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Patent records document a continuous development of trace gas/particle preconcentrators for use in particle detection systems. The most common application proposed for the inventions is the detection of biological agents, chemical agents, or explosives for security purposes although other applications are clearly possible. Existing particle detection systems such as gas chromatograph / mass spectrometer (GC/MS) systems do not have the required sensitivity for the characteristic application. Existing sensor technologies require pretreatment of the sample including preconcentration. There have been two classes of trace gas/particle preconcentrators: cycled and continuous. Preconcentrators that are based on adsorption membranes cannot operate on a continuous basis, because the gas must be stopped, a desired amount adsorbed, then released. These types of pre-concentrators may therefore not be able to maintain the time fidelity of the analyte gas concentrations. Hence, preconcentrators that can operate continuously may be useful for detecting in substantial real time variations in the concentration of the trace gases that are being analyzed. A recent patent of a meso-scale, continuous flow-through, trace gas preconcentrator can enable this specific application with the capability of achieving significant trace-gas concentration increases using one or two simple meso-scale mass diffusion separation stages.

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Continuous Preconcentrator for Trace Gas Analysis (Preprint)

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ABSTRACT:

Patent records document a continuous development of trace gas/particle preconcentrators for use in particle detection systems. The most common application proposed for the inventions is the detection of biological agents, chemical agents, or explosives for security purposes although other applications are clearly possible. Existing particle detection systems such as gas chromatograph / mass spectrometer (GC/MS) systems do not have the required sensitivity for the characteristic application. Existing sensor technologies require pretreatment of the sample including preconcentration. There have been two classes of trace gas/particle preconcentrators: cycled and continuous. Preconcentrators that are based on adsorption membranes cannot operate on a continuous basis, because the gas must be stopped, a desired amount adsorbed, then released. These types of pre-concentrators may therefore not be able to maintain the time fidelity of the analyte gas concentrations. Hence, preconcentrators that can operate continuously may be useful for detecting in substantial real time variations in the concentration of the trace gases that are being analyzed. A recent patent of a meso-scale, continuous flow-through, trace gas preconcentrator can enable this specific application with the capability of achieving significant trace-gas concentration increases using one or two simple meso-scale mass diffusion separation stages. The continuous trace-gas concentrator could increase the sensitivity for portable gas sensors/detectors by several orders of magnitude in a device – with a size less than several centimeters and with power consumption in the tens of milliwatts range. It can be operated continuously; instead of using adsorption-desorption cycles, and the response time is predicted to be more than one order of magnitude shorter than most currently available cycled techniques.

KEYWORDS: Preconcentrator, Gas Sensors, MEMS

INTRODUCTION

As MEMS technology progresses, the development of miniaturized gas sensors/detectors such as GC/MS (gas chromatography/mass spectrometer),[i,ii,iii,iv,v,vi,vii,viii,ix] and electronic noses,[x,xi,xii,xiii,xiv] have been significantly advanced. However, miniaturized gas sensors/detectors typically have limited performance for accurately detecting analyte (trace gas) with small concentration levels at the ppb (parts-per-billion) range. The detector errors arise primarily from carrier (diluent) gas interference and high noise to signal ratios. To increase the accuracy of any miniaturized sensor, passing samples through a preconcentrator is a promising method. Within a typical preconcentrator, a significant fraction of the trace gas analyte is separated from the carrier gas. The trace gas analyte is then introduced to the gas sensor with a higher concentration.

Conventionally, the preconcentration process is based on the adsorption and desorption mechanisms through porous materials identified as the adsorbent. Preconcentrators utilizing such mechanisms are characterized as the 'cycled' preconcentrators. Stopped by the adsorbent for some time until a desired amount of trace gas analyte has been collected, the gas sample is then released through thermal desorption with a higher concentration of the trace gas analytes to the connecting sensors. Patents on the adsorption-desorption cycled preconcentrators are reviewed in this paper. However, the drawback of these types of preconcentrators lies on the time fidelity of the analyte gas concentrations, which is closely related to the physical size of the preconcentrator. Hence, preconcentrators that can operate continuously may be useful for detecting in substantial real time variations in the concentrations of the trace gases that are being analyzed.

A recent patent of a micro/meso-scale, continuous flow-through, trace gas preconcentrator has addressed a specific application that the possibility of achieving significant trace gas concentration increases (for example from 10 ppb to 10 ppm) using one or two simple micro/meso-scale mass diffusion separation stages without interrupting the gas flows. Compared with the cycled preconcentrator, the continuous preconcentrator requires significantly less amount of operational time and possibly much higher trace gas concentration level with a smaller size device. Hence, extended efforts of this study are focusing on the newly innovated continuous preconcentration technology. Details on the design concepts and patent claims are discussed and followed by the future developments of the continuous preconcentrator.

TECHNOLOGIES AVAILABLE FOR TRACE GAS PRECONCENTRATION-CYCLED AND CONTINUOUS

Miniature trace-gas sensors/detectors are needed in many defense and civil environments. For defense applications, the detection of chemical warfare agents (CWAs) has been the focus. Exposure to certain CWAs including GA (tabun), GB (sarin), GD (soman), and GF (cyclosarin), would be lethal within a minute with trace concentrations of several to several tens of parts-per-billion (ppb).[xv] Toxic industrial chemicals (TICs) and volatile organic compounds (VOCs) with very low concentrations (from several ppb to several hundreds of ppb) gradually impact human health and raise concerns for the general public.[xv] In any of these cases, but particularly for CWA detection, trace gas sensors/detectors with portability, rapid response, low power consumption, and extremely high sensitivity are required. As will be described below, there also may be a distinct advantage to having a preconcentrator that operates continuously and thus retains the time fidelity of the sample stream supplied to system sensors/detectors.

