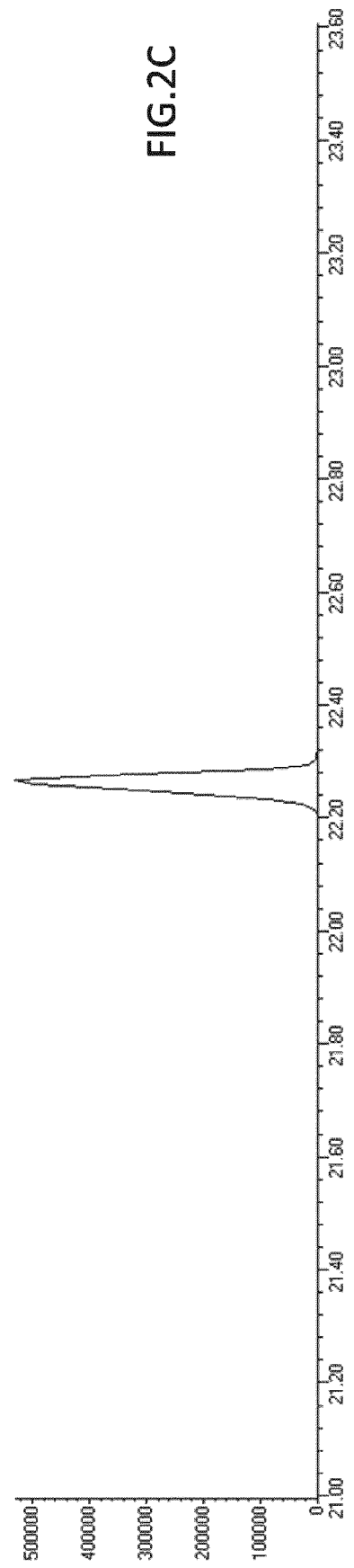
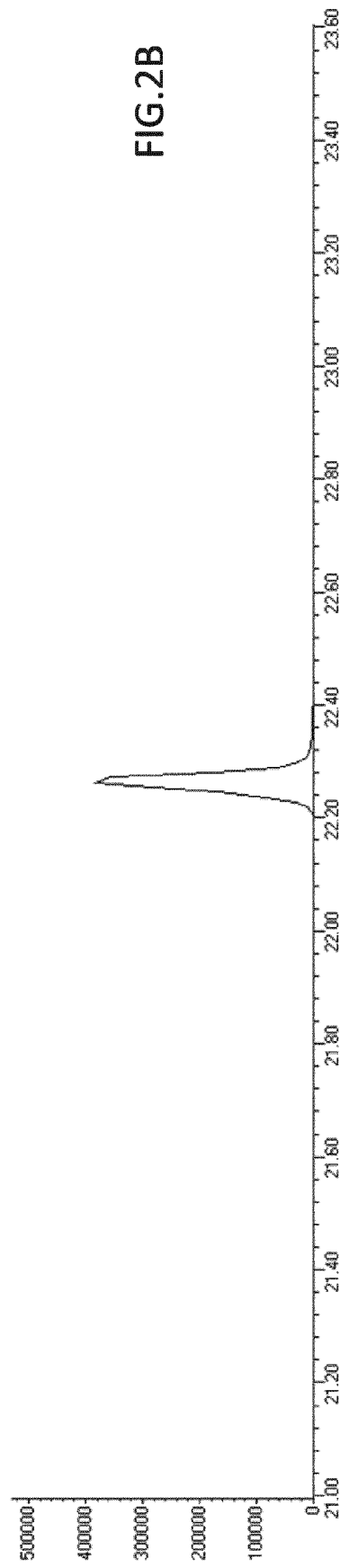
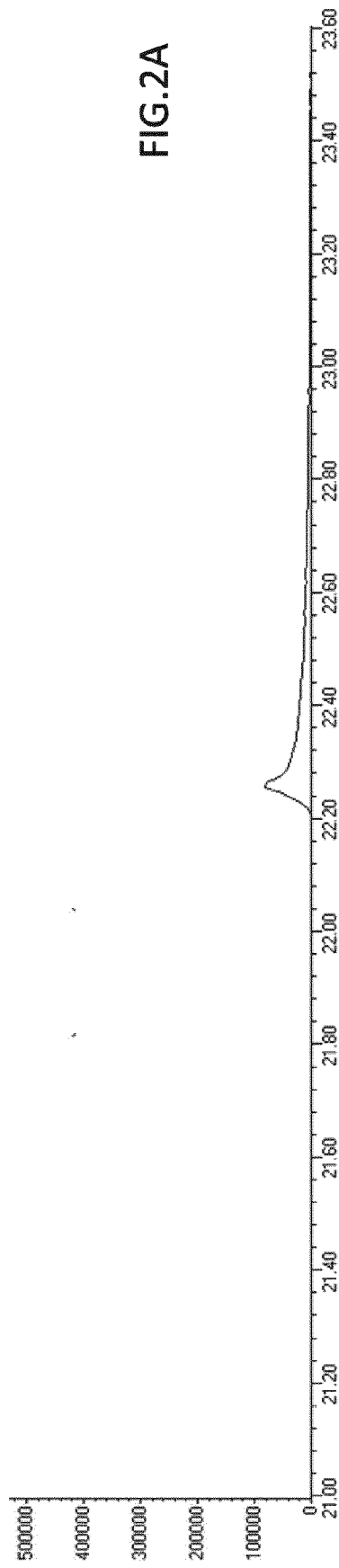


