(12) UK Patent Application (19) GB (11) 2627803 (13) A

(43) Date of A Publication 04.09.2024

(21) Application No: 2303109.9

(22) Date of Filing: 02.03.2023

(71) Applicant(s):
Smiths Detection-Watford Limited
Century House, Maylands Avenue, Industrial Estate,
Hemel Hempstead, HP2 7DE, United Kingdom

(72) Inventor(s):
Luca Marmugi
Alastair Clark
Andrew Hobson

(74) Agent and/or Address for Service:
Mathys & Squire LLP
The Shard, 32 London Bridge Street, LONDON,
SE1 9SG, United Kingdom

(51) INT CL:
G01N 21/65 (2006.01) ***G01J 3/44*** (2006.01)
G01N 1/02 (2006.01) ***G01N 1/22*** (2006.01)

(56) Documents Cited:
CN 113040831 A **CN 108867026 B**
CN 107643276 B **US 20180024067 A1**
US 20160161412 A1 **US 20040007673 A1**

(58) Field of Search:
INT CL **G01J, G01N**
Other: **WPI, EPODOC, SEARCH_PATENT**

(54) Title of the Invention: **Method and Apparatus**
Abstract Title: **Neutral gas surface enhanced raman spectroscopy system**

(57) A system 10 and corresponding method for collection of a sample of a sample of a neutral gaseous fluid desorbed from a solid or liquid sample of a substance of interest, the system comprising a sample collection substrate 1 having an activated surface for surface enhanced raman spectroscopy (SERS), the activated surface being configured for collection of the sample, a substrate receiving area 14, in which the substrate is disposed, a SERS analyser 12 for performing SERS on the substrate in the receiving area, a desorber for desorbing the sample from the substrate to provide a neutral gas suitable for further analysis.