Micro/meso-scale thermal desorption preconcentrators have been applied to a number of portable GC/MS and other gas sensing systems.[xvi,xvii,xviii,xix,xx,xxi] The major concern of the micro-scale thermal desorption preconcentrators is to obtain a volume (or mass) of the trace gas analyte sufficient for accurate quantitative analyses at the desired detection limits. Typically, the adsorption process requires several tens of seconds to accumulate sufficient trace-gas analyte from a sample stream with a flow rate of several hundreds of ml/min. Multiple adsorbents may be required for a broad spectrum of target analytes. Adsorbent materials, such as porous carbon-based adsorbents (eg. Carboxen)[xix,xx], porous polymers (eg. Tenax),[xvii,xix,xx,xxii] and single wall carbon nanotubes,[xxiii] have been studied for increasing preconcentrator efficiencies. Efficiencies have been improved from the traditional approach (namely Microtrap). [xvi,xvii,20,xxiii,xxiv,xxv] Microtrap consists of glass capillary or metal tubes packed with adsorbent materials. In the newer systems, a micromachined membrane-like grid [xviii,xxvi,xxvii] has been used to suspend the adsorbent materials in order to create a higher effective surface area. Also, coating the adsorbent materials onto the walls of a collector to create a high surface area, that in turn enables rapid heating, has been identified as an attractive approach for micro-scale thermal desorption preconcentrators. [xx,25,xxviii]

The minimum effective desorption temperature for porous polymers[xvii,xix,xx,xxii] and carbon-based[xix,xx] adsorbents is about 200 °C, but the single wall carbon nanotubes need to be heated to 460 °C.[xxv] The major power consumption of a thermal desorption preconcentrator comes from the heating element. An efficient built-in microheater with high heating rate and low thermal loss is essential in order to reduce the power consumption for all types of thermal desorption preconcentrators. Most of the microheaters adopted so far[xvii,xviii,xix, xxii,xxv] have a heating rate of 10 to 20 ^{o}C/sec with an input power of several watts. The desorption cycle normally requires from several to several tens of seconds after the heater temperature reaches a steady state. Combining two[xxiii,xxvii] or multiple[xx] single stage micro-scale thermal desorption preconcentrators in series, to form a cascade, has also been studied. The approach has been found to provide improvements in the trace-gas concentrations. According to Tian et al [xix,xx] the preconcentration factor (defined as the ratio of the volume in which the trace-gas was contained originally to that in which it is contained following thermal desorption) can be greater than 5600 for a three-stage thermal deposition preconcentrator. A further point to consider is the lack of time fidelity introduced by the adsorption-desorption process compared to continuous flow preconcentrators. For fast acting target gases the introduction of a few minutes delay and the complete corruption of the time dependency of target gas concentrations would have very serious consequences. Hence, preconcentrators that can operate continuously may be useful for detecting in substantial real time variations in the concentrations of the trace gases that are being analyzed.

The difficulties presented by thermal desorption preconcentrators are such that several alternative, entirely gas phase preconcentrators/separators have recently been suggested. One is the continuous trace-gas preconcentrator, which will be discussed in the following sections. The continuous gas phase separations technology[xxix,xxx,xxxi,xxxii,xxxiii,xxxiv] was originally acquired during the days of the post World War II U^{235} separation bubble from 1960 to 1980. It was a period when the nuclear power industry was expecting to grow rapidly. As a result, it was anticipated that there would be a large increase in the requirements for the economic production of fuel for nuclear power plants. The bubble burst in the late 1970’s and the 1980’s as a result of reactor accidents and nuclear waste disposal concerns. However, the technology investigated for gas phase separation is valuable in many other applications and the continuous trace-gas preconcentrator is now one of them.

A second artifact, from the same time period, has recently been reported by Li et al.[xxxv] The MEMS fabrication of micro-scale separation nozzles is discussed, a subject that was studied by E. Becker and his colleagues in the 1960's and 1970's at the Karlsruhe Nuclear Laboratory.[xxxvi,xxxvii,xxxviii,xxxix] The principal contribution of the Li et al work is the application of modern MEMS technology to the fabrication of separation nozzles. The preconcentrator studied by Li et al[xxxv] presented a fast response time (0.01 ms) with a continuous operation in separating SF_6 from a SF_6/N_2 gas mixture, but the volume fraction of SF_6 only doubled at the end of the preconcentrator. Although the separation nozzle preconcentrator (separator) can have comparative separation performance in theory, the experimental performance was much lower than what can be achieved by a single stage thermal desorption preconcentrator.

There are other gas phase isotope separation techniques involving aerodynamic separation processes such as the Jet Membrane separation method for isotope separation. An under expanded free jet through an orifice, in rarefied flow conditions, interacts with a background gas mixture containing gas species with different molecular weights. Along the jet centerline, background species densities are reduced from their equilibrium value far from the orifice by collisions with the jet species by penetrating back through the orifice. The separation effect relies on the preferential diffusion of the light specie moving away from the centerline of the jet. The separation factor is determined by the combining effects of the jet-background interaction and the diffusion separation. Like the separation nozzle, a Jet Membrane is rather complicated and consequently does not appear suitable for portable trace-gas detection systems.

The recently patented continuous trace-gas concentrator could increase the sensitivity for portable gas sensors/detectors by several orders of magnitude in a device – with a size less than several centimeters and with power consumption in the tens of milliwatts range. It can be operated continuously; instead of by adopting adsorption-desorption cycles, and the response time is predicted to be more than one order of magnitude faster than most currently available adsorption techniques.

PATENTS ON CONTINUOUS TRACE GAS PRECONCENTRATION-SUMMARIZING OTHER PATENTS

As indicated in the previous section, gas/particle preconcentrators found in the patent literature can be broadly classified into two separate categories: continuous and cycled. The patent literature also indicates, however, that the distinction between the two is being blurred as cycled preconcentrators are being developed with ever shorter collection times. It is worthwhile, therefore, to view preconcentrator technology as having a continuous distribution of collection times ranging from collections times that dominate the detection time to collection times that are insignificant compared to the detection time. It is typically the total analysis time (including all sample preparation and detection) that is the important speed metric for most applications. For any set of operating conditions detectors will require a minimum total amount of analyte to be able to conclusively detect a target specie indicating that both the preconcentrator and detector must be made continuous for true near real time measurements to be made. Even continuous preconcentrators will have to operate for some finite time before enough analyte reaches the detector to be detected. From this point of view preconcentrators can also be viewed as a system used to modify an incoming gas stream by increasing the concentration of analyte relative to the diluent which provides conditions at the detector that minimizes the total amount of analyte that is required for detection.

The vast majority of patents for such preconcentrator technologies have been for cycled technologies where the collection time is significant compared to the detection time. The large number of patents on the subject makes a complete comprehensive review impossible, but general characteristics will be discussed along with a description of several more recently patented concepts. In cycled preconcentrators the analyte and diluent mixture flows over a specific adsorbing material for a specified amount of time which adsorbs some quantity of gas/particles/vapor in the mixture. The adsorbing material is then heated at a controlled rate to release the adsorbed gas. The adsorbing material can be rapidly heated to yield a sharply defined plug of material that can be sent to a gas chromatograph for time differentiation or it can be slowly heated at a controlled rate in which case each specie desorbs at a different temperature and time which separates the species in time and aids in detection.