FIG.1



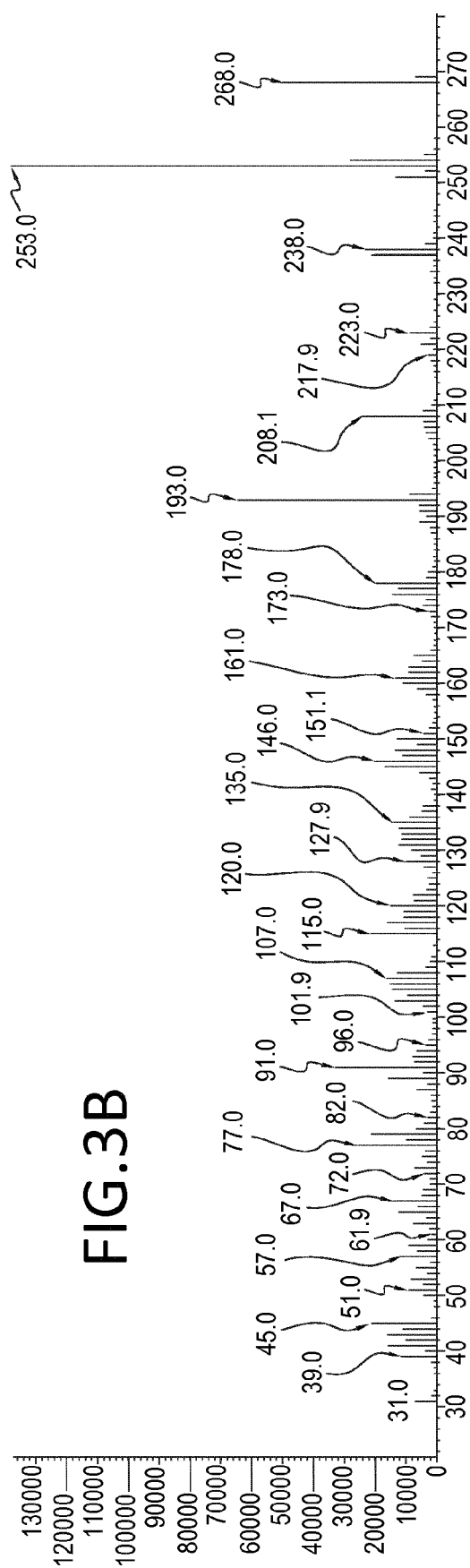
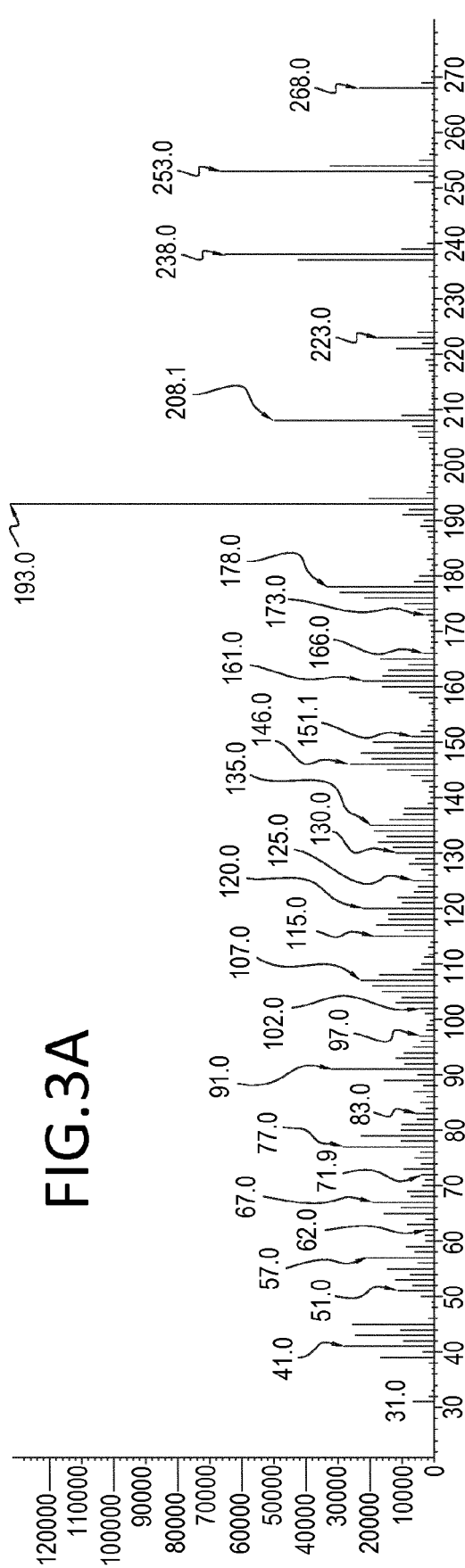