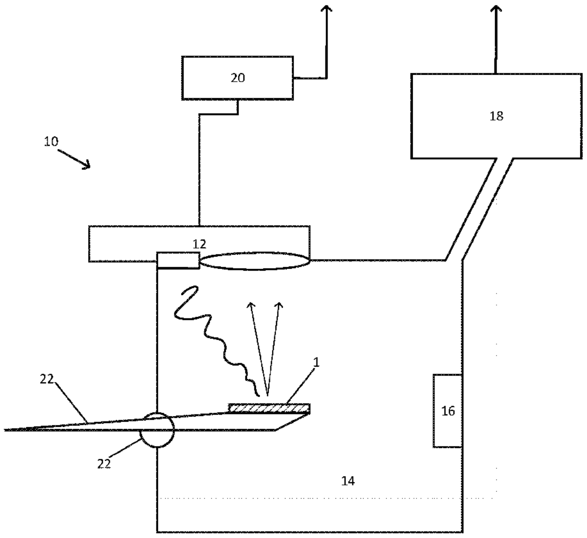

Figure 1

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

GB 2627803 A

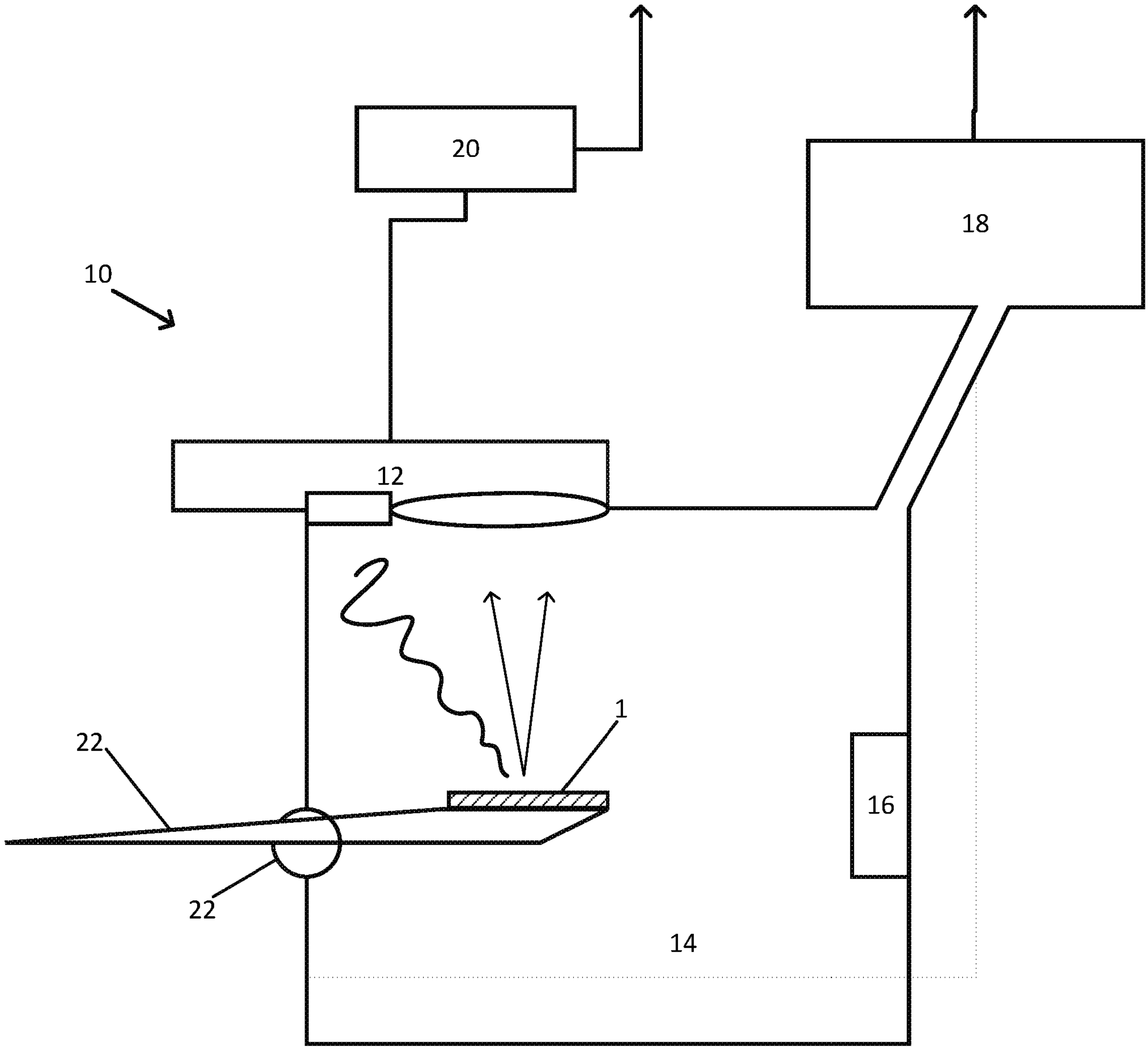

Figure 1

Method and Apparatus

Technical field

The present disclosure relates to methods and apparatus for the collection of solid and liquid samples, and to the analysis and processing of such samples for further analysis.

Background

A variety of approaches to sample collection and processing have been proposed. These include:

- P. D. Fedick et al., Forensic Sampling and Analysis from a Single Substrate: Surface-Enhanced Raman Spectroscopy Followed by Paper Spray Mass Spectrometry, Anal. Chem. 89, 10973-10979, 2017. DOI: 10.1021/acs.analchem.7b02798.
- Z. Gong et al., Fabrication of SERS Swab for Direct Detection of Trace Explosives in Fingerprints, ACS Appl. Mater. Interfaces 6, 21931-21937, 2014. DOI: https://doi.org/10.1021/am507424v.
- T. Liyanage et al., Fabrication of a self-assembled and flexible SERS nanosensor for explosive detection at parts-per-quadrillion levels from fingerprint, Analyst 143, 9, 2012–2022, 2018. DOI: https://doi.org/10.1039/C8AN00008E.
- C. H. Lee et al., Paper-Based SERS Swab for Rapid Trace Detection on Real-World Surfaces, ACS Appl. Mat. Inter. 2, 12, 3429-3435, 2010. DOI: https://doi.org/10.1021/am1009875.
- L. Lan et al., Inkjet-printed paper-based semiconducting substrates for surface-enhanced Raman spectroscopy, Nanotechnology 31, 5, 055502, 2020. DOI: 10.1088/1361-6528/ab4f11.
- M. S. S. Bharati, V. R. Soma, Flexible SERS substrates for hazardous materials detection: recent advances, Opto-Electr. Adv. 4, 11, 210048, 2021. DOI: https://doi.org/10.29026/oea.2021.210048.
- H.-C. Chen et al., Surface-enhanced Raman scattering substrate and manufacturing method thereof, US Patent No. 9,518,927 B2, December 13th 2016.
- Y. Shi et al., A positively charged silver nanowire membrane for rapid on-site swabbing extraction and detection of trace inorganic explosives using a portable Raman spectrometer, Nano Res. 9, 8, 2487–2497, 2016. DOI: 10.1007/s12274-016-1135-5.

- W.-C. Shih, Method of stamping surface-enhanced Raman spectroscopy for label-free, multiplexed, molecular sensing and imaging, US Patent No. 9,546,958 B2, April 29th 2015.