The slow extreme of patented preconcentrator technology is represented by the volume adsorption type preconcentrator. These devices typically send the gas and analyte through a tube containing a volume or bulk amount of adsorption material. The large volume of the adsorbing material yields efficient collection and allows a large amount of sample to be adsorbed. It also, however, leads to longer desorption times yielding a less sharply defined plug of gas for analysis. It also yields less accurate time differentiation in the controlled rate desorbing process due to nonuniform temperatures in the volume. Several recent patents have attempted to address this issue using different techniques. One recent patent uses a porous metallic foam substrate to house the adsorbing material.[xl] The primary purpose of the metallic substrate is to increase the thermal conductivity of the adsorbing bed which will lead to faster gas desorption and also a more uniform temperature distribution within the adsorbing bed. In another patented technology the adsorbing material is placed between two concentric cylindrical chambers which yields a more controlled temperature profile and faster, more efficient heating and cooling of the adsorption material.[xli] Volume desorption based preconcentrators are a well established technology and the general trend in their development is towards faster and more accurately controlled desorption systems.

A natural progression in the development of faster and better controlled desorption processes is to a thin film desorption layer either suspended or deposited on a surface. Thin films can rapidly adsorb and desorb the analyte of interest and typically maintain a more uniform temperature distribution. Thin film adsorption membranes are less efficient at adsorbing the analyte, however. A series of patents have been granted in relation to the development of a supported screen adsorption preconcentrator being developed at Sandia National Labs.[xlii,xliii,xliv,xlv] The preconcentrator is used to increase the concentration of particles and vapors in a diluent gas such as air primarily for the detection of explosives, narcotics, and chemical agents. The device operates by using a fan or similar device to drive a primary gas stream over a pervious woven wire or metallic felt screen. During the process some of the incoming particles accumulate on the screen. After a set period of time a diaphragm shutter valve is used to close off the incoming air. Then a cross-flow puff of gas parallel to the screen is used to dislodge the particles from the screen and send them to a detector such as an ion mobility spectrometer. The screen is typically electrically conducting and can then be heated by passing electrical current through it. The device detailed in Patent #6,345,545 includes multiple stages of a similar device to increase the concentration and to reduce the flow rate to levels that are acceptable for common detectors.

Similarly, another series of patents describe a preconcentrator concept developed at Sandia National Labs that captures selected particles or vapors as a fan drives the primary gas flow in one plenum port that is covered by a pervious screen.[xlvi,xlvii,xlviii,xlix] After a sufficient period of time the screen is moved across a third port to the detector. This technology, however, doesn't use a gas puff to release the molecules, but instead releases them by heating the screen. The released particles are then directed to a detection device such as an ion mobility spectrometer. This technology is also specifically designed to be human portable and significantly reduces the analysis time for cycled preconcentrator technologies. Patent

#6,978,657 also discusses the alternative possibility of using the mesh adsorbing material on a wipe that is wiped over an area of interest and then attached to the analyzer. Patent #7,299,711 adds tight control of the mesh temperature during the desorption phase to help in accurate particle detection. The temperature of the membrane is increased in 2-7 steps with the dwell time (1-7s) at least twice the rise time (0.5s).

Another example of a preconcentrator using a thin film adsorber is described in patent #6,171,378.[l] The preconcentrator consists of a thin semiconductor or dielectric membrane with a platinum resistive heating membrane element and a adsorptive layer deposited on it. The adsorptive layer can be made up of a variety of materials (microporous materials, sol-gel oxides, polymers) depending on the specific particles to be analyzed. The membrane can be rapidly heated which causes a sharp release of particles into the detector. The device can also employ a heat spreading layer to deliver a uniform temperature over the surface of the membrane and an integrated temperature sensor. The primary application for the technology is for lab-on-a-chips.

A similar technology described in patent #5,083,019 uses a collector that is a wire, filament, or ribbon made from a transition metal and may be coiled for increased surface area.[li] An active coating of ceramic, gel, glasses, zeolites, or salts is placed on the collector and performs the actual collection. The active surface element is transported using a sliding shuttle to the detection device without allowing any ambient air to enter the device. The collector is then heated and electrically biased to remove the adsorbed vapor or particles. The collector can also have an integrated temperature sensor. The preconcentrator has shown an increase in sensitivity for an ion mobility spectrometer of up to 3 orders of magnitude yielding a device sensitivity of 0.003ppt. This sensitivity is sufficient to detect practical amounts of nonvolatile vapors. Multiple probes could allow one sample to be analyzed while another sample is being collected thus operating in a quasi-continuous manner.

Several preconcentrators that operate in a continuous fashion have also been previously patented. These devices may decrease the overall analysis time of the sensor system, but they are not applicable to sensing technologies that require a timed release such as systems that use gas chromatography. One technology described in multiple patents is a novel liquid adsorbent based system patented by Zaromb.[lii,liii,liv,lv,lvi] The device is an elongated tube in which a significant fraction of the length of the tube is covered with a wettable material. An analyte-sorbing liquid is continuously injected in one side of the tube and flows down the length of the tube to the other where it is collected and discharged to the detector. The sorbing liquid is an aqueous solution of a soap, detergent, or other wetting agent. The wettable material can be a wick or liner and the system would typically be operated with the cylinder axis vertical so that gravity causes the fluid flow. The fluid flow can also be driven by osmotic gradient. The gas is introduced into the cylinder with a turbulent swirling motion to cause more interactions between the gas and the liquid to increase adsorption. The goal of the device is to be able to detect explosives which may have concentrations of the order of ppt or less. The device can also be used with high sensitivity colorimetric detection or chemiluminescence. The analysis can be completed using the container that the liquid is stored in or the liquid can be moved to the analyzer. The collection chamber is a conical cavity at one end of the device. The device has the specific described application of the detection of cocaine or heroin. The invention was also extended to the collection of aerosol-borne analytes. The device has low temperature operation making it viable for highly reactive compounds. Liquid-absorption sampling has proven effective in collecting many different analytes.

Another continuous preconcentrator described in the patent literature is a continuous powder preconcentrator developed by Elias.[lvii] In this device an adsorbent is used, but it is in powder form. The powder is reused continuously. It is first introduced to the incoming gas/analyte stream, it then adsorbs analyte, is separated from the gas stream using cyclonic action, and then is sent to a heating zone where the adsorbed gas is released. The device showed the capability of concentrating relevant vapors from the parts-per-trillion range to the parts-per-billion range which is more suitable for detection. Several heating zones may be required to remove the vapor of interest and then to remove any other adsorbed vapor.

