NMT – A new individual ion counting method: Comparison to a Faraday cup

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Abstract
Two sample detectors used to analyze the emission from Gas Chromatography (GC) columns are the Flame Ionization Detector (FID) and the Electron Capture Detector (ECD). Both of these detectors involve ionization of the sample molecules and then measuring electric current in the gas using a Faraday cup.

In this paper a newly discovered method of ion counting, Nanotechnology Molecular Tagging (NMT) is tested as a replacement to the Faraday cup in GCs. In this method the effective physical volume of individual molecules is enlarged up to 1 billion times enabling them to be detected by an optical particle counter.

It was found that the sensitivity of NMT was considerably greater than the Faraday cup. The background in the NMT was circa 200 ions per cm$^3$, corresponding to an extremely low electric current $\sim 10^{-17}$ A.

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1. Introduction

Detection of ions in the gas phase is widely employed in science and technology, e.g. in trace gas detectors such as Ion Mobility Spectrometry (IMS), Mass Spectrometry (MS), Gas Chromatography (GC). In nuclear physics the cloud chamber detector is used [1]. The quantification of ion concentrations in IMS and some GC detectors is accomplished by measuring an electric current using a Faraday cup [2]. The Faraday cup operates by measuring the current produced from the neutralization of an ion’s charge as it is captured by an electrode [3]. The Faraday cup detection technique is close to its physical detection limits due to the thermal fluctuations in the electron gas producing noise in the electronic amplification circuits [2,4]. In general MS does not use a Faraday cup but it requires a vacuum that causes sample loses at the atmospheric pressure – vacuum interface [3].

In practice, with the trace gas detectors available it is challenging to measure concentrations below the ppt level (circa $10^7$ molecules per cm$^3$) in the air. Currently to achieve sensitivity below the ppt level, enrichment of the sample gas through pre-concentration (by the absorption and then quick desorption of the sample) is employed [5]. Pre-concentration is a time-consuming process. Higher sensitivity within acceptable time frames would improve progress in trace concentration measurements in many areas, for example in life sciences and medicine.

As an example of medical applications, measurements of trace levels of Volatile Organic Compound (VOC) biomarkers for disease diagnostics is a rapidly growing area of metabolomics that promises to bring non-invasive fast diagnostics to points of care [6]. An increase in sensitivity will enable diagnosis of diseases at an earlier stage. This has been recently confirmed in vitro by quantification of VOC biomarkers emitted by various cells, e.g. HepG2 hepatocellular carcinoma cells [7] or lung cancer cells [8]. A single cell is responsible for generating $\sim 10^4$ biomarker molecules per hour in a head space [8]. Analysis at a low concentration level is desirable for many applications, e.g. for single cell or bacteria observations and drug development, but is not achievable with current technologies.

Ion Mobility Spectrometry (IMS) devices [5] are used for security applications including detection of explosives at airport checkpoints. The availability of low vapour pressure explosives, such as tetranitro-triazacyclohexane (RDX) [5], and the need to detect concealed explosives requires new technologies that detect lower concentrations of explosives in the air.

A newly discovered method of ion counting, Nanotechnology Molecular Tagging (NMT), is a fast-developing technology that enables ions in the air to be individually counted [9,10]. This method has a fundamental advantage over the Faraday cup because it does not require electronic circuit amplification. Instead the volume of individual molecules is enlarged up to 1 billion times.
by tagging them with specially generated nano-objects with radius ≥100 nm, enabling them to be detected individually by widely available optical particle counters [9,11]. An ultimate sensitivity of measurements down to 1 elemental charge can in principle be achieved. The NMT technology has been tested with IMS and GC in a variety of environments. It is anticipated that this concept opens doors for considerable improvement of detection capability in many applications across diverse fields such as airport security, atmospheric science, trace compound detection e.g. in lab-on-a-chip devices, life science and medicine (e.g. for monitoring and diagnostics of early stages of lung cancer and other diseases).

2. Description of the NMT technology sensor

The NMT is a novel concept of measuring ultra-low concentrations of ions and molecules in a gas phase [9]. As with the Faraday cup, for the detection of molecules with NMT the molecules are required to be ionized. The NMT sensor contains 5 main modules, as shown in Fig. 1:

1. An ionization chamber if molecules of interest are uncharged;
2. A generator of electrically uncharged tags;
3. A tagging chamber where ionized molecules are tagged;
4. A tagged ion extractor where tagged ions (tags that are now charged) are separated from unused neutral tags and
5. An optical particle counter (OPC).