A variety of analysis techniques are known. For example, Surface-Enhanced Raman spectroscopy or surface-enhanced Raman scattering (SERS) is a surface-sensitive technique that enhances Raman scattering by molecules adsorbed on suitably decorated surfaces with nanostructures such as plasmonic nanoparticles. The most common method for performing SERS measurements is by depositing a sample onto a silicon or glass surface with nanostructured noble metal inclusions. Surfaces are often prepared using a distribution of metal nanoparticles on the surface. The most commonly used metals for visible light SERS are silver and gold. The use of aluminium has also been proposed for UV SERS. To reduce cost, SERS active particles may be provided on a substrate – for example nanoparticles may be provided on a substrate so that SERS can be performed on a sample on that substrate.

Other analytical techniques are also known – for example ion mobility spectrometry and mass spectrometry and other techniques are also used for the analysis of ions obtained from samples.

Embodiments of the disclosure provide a single sample collection substrate (such as a ‘swab’) which provides a suitable desorption mechanism and an arrangement for the transport of samples. Embodiments may address or at least ameliorate some or all of the following problems:

- Efficient collection of solid or, potentially, liquid substances for detection and screening of hazardous, explosive, polluting or illicit substances;
- In situ non-destructive rapid detection and identification (chemical fingerprinting) via SERS;
- Possible sample transfer such as for for *ex situ* analysis;
- Desorption and extraction of sample in the vapour-phase for further analytical characterisation and/or forensics analysis, for example (but not exclusively) using analytical instrumentation or optical spectroscopy.

In an embodiment a swab according to the present disclosure (such as any SERS active swab described or claimed herein) may be inserted into a desktop or handheld trace detection system, such as an explosive trace detector (sometimes referred to as an ETD). So, when the user inserts a swab, a SERS analysis is performed and then the swab is thermally desorbed for analysis in the IMS.

Summary

Aspects of the invention are set out in the independent claims. Embodiments are set out in the dependent claims.

An aspect provides a system for collection of a sample of a neutral gaseous fluid desorbed from a solid or liquid sample of a substance of interest, the system comprising:

a sample collection substrate having an activated surface suitable for surface enhanced Raman spectroscopy, SERS, the activated surface being configured for collection of the sample of a substance of interest;

a substrate receiving area, in which the sample collection substrate is to be disposed;

a SERS analyser configured for performing SERS on the surface of the substrate in the substrate receiving area;

a desorber configured for desorbing the substance of interest from the sample collection substrate to provide a sample of a neutral gaseous fluid.

The system may comprise a gaseous sample collection arrangement arranged to collect gaseous fluid desorbed from the sample carried by the swab and to provide the gaseous fluid to a receptacle, such as a container, or to an inlet of a detector.

The system may further comprise the detector, and the detector may be configured to ionise the gaseous fluid. Examples of such detectors include ion mobility spectrometers (IMS) and mass spectrometers. Other detectors may be used.

An aspect provides a sample collection substrate having an activated surface suitable for surface enhanced Raman spectroscopy, SERS, the activated surface being configured for collection of a sample of a substance of interest, wherein the substrate is further configured for the desorption of said substances from the substrate to provide gaseous fluid.

The substrate may be of a flexible material. Examples of such materials include a plastic film, a colloidal dispersion on a solid substrate, a paper-based material, a structured material such as a porous glass or porous alumina, silica or other glass-based films or fibres, homo- or hetero-structured semiconductor films, nanostructures and graphene, as well as cloth-like substrates such as carbon cloth.

The substrate is generally SERS activated and/or enhanced by at least one of nanoparticles, nanostructures, and photonic crystals.

An aspect provides a method of collecting a sample of a neutral gaseous fluid for analysis, the method comprising:

collecting a solid or liquid sample of a substance of interest on a sample collection substrate having an activated surface suitable for surface enhanced Raman spectroscopy, SERS;

desorbing the sample from the substrate to provide a sample of neutral gaseous fluid; and collecting the sample of neutral gaseous fluid for analysis.

The method may further comprise performing SERS on the surface of the substrate to obtain SERS data corresponding to the sample.

Collecting the sample of gaseous fluid for analysis may comprise providing the neutral gaseous fluid to one of (a) a container for storage and/or transport; and (b) an inlet of a detector.

Desorbing the sample from the substrate may comprise at least one of (a) heating the substrate; (b) chemical modification such as acid volatilisation.

General methods of desorption may be used (e.g., thermal desorption and/or electric current based desorption, vacuum desorption, etc). However, in some cases, methods which are specific to a substance or class of compounds may be used. Examples include chemical extraction, acid volatilisation, optical resonant and non-resonant desorption, etc. The extraction can happen in a separate device or reactor, followed by transfer for further analysis, or directly in instruments equipped with suitable desorbers. For example, the SERS-active swab can be exposed to a thermal desorption cycle in an IMS or MS.