The patent literature also contains component technologies that could be advantageous for multiple types of preconcentrator technologies. Thermal control systems that are responsive and accurate would greatly benefit desorption based preconcentrators. Patent# 7,282,676 describes a method used to accurately control the electrical resistance and heating of the metallic screens used in many preconcentrators.[lviii] The net temperature rise is calculated in real time by performing the integral over the square of the voltage across the screen. Accurately measuring the quantity of adsorbed gas would also improve performance by enabling the preconcentrator to collect analyte only until sufficient analyte has been collected instead of for a predetermined estimated amount of time. Patent #7,168,298 deposits the adsorbing layer on the end of the paddle of a pivot plate resonator microbalance.[lix] The mass of the adsorbed particles can then be accurately measured as a function of time and the adsorption phase can then be run for the optimal amount of time. Patent #6,527,835 describes a preconcentrator that includes a thermal mass flow sensor.[Ulx] Accurate measurements of the fluid flow rate aids in the characterization of different analytical systems in response to flow and analyte properties.

A wide variety of gas preconcentrator technologies have been developed and patented. The obvious general trend of the most recent patents is towards greatly increased speed of the preconcentration process. Continuous preconcentrators, like the one described later in detail, represent the logical conclusion of this trend.

THE CURRENT PATENT ON CONTINUOUS TRACE GAS PRECONCENTRATION-

A continuously operating pre-concentrator for trace gas analysis includes a flow channel, a pumping chamber, and a separation membrane between the flow channel and the pumping chamber. The flow channel has a width that decreases from the inlet to the outlet in such a way that the trace gas and the carrier gas maintain a substantially constant flow speed through the flow channel. The separation membrane is configured to preferentially remove molecules of the carrier gas from the flow channel, as the sample gas flows from the inlet to the outlet, thereby increasing concentration of the trace gas in the sample gas. The separation membrane includes a substantially non-adsorbing material that allows the gas sample to flow substantially continuously through the flow channel, so that a variation in concentration of the trace gas can be detected in substantial real time.

(1) CLAIMS

The continuous trace-gas preconcentrator mainly claims a method in trace gas analysis of increasing concentration of a trace gas within a gas sample that includes the trace gas and a carrier gas. The method comprising: passing the sample gas at a substantially uniform flow speed through a pre-concentrator that causes the carrier gas to be preferentially removed from the sample gas through filtering membranes that do not adsorb the carrier gas and the trace gas, thereby raising concentration of the trace gas within the sample gas to a level sufficient for detection of the trace gas by a detector.

Physically, a continuous pre-concentrator for analysis of a trace gas, the pre-concentrator comprises a flow channel having an inlet and an outlet and configured to receive at the inlet a sample gas containing the trace (target) gas and a carrier (diluent) gas. The flow channel having a width that decreases from the inlet to the outlet in such a way that the sample gas maintains a substantially constant flow speed through the flow channel; and at least one separation membrane defining a portion of a side-wall of the flow channel between the inlet and the outlet. The separation membrane configured to preferentially remove molecules of the carrier gas from the flow channel so as to increase concentration of the trace gas as the sample gas flows from the inlet to the outlet, the separation membrane including a substantially non-adsorbing material that allows the gas sample to flow substantially continuously through the flow channel without being stopped by adsorption so that a variation in concentration of the trace gas within the sample gas can be detected in substantial real time.

The pre-concentrator further comprises at least one pumping chamber connected to the separation membrane and separated from the flow channel by the separation membrane, the pumping chamber configured to create and maintain the pressure difference between the lower surface of the membrane and the upper surface of the membrane so that the carrier gas molecules preferentially diffuse from the lower surface of the membrane to the upper surface of the membrane and into the pumping chamber.

The separation membrane has a strength sufficient to withstand the pressure difference between the lower surface of the membrane and the upper surface of the membrane. The separation membrane comprises an array of capillaries, which have a diameter size of about several nanometers, and wherein the preferential removal of the carrier gas molecules through the separation membrane occurs by diffusive filtering, size filtering and quantum separation. The separation membrane has an open area fraction greater than 0.01.

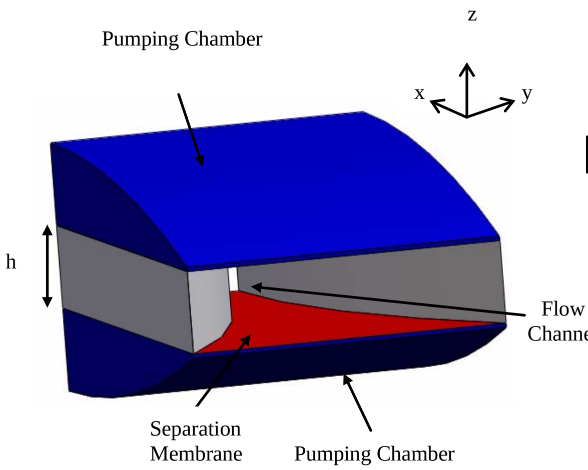
The flow channel height, length and width are to be designed according to the requirements of the analyzer. For example, type of target gas molecule (gives the molecular weight, size of the molecule, etc.), power budget, size constraint, separation channel size, and the required concentration of the target molecules are the main issues to determine the sizes of the flow channel.

A multi-stage pre-concentrator system for analysis of a trace gas, comprising: a plurality of pre-concentrators connected to each other so that concentration of the trace gas within a sample gas containing the trace gas and a carrier gas increases progressively as the sample gas flows through each one of the plurality of pre-concentrators in sequential order; wherein each pre-concentrator comprises: a flow channel having an inlet and an outlet and configured to receive at the inlet a sample gas containing the trace gas and a carrier gas, the flow channel having a width that decreases from the inlet to the outlet in such a way that the trace gas and the carrier gas maintain a substantially constant flow speed through the flow channel; and at least one separation membrane defining a portion of a side wall of the flow channel between the inlet and the outlet, the separation membrane configured to preferentially permit removal of molecules of the carrier gas from the flow channel so as to increase concentration of the trace gas as the sample gas flows from the inlet to the outlet, the separation membrane including a substantially non-adsorbing material that allows the gas sample to flow substantially continuously through the flow channel without being stopped by adsorption so that a variation in concentration of the trace gas within the sample gas can be detected in substantial real time.

(2) DESCRIPTIONS OF THE PATENT

Continuously operating preconcentrators for trace gas analysis do not use adsorbing materials, but are configured to raise the concentration of the analyte trace gas by causing the gas sample to preferentially lose the carrier gas through separation membranes. By passing the gas sample at a substantially uniform flow speed through a pre-concentrator, the carrier gas can be preferentially removed from the gas sample through separation membranes that do not adsorb the carrier gas and the trace gas. Consequently, the concentration of the trace gas within the gas sample can be raised to a level sufficient for most of the miniature gas sensors.