In the first module (the ionization chamber), the molecules of interest in a sample flow are ionized by an ionization source (e.g. 241Am, 63Ni or a corona discharge). The ionization chamber is not required if the sample is already ionized. A tag generator forms a flow of electrically neutral tagging objects (or simply “tags”) in the second module. Tags are formed by homogeneous nucleation from a semi-volatile organic compound, e.g. Bis(2-ethyl-hexyl) sebacate. Tags are spherical particles with radius ~100 nm or more [9,14]. The flow containing the tagging objects and the flow containing the ions are mixed in the tagging chamber (module 3). To minimise the probability of multiple ions attaching to a single tag, the number of tags introduced to the chamber greatly exceeds the number of ions. In the 4th module the tags, which have gained charge (the tagged ions) are separated from the tags which did not interact with ions and thus remained neutral. The charged tags are separated in an electric field, being moved into an adjacent clean laminar gas flow [15]. Finally, the flow with the charged tags (tagged ions) is directed to an optical particle counter where a laser diode counts single tags using photon scattering [11]. This is a conceptually new way of measuring ultra-low concentrations of chemical compounds in gas samples or flows. Amplification of small changes in electric currents is replaced by tagging that increases the physical volume of ions by factor of ~109. This eliminates the thermal electronic noise present in methods based on the Faraday cup and has the potential to achieve much lower detection limits. Therefore, an ion sensor utilizing the NMT technology should be more sensitive than a conventional detector. In this paper we report results of a comparison of an NMT ion sensor with a typical Faraday cup detector used with GC.

3. Experimental

3.1. NMT

An NMT ion sensor was built according to [9] as shown in Fig. 1 but the ionization chamber was not used. The tag generator uses homogenous nucleation and comprises a PTFE volume containing a heater as a saturator, followed by an aluminum tube as a condenser [14]. The tagging chamber is a brass cylinder of 2 cm3 volume with two inlets and an outlet. A sample flow (0.05 l/min) containing ions enters the tagging chamber through one inlet and the flow containing tags (0.2 l/min) enters the chamber through the other inlet. A third tube removes 0.25 l/min, this flow contains a mixture of tagged ions and neutral unchanged tags, and is directed to a charged tag extractor. The rectangular charged tag extractor (third module) is formed by two aluminum plates (4 cm × 11 cm) separated by a 0.5 cm spacer [10,15]. Inside the extractor two parallel laminar flows are formed, see Fig. 1. One of the laminar flows is the flow from the tagging chamber. This flow contains tagged ions and electrically neutral tags. The second laminar flow contains no tags. Using an electric field the tagged ions are moved into the second laminar flow. This results in a spatial separation of the charged and uncharged tags. This second laminar flow which now contains the charged tags is then directed to an OPC. Finally, the tagged ions are counted in the OPC individually. Because the number of charged tags is equal to the number of ions, the OPC reading provides the ion number [9]. The NMT interface was set to detect negative ions for the comparison study below.

3.2. Faraday cup

The Faraday cup was taken from an off-the-shelf GC detector (SRI electrometer model 110). Aluminum shielding was put in place to ensure background electrical noise picked up by the elec-

![Fig. 1. Schematic of the NMT molecule counting device. The neutral tagging objects are represented by the green line. The ions from the ionization chamber with a purple line. The ions attached to a tag by a red line. The lines are representative of trajectories, in reality the flows are more turbulent especially in the Tagging Chamber. The bold lines at the Tagged Ion Extractor represents the electrodes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
trometer was low. The voltage difference applied to the central electrode of the Faraday cup was +24 V. The amplifier circuit for Faraday cup (GC electrometer) was functioning in negative mode.

3.3. Ion generating set-up

The same source of ions was used to compare performance of the Faraday cup and the NMT sensor. A gas flow was used to transport the ions from the ion source to the detector being tested. To achieve a controllable range of ion concentrations, the length over which the ions were transmitted was varied. This was achieved by varying the length of a copper tube with 4 mm inner diameter placed between the ion source and the sensor being tested, see Fig. 2. The number of ions reaching the sensor at the end of the tube is varied due to ion losses. Ion losses occur during transmission via any mechanism which neutralizes the ion, including recombination with an ion of the opposite charge, or collision with an object that can disperse the charge, such as the conductive tube wall. Therefore, although ion concentrations were not known a priori, it was possible to compare two sensors across a range of controlled ion concentrations.

A 0.05 l/min air flow was generated by a diaphragm pump (Schwarzer Precision SP 270 EC-TH) and monitored with a flow meter (Omega FLDA3525S). Ions in the sample air flow were formed by a 37 kBq $^{241}$Am radiation source, see Fig. 2. A radiation source is a convenient and stable method of producing negative and positive ions in atmospheric air.

The NMT and Faraday cup sensors were placed a set-copper tube length away from the radiation source and their response recorded (one at a time). The length of the copper tube was varied between 0 mm and 100 mm. The NMT sensor entrained the 0.05 l/min flow from the radiation source directly into the tagging chamber. Readings of the number of counts were taken at various lengths of the copper tube in the same way as readings for the Faraday cup sensor.