For example, graphene and semiconductor-based substrates could be suitable for electric current-induced desorption, potentially allowing for conductivity/resistivity measurements. Chemically inert materials such graphene or graphite, silica-based glasses or other glasses can be suitable for selective or non-selective chemical extraction, for example via acidic volatilisation. Optically transparent materials might be used in conjunction with light- or laser-induced desorption, resonant or non-resonant, whereby the one could also make use of the SERS-active nanoparticles for plasmon-enhanced optical desorption.

As another example the desorbing step may be performed in a desorber of a detector such as an IMS or mass spectrometry device.

Embodiments of the present disclosure provide an apparatus comprising a Surface-Enhanced Raman Spectroscopy (SERS)-active sample collection substrate for collecting a solid or liquid sample, and a desorber arranged to desorb the sample to obtain a sample of gaseous fluid. Generally the sample of gaseous fluid is electrically neutral – for example it is substantially not ionised.

The desorber may comprise a thermal desorption means, such as a heater. In some embodiments additional means may be provided for chemical desorption, such as an apparatus for acid volatilisation of the sample. For example means may be provided for acid volatilisation which provides an acid to the solid or liquid sample on the swab to chemically produce a more volatile material. The more volatile material may still be bound on the swab and thermal desorption may still be required to desorb the more volatile material, e.g., for desorbing the (now more volatile) substance of interest from the sample collection substrate to provide a sample of a neutral gaseous fluid

Embodiments of the disclosure aim to provide rapid *in situ* SERS detection and chemical identification, storage and transport. For example samples may be collected on SERS active substrate and then desorbed into a container for holding the sample of gaseous fluid. Examples of such containers include bags and other types of packaging which may be sealed. The *ex situ* release of sample to the gaseous phase (e.g. gas or vapour) may permit further analytical or optical analysis. Embodiments may thus provide multi-step detection and analysis protocols.

For example in an embodiment there is provided a method comprising collecting a sample of a solid or liquid using a SERS active sample collection substrate, such as a swab, performing a SERS analysis of the sample in situ on the sample collection substrate, and desorbing the sample from the substrate to obtain a sample of gaseous fluid for analysis.

The sample of gaseous fluid may be provided to a detector for further analysis such as by Ion Mobility Spectrometry (IMS), Mass Spectrometry (MS), Gas Chromatography, as well as conventional Raman or optical spectroscopy of vapours or any suitable combination of these.

Embodiments of the disclosure may allow for spatial and/or temporal separation of identification of a specimen in the field and further analytical or forensics investigations at a mobile or fixed facility.

Embodiments of the disclosure may allow a single collection method to support a variety of different analytical and/or spectroscopic investigations, including a rapid SERS detection. Embodiments may provide a SERS-based chemical fingerprint followed by a suitable desorption mechanism (including, but not limited to thermal desorption or acid volatilization) and other destructive or non-destructive analysis.

The desorption may be configured to provide gaseous fluid comprising only neutral species (i.e., the sample is not directly ionized in the process of desorption).

Embodiments of the disclosure may be of particular utility in the detection of explosives, toxic or illicit substances such as Chemical Warfare Agents (CWAs), Toxic Industrial Chemicals (TICs) or narcotics in solid phase or in solution.

Brief Description of Drawings

Embodiments of the disclosure will now be described with reference to the accompanying drawings, in which Figure 1 shows a schematic diagram of an apparatus according to the present disclosure.

Specific Description

Figure 1 shows an apparatus 10 comprising a chamber 14 for introduction of a substrate 1 having a SERS-active surface, a SERS analyser 12, a desorber, and a gaseous sample collection arrangement 18.

The substrate 1 is adapted for physical collection ('swabbing') of particulate residuals and/or deposition from liquid solutions. For example, it typically is flexible and may comprise a cloth-like material or other appropriate material to allow it to be wiped against a surface to collect a sample of a substance of interest from the surface. The substrate material typically is adapted to allow it to be subjected to a desorbing process, for example it may be non-combustible and/or capable of being heated to at least 200°C without substantial off-gassing. The surface of the substrate 1 is SERS active. For example, it carries a material suitable for performing SERS – such as silver nano particles.

As illustrated in Figure 1 the substrate 1 may be carried on a sample collection wand 22 or similar. As shown, the substrate 1 may be introduced into a chamber 14 of the apparatus on such a wand 22, or by other means. The chamber 14 may provide an enclosure so that gaseous fluids, such as vapour or gas, desorbed from the sample can be collected. In the example shown in Figure 1 the chamber 14 of the apparatus 1 comprises a port 24 to allow the substrate 1 to be introduced to the chamber, for example so that a sample collection wand 22 can be inserted into the chamber 14 carrying the substrate 1.

A desorber 16 can be also be provided in the chamber 14. In the embodiment shown in Figure 1, the desorber 16 comprises a heater arranged so that, when the substrate 1 is introduced to the chamber 14 and following the SERS analysis, heat can be applied to the substrate 1 to desorb the sample from it.