The continuous trace-gas preconcentrator could make use of one or several of four possible separation mechanisms: mass diffusion separation, potential well (between a gas specie and the wall material) and sampled by thermal creep flows) separation, quantum separation, and size separation.



Note: Scale is distorted in this sketch
Fig. 1 (a) Continuous Pre-Concentrator

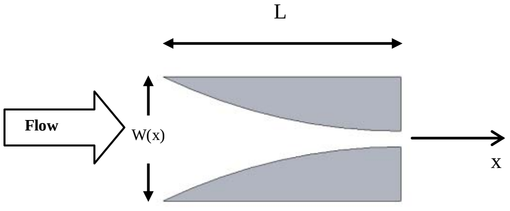


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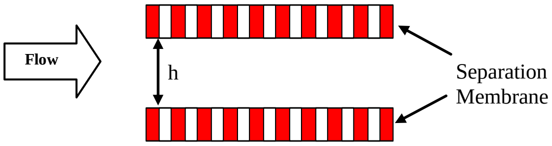
Fig. 1 (b) Flow Channel Top View



Note: Scale is distorted in this sketch
Fig. 1 (c) Flow Channel Side View

Fig. 1(a) is a schematic diagram of the continuous trace gas preconcentrator in accordance with one embodiment of the patent disclosure. In overview, the pre-concentrator includes a flow channel, at least one pumping chamber, and at least one separation membrane between the flow channel and each pump chamber. The separation membrane defines at least a portion of the surface of the side-wall of the flow channel.

As shown in Fig. 1 (b), the preconcentrator's flow channel has a constant height and varying width, while the pumping chambers have constant widths and varying heights. Separation membranes with nanometer size channels form the upper and lower surfaces of the concentrator's flow channel. Pumping chambers back each of the separation membranes. Sampled gas is continuously drawn into the flow channel from the local atmosphere or other source. In order to minimize pumping energy requirements both the flow speed of the sampled gas and its number density remain essentially constant throughout the flow channel. The sampled gas is overwhelmingly a carrier gas, with trace concentrations (1 to 10^{-3} ppb) of target molecules. It is of interest to enhance the trace concentrations of the target molecules. As the sampled gas travels down the flow channel the generally lighter and smaller carrier gas molecules preferentially escape through the separation membranes into the pumping chambers. Pre-concentration by the pre-concentrator is performed by preferentially removing through the separation membrane molecules of the carrier gas from the flow channel, as the sample gas flows from the inlet to the outlet. In other words, as the sampled gas travels down the flow channel, the generally lighter and smaller diluent (or carrier) gas molecules preferentially escape through the separation membranes into the pumping chambers. In this way, concentration of the trace gas within the sample gas is increased.

Fig. 1(c) illustrates an embodiment in which an upper separation membrane and a lower separation membrane are provided on an upper portion and a lower portion of the side wall of the flow channel, each membrane connected to a respective pump chamber and (practically, one pumping chamber, which provides the same low pressure environment at both of the separation membrane outlets, will be needed. Using one pumping chamber also cuts down the energy consumption.). In this embodiment, the separation membranes form the upper and lower surfaces of the side wall of the flow channel, respectively. Different configurations of the membranes and the pumping chambers may be used, in different embodiments of the present disclosure.

The pumping chamber creates and maintains a pressure difference across the membrane, i.e. between the lower surface of the membrane (connecting to the flow channel) and the upper surface of the membrane (connecting to the pumping chamber) so that the carrier gas molecules are pushed from the lower surface of the membrane to the upper surface of the membrane and into the pumping chamber, as the gas sample travels through the flow channel. The separation membrane has a strength sufficient to withstand this pressure difference between a lower surface of the membrane and an upper surface of the membrane, and to maintain its shape substantially constant during the flow of the sample gas through the channel.

As a consequence of diffusive mass selection and/or size selection, the membranes inhibit target molecules from passing through the separation membrane channel (not necessarily capillaries) while allowing the diluent gas to pass more freely. The separation membrane is made of a substantially non-adsorbing material. This is so that the gas sample can flow substantially continuously through the flow channel without being stopped by adsorption. For the pre-concentrator to work continuously for long periods, it is most convenient if the target molecules do not condense in the separation membrane channels due to the phenomenon of pore condensation. Thus, the rejection of these molecules from the separation membrane channel may be important.

The width of the flow channel decreases along its length such that the flow speed is constant, with typical values of 2.5 to 10 cm/s. Preconcentrator flow channels are typically 1 to 2 cm long and 0.1 to 0.5 cm wide. Representative transit times are a few tenths of a second. The flow channel has a height of around 100 μm and the flow is well into the continuum flow regime for pressures of one Earth atmosphere, while the flow through the separation membranes is in the molecular flow regime. In the pumping chambers backing the membranes, carrier gas number densities are a fraction (0.75 to 0.5) of the number density at the entrance to the flow channel. The cross-sectional area of the pumping chambers, perpendicular to the downstream x direction in the channel, is adjusted by changing the height of the chambers according to continuity requirements. The result is both a constant flow speed in the x direction and an approximately constant carrier gas number density throughout the pumping chambers.

For the available analysis of the basic flow field of the pre-concentrator, concentrations of the target molecules are assumed to be so small that they have no influence on the flow dynamics in the channel. Once the carrier flow field is determined, the target molecules are introduced by linear superposition. The separation membranes are arrays of aligned, reasonably uniform size capillaries, that can vary from tens of nanometers to subnanometer size. For the larger sizes, transitional flows can occur inside of the separation membrane's channel at one Earth atmospheric pressure. The capillaries in the separation membrane should have relatively short lengths as the proper length to diameter ratio has a great influence on the preconcentrator's performance.

An additional assumption is that the target and carrier gas molecules remain well mixed as they travel together down the preconcentrator's flow channel. Since the conductance (as well as diffusivity) of a normal separation membrane will generally be greater for the carrier gases (lighter), an increased concentration of target molecules will appear near each separation membrane. A preliminary analysis of the extent to which diffusion can be expected to reduce gradients in target gas molecules, perpendicular to the membranes in the flow channel, was performed[1] and indicated that the target gas would remain uniformly distributed. Consider the flow channel illustrated in Fig. 1. Assume the flow is driven by an extremely small pressure difference that is available as needed to draw the flow into the channel, as well as to overcome viscous effects in the channel flow. As the gas travels through the channel, the carrier gas preferentially diffuses through the separation membranes, which have an average conductance for the carrier molecules of $(c_aF_aa_a)/4$ per unit membrane area. Here c_a is the mean thermal speed of the carrier molecules, F_a is the fractional open area of the membrane surfaces, a_a is the probability that once in a capillary a molecule will pass through the membrane and end up in one of the pumping chambers. A preliminary analytical analysis[1] shows that the total loss N_a of carrier molecules, per unit distance in the axial direction, through the two membranes at a position x may be approximated as

$$N_a(x)=n_{a,i}\exp\{-c_aF_aa_a(1-\eta_a)\,x\,/\,(4hu_{a,i})\}. \qquad (1)$$

Here $n_{a,i}$ and $u_{a,i}$ are the inlet number density and velocity, h is the flow channel height, and η_a is the pressure ratio of the pumping chamber to the flow chamber.