FIG.4A

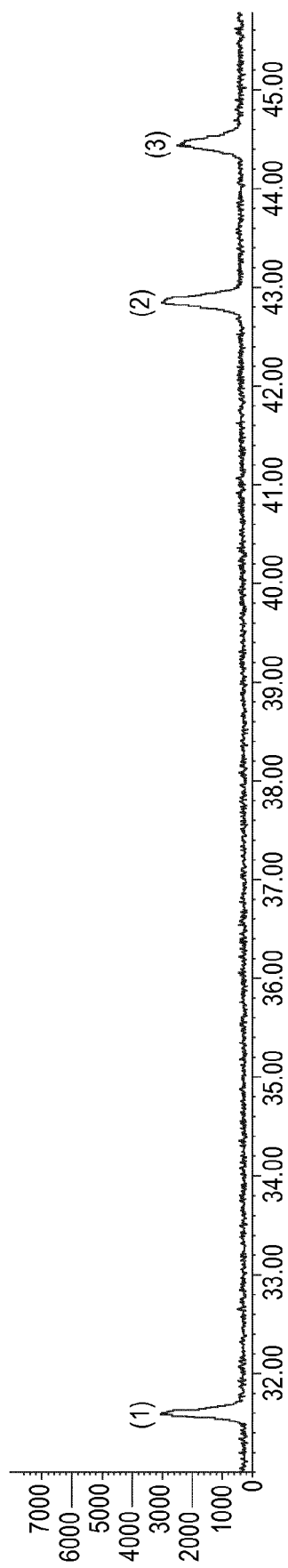
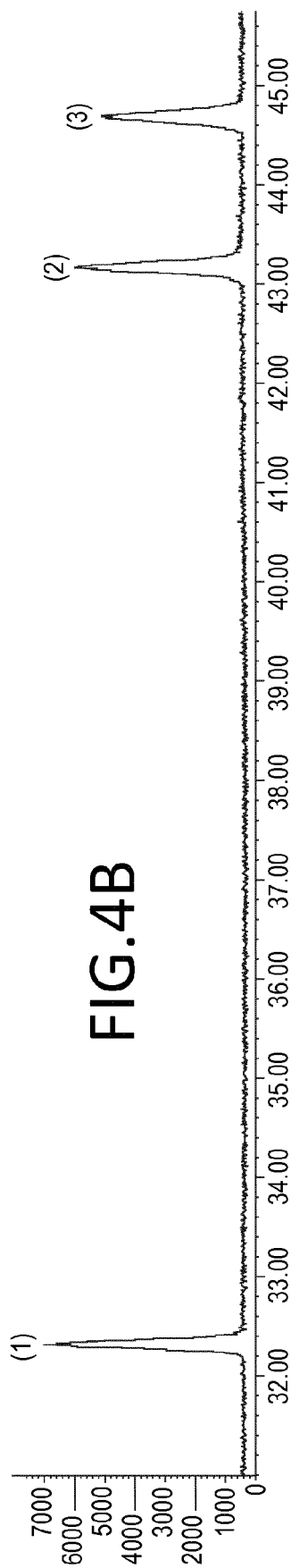


FIG.4B





EUROPEAN SEARCH REPORT

Application Number
EP 18 19 2990

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X	WO 2016/083964 A1 (CISTERNI MARCO [IT]) 2 June 2016 (2016-06-02) * claims 1,2,4,6,7,16 * * page 8, line 1 - line 2 * * figure 2 * -----	1-15	INV. H01J49/14
			TECHNICAL FIELDS SEARCHED (IPC)
			H01J
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 9 January 2019	Examiner Peters, Volker
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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