A gaseous sample collection arrangement 18 is coupled to the chamber for collecting gaseous fluids desorbed from the substrate 1 by the desorber 16. Typically, this sample collection arrangement 18 comprises an air mover such as a pump connected to move gaseous fluid from the chamber 14 to a receptacle, such as a container or the inlet of a detector.

In addition the apparatus also comprises a SERS analyser 12. As illustrated this comprises optics for providing radiation to the sample, and for collecting Raman scattered radiation from the sample.

A controller 20 may be connected to the SERS analyser 12 for obtaining SERS data from the SERS analyser 12. The controller 20 may have a data output interface for providing the SERS data to a further device, such as a detector which may use the SERS data together with analysis of the neutral gaseous fluid and/or ionized species obtained therefrom.

In operation, the SERS-active substrate 1 is rubbed against a surface to collect substances in the solid or liquid phase on the SERS-active substrate. The substrate carrying the solid or liquid sample is the introduced to the chamber 14 and positioned so that the SERS active surface of the substrate 1 and the sample are presented to the SERS analyser 12. The SERS analyser 12 is then operated to provide exciting radiation of in typical bands for Raman, for example near-infrared (e.g., 850 nm or 780 nm), visible (e.g., 635 nm or 532 nm) and, potentially, UV (e.g., 250 nm) to the active surface of the substrate. The SERS analyser 12 collects radiation scattered by the substrate 1 and analyses this scattered radiation to provide spectroscopic data corresponding to a chemical Raman signature of the sample. This spectroscopic data may be provided to the controller 20 which may store the data or provide it for communication to a further device.

The desorber 16 is then operated – according to its operating principles (e.g., thermal, optical and optionally additional chemical desorption) to volatilize the sample carried by the substrate 1. This process generates a gaseous fluid comprising vapour and/or gas. Generally, this is done so that the gaseous fluid remains neutral (i.e. not ionised). The neutral gaseous fluid is then collected and provided to a receptacle such as a container for storage or the inlet of a detector. Examples of appropriate detectors for this purpose include Ion Mobility Spectrometers (IMS), Mass Spectrometers, and other types of detector in which neutral gaseous can be taken into an inlet of the device for analysis.

This enables multi-stage analysis, where one of the stages is SERS, either automated or manually controlled by an operator. The substrate containing the collected substances will be used for SERS spectroscopy for rapid identification of the chemical and, with a suitable desorption or extraction mechanism in place, for at least another optical or analytical analysis requiring the use of gas phase. As the extracted molecule will be primarily in a neutral charge state, the envisaged following analyses may include ionisation of the extracted/vaporised species. It can thus be seen that the collection substrate described herein may provide significant advantages in matching the requirements for both SERS and subsequent extraction for chemical or physical analysis by detection methods such as IMS and other techniques.

The apparatus shown in Figure 1 uses a sample collection wand but any appropriate means may be used to hold the SERS-active substrate (‘swab’). Swabs can be either installed in suitable sampling tools (e.g., sampling rods or tweezers) or instruments (e.g., but not exclusively, any mechanical construct capable of autonomous or guided movement), but can be also simply hand-operated by an individual.

The SERS-active substrate can be designed in any form factor suitable for matching requirements of the instruments that one prefers to use. The same applies to materials: depending on the envisaged applications and/or the chosen mechanism for desorption (see below), the SERS-active swabs can be realized, for example (but not limited to) plastic films and organics polymers, colloidal dispersions on solid substrates, paper-based materials, structured materials at the microscopic level (e.g., porous glasses, porous alumina), silica or other glass-based films or fibres, homo- or hetero-structured semiconductors films or nanostructures and graphene, as well as cloth-like substrates such as (but not exclusively) carbon cloth.

SERS activity can be introduced and/or enhanced with any of the known techniques, including for example (but not limited to) decoration with nanoparticles or nanostructures, photonic crystals, etc.

The methods for extracting the collected substances for follow-up investigations with instrumentation other than SERS spectrometers can be either general (e.g., thermal desorption and/or electric current based desorption, vacuum desorption, etc) or specific to a substance or class of compounds (e.g., chemical extraction, acid volatilisation, optical resonant and non-resonant desorption, etc.). The extraction can happen in a separate device or reactor, followed by transfer for further analysis, or directly in instruments equipped with suitable desorbers. For example, the SERS-active swab can be exposed to a thermal desorption cycle in an IMS or MS.

For example, but without limiting the scope of this invention to these materials and method of operations, graphene and semiconductor-based substrates could be suitable for electric current-induced desorption, potentially allowing for conductivity/resistivity measurements. Chemically inert materials such graphene or graphite, silica-based glasses or other glasses can be suitable for selective or non-selective chemical extraction, for example via acidic volatilisation. Optically transparent materials might be used in conjunction with light- or laser-induced desorption, resonant or non-resonant, whereby the one could also make use of the SERS-active nanoparticles for plasmon-enhanced optical desorption.