Based on the typical extremely low concentrations of target gas molecules, even after preconcentration, there is no possibility that the target molecules can affect the flow dynamics in the preconcentrator's flow channel. There will be a tendency for target molecules to collect near the inner walls of the separation membranes. Because typical channel heights are from 50 to 100 mm, the target gas concentration was assumed to remain effectively uniform over the channel height. Also, there should be no significant diffusion of target gas molecules in the flow direction due to the much greater length scale. The target gas number density increases along the x direction as

$$n_t(x)/n_{t,i} = \exp\{(x/2hu_{t,i})[c_aF_aa_a\,(1-\eta_a)-c_tF_ta_t(1-\eta_t)]\}. \qquad (2)$$

Here, c_t is the mean thermal speed of the target molecules, and $a_t = \kappa a_a$, with $\kappa<1$.

To understand the performance of the separation membrane, based on eq (2), Ar/N_2, Xe/N_2 and SF_6/N_2 mixtures were studied and shown in Figs. 2, 3, and 4 respectively. Assuming a mixture flow with a uniform speed of 2.5 cm/s passes through the continuous trace gas preconcentrator shown in Fig. 1. The capillary channels of the separation membrane with an estimated 3% of open area have a mean diameter of 7.5 nm and a length of 50 μm. The pressure ratio between the pumping chamber and the flow channel is 0.5. The transmission probabilities (aa and at in the Figures) are one of the future research interests. In the Figs. 2, 3 and 4(a), values of a_a were estimated based on Knudsen flow through long capillaries and a range of a_t

values were obtained as 1 a_a, 0.9 a_a and 0.1a_a. The heavier the trace gas molecule is, the higher concentration of the trace at a fixed length (eg. x =0.1m). The trace concentration increases are also sensitive to the transmission probabilities of the trace and carrier gas molecules. For Ar/N_2 mixture, when a_t = 0.1 a_a, the increase of the trace gas concentration is more than two orders of magnitude greater than what was obtained when $a_t = a_a$. These results indicate importance of the transport of the trace and carrier gas molecules. Studies on transport properties of gas molecules through carbon nanotubes have indicated significant mass flow increases above the Knudsen flow predictions. If the transmission probability a_a increases by a factor of ten, for SF_6/N_2 mixture, the trace concentration changing along the x-axis is shown in Fig 4(b). For cases with the transmission probability being two orders of magnitude higher than the Knudsen flow, the trace gas concentration increases are shown in Fig. 4(c). The trace concentration shows very significant increases when the transmission probability varies. With a suitable membrane, the continuous gas trace preconcentrator can easily have a factor of 100 to 1000 times increase in the target molecule concentration.

Because the gas sample flows substantially continuously, without being adsorbed and without pore condensation, the pre-concentrator operates continuously. In this way, any variation in concentration of the trace gas within the sample gas that enters the inlet of the flow channel can be detected in substantial real time at the outlet of the flow channel.

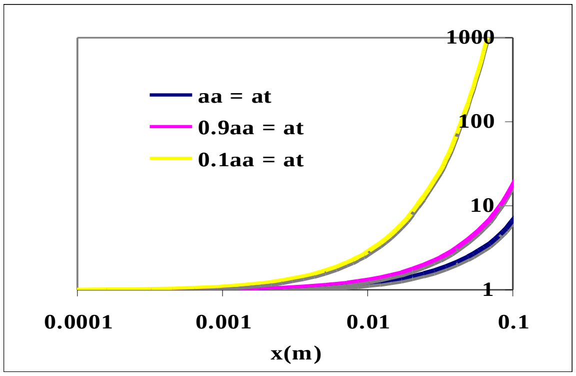


Figure 2: Ar/N2 mixture

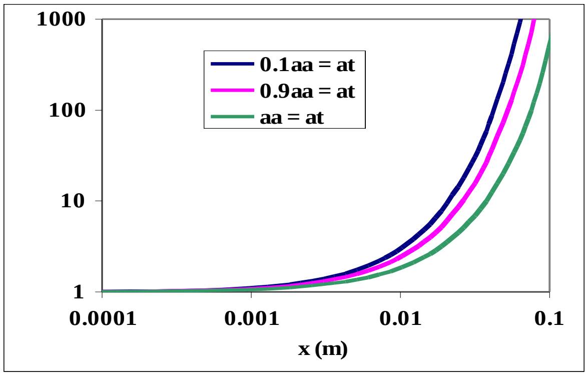


Figure 3: Xe/N2 mixture

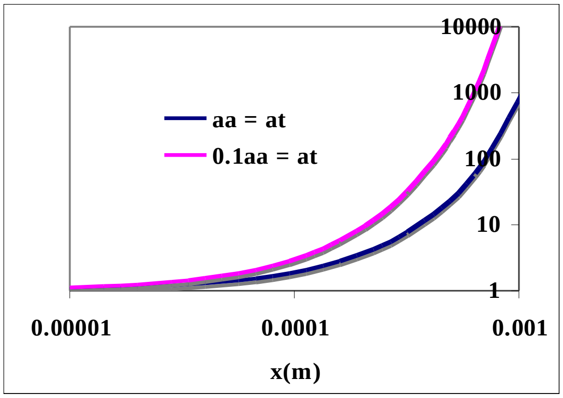


Figure 4 (a): SF$_6$/N$_2$ Mixture - Transmission Probability is One Hundred Times Higher than predictions from the Knudsen Flows

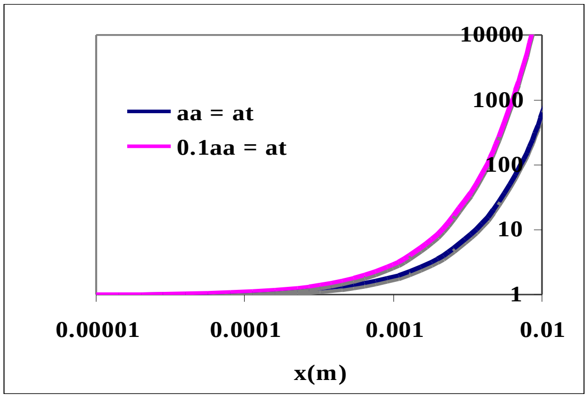


Figure 4 (b): SF$_6$/N2 mixture - Transmission Probability is Ten Times Higher than predictions from the Knudsen Flows

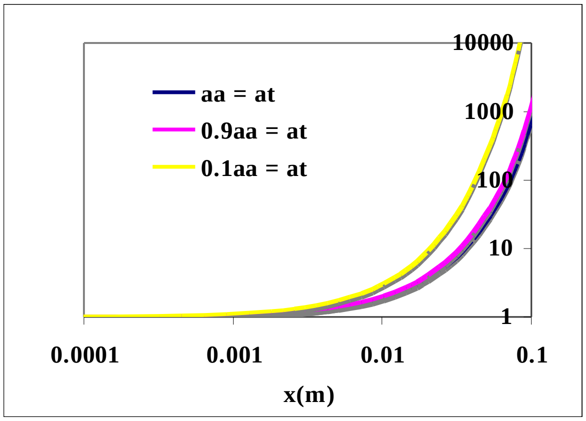


Figure 4 (c): SF6/N2 mixture Transmission Probability as Predicted by Knudsen Flows

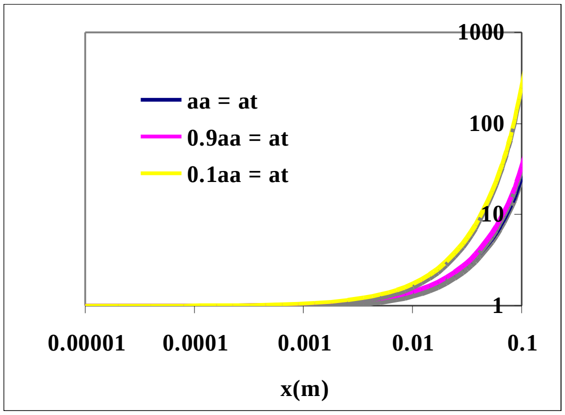


Figure 5: SF6/N2 mixture (with a pressure ratio between the pumping chamber and the flow channel = 0.75)

CURRENT AND FUTURE DEVELOPMENT

(1) NANO-SCALE MEMBRANE TECHNOLOGIES

The principal difficulty in creating a plausible mass diffusion separation scheme using membranes is the availability of arrays of nanometer diameter capillaries or apertures. The arrays must satisfy the following requirements: be short enough to have relatively high transmissions or pumping speeds; have an open area fraction of at least 1%; and be strong enough to support moderate pressure differences. Recently several techniques for assembling arrays of nanometer scale capillary channels with acceptably small length to diameter ratios for use in transmission membranes have been reported.[lxi,lxii,lxiii,lxiv,lxv,lxvi]

Martin et al reported on template-synthesized nanotube membranes. Based on commercially available nanoporous membrane as a template, polymer is synthesized by oxidative polymerization of the corresponding monomer within the pores. This may be accomplished either electrochemically or with a chemical oxidation agent. The inner pore diameter of the template-synthesized membrane can be smaller than 3 nm and the thickness of the membrane can be easily controlled according to selected templates. However, the fraction of open area can barely meet the 1% requirement. Unless a higher pore density and smaller pore diameter of the templates can be achieved, the template-synthesized membranes would not be able to provide satisfactory results as preconcentrator membranes.

Aligned multiwalled carbon nanotube membranes reported by Hinds et al [lxii] and Holt et al[lxv] are obtained by filling space between CNTs with a continuous polymer or Si_3N_4 film before the tips of nanotubes are etched open. The length of the nanotubes within the polymer can be reduced by selective electrochemical oxidation. This makes the membrane thickness robust. A membrane with 5 mm thickness, 7.5 nm inner tube diameter, and a fractional open area of 2.7% has successfully been demonstrated. The great improvement of the fractional open area from the template-synthesized polymer membrane to the multiwalled carbon nanotube membrane strongly suggests the choice of carbon nanotube membranes as preconcentrator membranes. Another carbon nanotube membrane is the “bed-of nails’ membrane of single-wall carbon nanotubes developed by Smalley’s group. [lxiv] Suspended in a fluid, SWNTs can be oriented by applying a magnetic and/or electric field. SWNTs become aligned with their longitudinal axes parallel to the applied field. Then the aligned SWNTs are removed from the suspension in such way that they are assembled while maintaining the alignment. The desirable properties of this membrane are ultrahigh pore density up to 10^{14}/ cm^2 and a narrow distribution of pore sizes that is tunable from 0.4 to 3 nm. Ref 62 present a membrane with size up to 15 mm x 15 mm, thickness of 75 nm or less and a resulting fractional open area of 0.7%. Using similar techniques, a membrane area of more than 1 cm^2 and a thickness of more than 1 mm has been produced.[64] This promising result demonstrates the rapid progress of carbon nanotube membrane technology. It is encouraging for the size separation option (<1nm) of the preconcentrator membranes. Also, simulation results[lxvii,lxviii,lxix,lxx] have shown that the transport diffusivities are about three orders of magnitude greater in carbon nanotube membranes than in silicalite membranes with the same thickness. The mass diffusion separation of the preconcentrator's membrane can be demonstrated with membranes of much larger pore diameter, since in many cases the molecular weight of the target gas is much heavier than that of the carrier gas. Ever since carbon nanotubes (CNTs) were discovered in 1991,[lxxi] researchers have been fascinated by their promising properties such as; superior mechanical strength, high electrical current density and super conductivity at low temperatures.[lxxii] As described in the previous section, with the development of methods capable of synthesizing aligned CNTs, filling the gaps with various compounds, and cutting them into open-ended tubes, CNTs have become an attractive material selection for nanofluidic and nano gas dynamic applications.

Molecular Dynamics simulations regarding transport phenomenon through CNTs have predicted significant (several orders of magnitude) increases of mass flows for small molecules such as CH_4, H_2, Ar, Ne, CO_2 and N_2. Some simulation results, which adopted the rigid lattice model, suggested that the fast transport exists due to the well-defined inner diameters and the ultra smoothness (on atomic scale) of the CNT surface.[lxvii,lxviii,lxix] Skoulidas et al[lxvii] have shown that with a 1.38 bar pressure drop, the CH_4 mass flux through 1.36 nm diameter (10,10) CNTs is more than three orders of magnitude higher than the mass flux through zeolites with comparable pore sizes. Ackerman et al[4] predicted the mass flux of Ar and Ne to be four orders of magnitudes higher through CNTs than through silicate membranes with the same thickness (10 mm). However, the real reasons for such fast transport phenomena through CNTs are still debated. Recently, simulation results including considerations of nanotube lattice flexibility, which implies more surface corrugation, have been reported.[lxx,lxxiii] Chen et al[lxx] concluded that the mass flux with the inclusion of the lattice flexibility only decreases by a factor of two relative to the rigid lattice assumption for CH_4 at 1 bar. Fast mass transport phenomenon still exists in 'flexible' CNTs.