The gaseous sample collection arrangement may provide a system for preserving the integrity of the collected samples (e.g., a sealed vapour bag) and for extracting neutral molecules from the collected sample via suitable desorbing mechanisms such as thermal desorption, light-induced desorption or chemical volatilization.

It is a significant advantage that samples of neutral gaseous fluid provide the possibility to transfer the collected samples after rapid SERS characterisation to an *ex situ* facility. SERS data collected with the relevant sample may be provided with the sample itself.

As explained above with reference to Figure 1, a combination of SERS with IMS is one preferred embodiment of the invention. Such embodiments may be provided in a single integrated system, in which both types of analysis are performed by a single device. However, other embodiments are contemplated. I For example, following SERS analysis of a sample of solid or liquid carried on the swab, desorption and analysis with instruments and techniques other than SERS may be performed separated (in space and/or time) from the instrument used for SERS detection. This may also imply the possibility of transferring the SERS-active substrate (‘swab’) after the SERS analysis to a different location.

As noted above, the present disclosure provides a sample collection substrate having an activated surface suitable for surface enhanced Raman spectroscopy, SERS, the activated surface being configured for collection of a sample of a substance of interest, wherein the substrate is further configured for the desorption of said substances from the substrate to provide gaseous fluid.

Such a substrate may be configured for high collection efficiency.

In an embodiment the substrate may have a superficial porosity and/or low adsorption energy and/or chemical affinity with compounds of interest. It may be disposable and configured for single use.

It may be configured for desorption mechanisms such as thermal desorption, and/or electric current based desorption, vacuum desorption, etc) or techniques specific to a substance or class of compounds (e.g., chemical extraction, acid volatilisation, optical resonant and non-resonant desorption, etc.).

Generally the substrate and the material from which it is made is flexible to promote surface adhesion of the solid or liquid sample. It may be configured to inhibit adsorption of background gases and/or it may provided in sealed packaging. Typically the active (e.g. SERS active) surface of the substrate has an area of at least 1cm^2.

The material and/or the substrate may be configured for attachment to a sample collection wand, or it may be configured to be applied to a surface by hand.

Generally the substrate comprises a hydrophobic material.

The substrate may be configured for thermal desorption of the solid or liquid sample. Typically, such a substrate may be configured for single use, for example it may comprise at least one carry a heat sensitive use indicator. Such an indicator may be configured to be degraded in response to being heated above a selected temperature threshold. For example it may at least partially discolour to provide a visual indication of prior use and/or at least partially disintegrate to inhibit reuse of the substrate.

A substrate configured for thermal desorption may have a melting point much greater than 200°C, for example at least 600°C, for example at least 800°C, for example 1500°C or more. Typically, such a substrate has a glass transition temperature greater than 200°C.

Typically, a substrate configured for thermal desorption consists solely of materials which have limited or negligible outgassing at desorption temperatures. Typically, a substrate configured for thermal desorption has a surface extraction potential which is less than the ionisation potential of species of interest, such as chemical warfare agents, illicit drugs, toxic industrial chemicals and so forth. For example a substrate configured for thermal desorption may have a low adsorption energy, for example having an order of magnitude of about 0.1 eV. Typically, a substrate configured for thermal desorption has a thickness of less than 1mm.

The substrate may be configured for electric desorption of the solid or liquid sample. Such swabs may comprise electrically conductive members, such conductive members may be at least partially electrically insulated for example such that they carry electrical current preferentially along their lengths, e.g. between uninsulated contact points disposed at opposite ends of the conductive members. Such swabs may be suitable for clamping between electrodes and may comprise contact regions, which may be arranged fo providing electrical contact between the conductive members and a power supply of a desorber. The contact regions may be arranged for electrical contact with a clamp which holds the swab to the desorber. The conductive members may be incorporated into the substrate, for example by weaving or embedding into the material of the substrate. Typically, a substrate configured for electrical desorption has a thickness of less than 1mm. Typically, a substrate configured for electrical desorption consists solely of materials which have limited or negligible outgassing at desorption temperatures.

The substrate may be configured for acid volatilisation of the solid or liquid sample. Typically such a substrate is chemically inert and stable, for example it may be unreactive with acids such as the acid to be used for volatilisation. The substrate may comprise a material that is amenable to coating with a polymer such as Nafion. In some embodiments the substrate comprises a polymer coating. Such substrates may be adapted for humidification prior to desorption. Substrates configured for acid volatilisation may be further configured for electrical and/or thermal desorption as outlined above.

The substrate may be configured for optical desorption of the solid or liquid sample. For example it may be substantially light-transmissive in a short-wavelength visible range. In some examples the wavelength may be in the near ultra-violet range. For example it may be substantially light-transmissive for wavelengths less than or equal to about 540 nm, for example less than or equal to about 532nm (i.e., $\lambda \leq 532$ nm). It may be substantially light-transmissive for wavelengths greater than or equal to about 300 nm. A substrate configured for optical desorption may have a low adsorption energy, for example having an order of magnitude of about 0.1 eV (Eads~10-1 eV).

All substrates of the present disclosure may be configured for single use. For example they may carry elements configured to inhibit reuse of the substrate, such as elements which change state in response to a desorption process carried out on the swab, for example elements which are degraded or discoloured by the desorption process.

Substrates of the present disclosure may be decorated with SERS active nanoparticles such as gold (Au) nanoparticles. The nano particles may be provided in regular arrangements on the substrate.

Substrates of the present disclosure may comprise (or consist solely of) a material which provides reduced or substantially no background fluorescence at the SERS wavelengths for example between 850 nm and 400 nm, for example less than 780 nm, for example less than 633 nm, for example less than 532 nm, for example more than 400nm. The material may be transparent, for example substantially transparent, for example partially transparent at such wavelengths.

Substrates of the present disclosure may comprise (or consist solely of) a material which provides reduced or substantially no background fluorescence at the SERS wavelengths for example between 400 nm and 850 nm, for example more than 532 nm, for example more than 633 nm, for example more than 780 nm, for example less than 850nm. The material may be transparent, for example substantially transparent, for example partially transparent at such wavelengths.

Typically the material is sufficiently robust to be manipulated by hand or by a wand. The SERS activated area is typically about 1 cm^2

Preferably the material(s) have superficial porosity and/or low adsorption energy and/or chemical affinity with compounds of interest. Preferably the swab is configured for single use and capable of retaining a sample for at least a day, for example at least 5 days, for example at least 28 days, for example 90 days. Preferably, the material is suitable for at least one of desorption mechanisms listed above. Preferably the material is flexible and exhibits low-outgassing levels, for example substantially no outgassing at the temperatures used for thermal desorption. Preferably the material is decorated with nanoparticles across a SERS activated area. The nanoparticles may be gold or silver.

In some embodiments the swabs of the present disclosure have a shelf-life longer than 3 months and are suitable for both manual and wand sampling.

The material may comprise or consist essentially of paper-based and other cellulose-based substrates decorated with Au (or Ag) nanoparticles.

The material may comprise or consist essentially of membrane-based substrates decorated with Au (or Ag) nanoparticles, such as PTFE, micro/nano-porous glass, etc. One commercial example of such a material is Zitex G by Saint-Gobain.

The material may comprise or consist essentially of cloth-based substrates decorated with Au (or Ag) nanoparticles. e.g., carbon cloth.

The material may comprise or consist essentially of a graphene or graphite sheets, decorated with Au (or Ag) nanoparticles.

In some embodiments silicon or semiconductor structures, decorated with Au (or Ag) nanoparticles may be used.

The above materials might provide useful performance even with different nanostructures providing plasmonic-like response that might lead to SERS enhancement.

The controller of the apparatus described herein may comprise an ADC, and digital logic configured to perform the operations described herein. In some examples the functionality of the controller may be provided by a general purpose processor, which may be configured to perform a method according to any one of those described herein. In some examples the controller may comprise digital logic, such as field programmable gate arrays, FPGA, application specific integrated circuits, ASIC, a digital signal processor, DSP, or by any other appropriate hardware. In some examples, one or more memory elements can store data and/or program instructions used to implement the operations described herein. Embodiments of the disclosure provide tangible, non- transitory storage media comprising program instructions operable to program a processor to perform any one or more of the methods described and/or claimed herein and/or to provide data processing apparatus as described and/or claimed herein. The controller may comprise an analogue control circuit which provides at least a part of this control functionality. An embodiment provides an analogue control circuit configured to perform any one or more of the methods described herein.

It will be appreciated from the discussion above that the embodiments shown in the Figures are merely exemplary, and include features which may be generalised, removed or replaced as described herein and as set out in the claims.

With reference to the drawings in general, it will be appreciated that schematic functional block diagrams are used to indicate functionality of systems and apparatus described herein. It will be appreciated however that the functionality need not be divided in this way, and should not be taken to imply any particular structure of hardware other than that described and claimed below. The function of one or more of the elements shown in the drawings may be further subdivided, and/or distributed throughout apparatus of the disclosure. In some embodiments the function of one or more elements shown in the drawings may be integrated into a single functional unit.