Experimentally, Hintz et al[62] and Holt et al[65] both observed the fast mass transport through CNT membranes for both liquid and gas molecules. Hintz et al[62,63] measured the flow rates of water and several solvents through CNTs and found that the flow speeds are four to five orders of magnitude faster than conventional fluid flow would predict through pores of 7 nm diameter at 1 bar. The mass flow rates of air through CNT membranes (diameters ~ 1.3 to 2 nm) observed by Holt et al[lxv] are one to two orders of magnitude larger than what were predicted by the Knudsen diffusion model. Utilizing a CNT's property of fast mass transport in a membrane is expected to substantially increase the preconcentrator efficiency.

(2) Carbon Nanotube Membrane Fabrication

Fabrication of single-walled carbon nanotube (SWNT) membranes involves the following processes. First, silicon substrates with suspended 100 nm SiN membranes using standard silicon micromachining techniques were produced. Fe films (1~2Å) were then deposited onto the substrates and annealed at 500°C for 10 minutes to produce Fe nanoparticles that can work as catalysts for single-walled nanotube growth. A special home-made PECVD (plasma enhanced chemical vapor deposition) setup was subsequently employed to synthesize vertical aligned SWNT with high density and uniform diameter atop the silicon substrates.[lxxiv] For a typical process, the substrate was first placed in the quartz tube reactor housed in a tube furnace; it was then heated to the growth temperature (~ 720 °C) with H_2 (100 sccm) flowing, followed by nanotube growth with a gas flow of 160 sccm CH_4, 30 sccm H_2, and 2.5 sccm at 0.3 ~ 0.4 torr pressure. An RF plasma was generated at a power of 60- 70 W for 10-30 minutes for the nanotube growth. Figure 6c shows two SEM images, where one can clearly see the vertical aligned carbon nanotubes. These nanotubes have been thoroughly examined using AFM, TEM, and Micro Raman, and are confirmed to be mostly single-walled carbon nanotubes. The average diameter of carbon nanotubes can be tuned by depositing Fe films of different thickness and annealing at different temperatures.

After the growth of CNTs on the silicon substrates with SiN membranes, the voids between the CNTs have to be filled. Techniques have been demonstrated including spin-coating polymer - polystyrene (PS) in a toluene solution,[lxii] and LPCVD (low-pressure chemical vapor deposition) silicon nitride (SiN).[65] Using PS to fill the voids is an easier choice and it has been proven to be able to effectively filling the voids. [62] Currently, experiments adopting the spin-coating polymer technique are ongoing. A PS (50% weight ratio) in toluene solution was spin-coated over the surfaces of aligned CNT samples. To slowly eliminate toluene and to enhance the adhesion of PS and CNT, samples were then dried in vacuum oven at 70°C for 5 days under 640 Torr pressure.

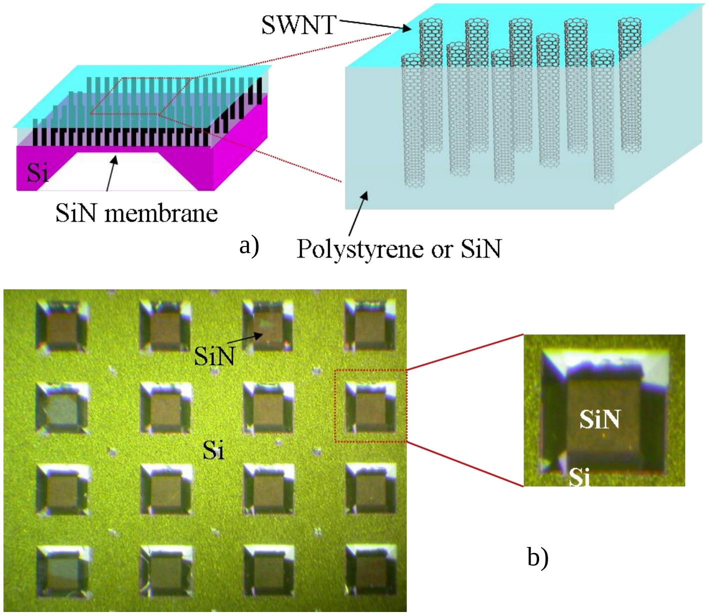


Figure 6: a) Schematic diagram of SWNT membranes on Si substrate with SiN membrane.
b) Photograph of Si substrate with SiN membrane achieved by wet etching of silicon wafers

Figure 6a shows a schematic diagram of the carbon nanotube membranes on top of the SiN membrane, while Figure 6b shows photographs of an array of fabricated SiN membranes. Once the voids have been filled, the backside SiN membranes on Si substrate will be removed by CF_4 reactive ion etching. CF_4 plasma will only etch SiN but keep carbon nanotubes and PS unharmed. The freestanding carbon nanotube membranes can then be reduced to the desired thickness by O_2 plasma etching from both the front side and the back side. This etching process will also open up both ends of the carbon nanotubes and remove excess PS. Carbon nanotubes will be the only open channels for gas flows through the membrane.

The fraction of the open area of the carbon nanotube membrane can be larger than reported previously.[lxii,lxv] It can be more than 2.7% with the mean nanotube inner diameter of 1~ 2 nm. One future goal of the carbon nanotube membrane construction is to optimize the fraction of the open area of the membrane and the nanotube diameters for trace-gas preconcentrator operations. Conventionally, at one atmospheric pressure, Preconcentrators can be operated more efficiently using membranes with larger inner diameters of nanotubes. A higher fraction of open area can provide more mass flow through the membrane. Adjustments of the membrane open area and nanotube diameters can be achieved by carefully patterning and controlling the thickness of the Fe film.

(3) Continuous Trace Gas Preconcentrator with Carbon Nanotube Membrane

The recently patented micro/meso-scale, continuous flow-through, trace gas preconcentrator has been predicted to be capable of achieving significant trace gas concentration increases using one or two simple micro/meso-scale mass diffusion separation stages without interrupting the gas flow. Combined with recent advances in carbon nanotube membrane fabrication techniques, the continuous preconcentrator, which requires significantly less operational time, can possibly achieve much higher trace gas concentration levels with a comparably smaller sized device. Research efforts for the continuous trace gas preconcentrator will focus on validating the performance of the carbon nanotube separation membrane.

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