The above embodiments are to be understood as illustrative examples. Further embodiments are envisaged. It is to be understood that any feature described in relation to any one embodiment may be used alone, or in combination with other features described, and may also be used in combination with one or more features of any other of the embodiments, or any combination of any other of the embodiments. Furthermore, equivalents and modifications not described above may also be employed without departing from the scope of the invention, which is defined in the accompanying claims.

Claims:

1. A system for collection of a sample of a sample of a neutral gaseous fluid desorbed from a solid or liquid sample of a substance of interest, the system comprising:

    a sample collection substrate having an activated surface suitable for surface enhanced Raman spectroscopy, SERS, the activated surface being configured for collection of a sample of a substance of interest;

    a substrate receiving area, in which the sample collection substrate is to be disposed;

    a SERS analyser configured for performing SERS on the surface of the substrate in the substrate receiving area;

    a desorber configured for desorbing the substance of interest from the sample collection substrate to provide a sample of a neutral gaseous fluid suitable for further analysis.

2. The system of claim 1 comprising a gaseous sample collection arrangement arranged to collect the sample of the neutral gaseous fluid and to provide the sample to a receptacle.

3. The system of claim 2 wherein the receptacle comprises a container.

4. The system of claim 2 wherein the receptacle comprises an inlet of a detector.

5. The system of claim 4 further comprising the detector, and wherein the detector is configured to ionise the gaseous fluid.

6. The system of any preceding claim in which the substrate is flexible.

7. A sample collection substrate having an activated surface suitable for surface enhanced Raman spectroscopy, SERS, the activated surface being configured for collection of a sample of a substance of interest, wherein the substrate is further configured for the desorption of said substances from the substrate to provide gaseous fluid.

8. The sample collection substrate of claim 7 wherein the substrate is of a flexible material.

9. The sample collection substrate of claim 7 or 8 wherein the substrate comprises at least one of: a plastic film, a colloidal dispersion on a solid substrate, a paper-based material, a structured material such as a porous glass or porous alumina, silica or other glass-based films or fibres, homo- or hetero-structured semiconductor films, nanostructures and graphene, as well as cloth-like substrates such as carbon cloth.

10. The sample collection substrate of any of claims 7 to 9 wherein the substrate is SERS activated and/or enhanced by at least one of nanoparticles, nanostructures, and photonic crystals.

11. A method of collecting a sample of a sample of a neutral gaseous fluid desorbed from a solid or liquid sample for analysis, the method comprising:

collecting a solid or liquid sample of a substance of interest on a sample collection substrate having an activated surface suitable for surface enhanced Raman spectroscopy, SERS;

desorbing the solid or liquid sample from the substrate to provide a sample of neutral gaseous fluid; and

collecting the sample of neutral gaseous fluid for further analysis.

12. The method of claim 11 further comprising performing SERS on the surface of the substrate to obtain SERS data corresponding to the sample.

13. The method of claim 11 or 12 wherein collecting the sample of gaseous fluid for analysis comprises providing the neutral gaseous fluid to one of (a) a container for storage and/or transport; and (b) an inlet of a detector.

14. The method of any of claims 11 to 13 wherein desorbing the sample from the substrate comprises at least one of (a) heating the substrate; (b) chemical extraction such as acid volatilisation; (c) optical desorption; (d) current flow induced desorption.

15. The method of any of claims 11 to 14 wherein the desorbing step is performed in a desorber of a detector such as an IMS or mass spectrometry device.

16. The system of any of claims 1 to 6 wherein the desorber is provided in a separate device, separate from the SERS analyser.

17. The system of any of claims 1 to 6 or claim 16 wherein the further analysis is spatially and/or temporally separated from the SERS analysis.

Application No: GB2303109.9 **Examiner:** Mr Luke Frodsham
Claims searched: 1-17 **Date of search:** 19 December 2023

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X	1-4, 7-14	US 2016/0161412 A1 (EWING et al.), See figure 1, paragraphs 8, 13
X	7-10	CN 107643276 B (PHANSCO), See figure 1 and associated description
X	7-10	CN 108867026 B (NATIONAL DONG HWA UNIVERSITY), See whole document
A	-	CN 113040831 A (MICROMASS), See figure 11 and associated description
A	-	US 2018/0024067 A1 (MEINHART et al.), See figures 1A-D, column 24 lines 22-39
A	-	US 2004/0007673 A1 (HARRISON et al.), See paragraphs 8-9

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

Worldwide search of patent documents classified in the following areas of the IPC

G01J; G01N

The following online and other databases have been used in the preparation of this search report

WPI, EPODOC, SEARCH_PATENT

International Classification:

Subclass	Subgroup	Valid From
G01N	0021/65	01/01/2006
G01J	0003/44	01/01/2006
G01N	0001/02	01/01/2006
G01N	0001/22	01/01/2006