4. Results

Data with and without the radiation source present were recorded for both the NMT sensor and for the Faraday cup sensor. The NMT sensor data obtained at a set distance downstream of the radiation source were consistent and repeatable, see Fig. 3. Without the radioactive source the NMT background ion count per second was 216 ± 73 per second. With the radioactive source the NMT ion counter detected much greater ion count rates. At the 0 tube length the ion count rate was 50,328 per second. At 40 mm tube length the count rate was 8000 per second. Even at 90 mm tube length the count rate was 493 per second. The NMT ion count rate depends on the copper tube length over the entire length range, and therefore it depends on ion concentration down to a minimal concentration corresponding to a 100 mm tube length.

Fig. 4 shows the Faraday cup data, graphing voltage vs. the tube length. Data obtained with the Faraday cup were unstable and showed a drift in the signal which occurs over a period of minutes. This leads to occasional negative signals both with and without the radioactive source. Without the radioactive source, the signal from the Faraday cup sensor at the 0 mm length of the copper tube is ~7 mV, see Fig. 4. When a radioactive source is placed in a tube with an air flow passing over it, the ion concentration occurring at the same tube length is 49 mV. There is a difference in the signal that can be associated with the presence of ions. At 30 mm tube length with the radioactive source the signal is 24 mV but without the source it is negative ~43 mV. This is considerably lower than the background noise level measured without the radioactive source at other tube lengths. Therefore, the instability of the background measurements might affect both readings.

For larger tube lengths from 40 to 100 mm there is no clear difference between the signals with or without the radioactive source. Thus, the effect of ions from the radioactive source on the signal can be observed only when the tube length is less than 40 mm. This indicates that 40 mm length corresponds to a certain ion concentration that does not enable ions to be detected reliably by the Faraday cup sensor. The value of the ion concentration occurring at this threshold cannot be retrieved reliably from the Faraday cup measurements.

5. Discussions

The NMT sensor showed an ability to detect ions reliably from the radiation source down to 90 mm tube length. The Faraday cup based sensor enabled detection down to 30 mm tube length. There is a clear advantage of NMT performance in comparison to the Faraday cup device. To quantify this advantage, we need to refer to a unique ability of the NMT technology to provide direct data on ion current. The NMT method is an ion counting method and therefore the origin of the NMT signal is numerical (number of elementary charges). The number of elementary charges is linked to the electric current. The range of change in the effective electric current over the copper tube length is from 8 × 10$^{-15}$ A (at 0 tube length) to 3 × 10$^{-17}$ A (at 100 mm tube length), see Fig. 5.

The specification of the tested Faraday cup is unknown, however by using the NMT results as a guide it appears that it enables roughly 2 femto-amperes to be reliably measured, this is broadly consistent with the current state-of-the-art for Faraday cup detectors. On the contrary, the NMT device provides measurements in the atto-ampere range (3 × 10$^{-17}$ A). This also illustrates an advantage of the NMT sensor – being a direct counting method it does

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**Fig. 2.** Schematic of the set-up for the comparison of the NMT and Faraday cup based electrometer detection of ion concentrations in the same flow. The "radiation" rectangle indicates the ionization chamber with 241Am.
Fig. 3. Ion count rate data from the NMT ion counter vs. the copper tube length. Blue squares represent the count obtained with 241Am radiation source present, red circles for 241Am radiation source absent. The errors bars represent the standard deviation of measurements using the NMT. The errors for the blue squares are smaller than the size of the squares. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 4. Data from the electrometer based on the Faraday cup vs. the copper tube length. Blue squares represent the count occurring when the 241Am radiation source is present, red circles for when the 241Am radiation source was absent. The errors bars represent the standard deviation of 9 measurements using the electrometer. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
not require calibration as required for example in the case of a Faraday cup based sensor.

The sensitivity of a detection technology can be also evaluated from signal to background noise ratio. Preferably it should be done at the same ion concentration. The most suitable choice is the maximal ion concentration at 0 mm tube length where both methods provide reliable data. The signal is taken as the count occurring with radiation source minus the count occurring without the radiation source. The background noise level is taken as the standard deviation of the signals obtained without a radiation source. Therefore at 0 mm tube length the Faraday cup signal is 55.6 mV, with a background noise level of 20.2 mV. This gives a signal to noise ratio of 2.75.

For the same ion concentration (0mm tube-length) the NMT signal is 50,112 counts per second with a background noise level of 62 counts per second. Therefore, for NMT the signal to noise ratio is 808. Thus, the NMT technology enables ion counts with much greater precision and at considerably lower levels.

Another advantage of NMT technology is its ability to count absolute numbers of ions in the gas sample. The ion sample flow rate is 0.05 l/min (0.83 cm³/s). The highest ion number concentration detected in the experiment (at 0 mm tube-length) was 60,393 cm⁻³. The lowest ion number concentration detected in the experiment (radiation source present at 100 mm tube-length) was 270 cm⁻³. The figure of 270 cm⁻³ is at a similar concentration to the without radiation level; it represents ions from background radiation sources such as cosmic rays [16] and thus provides an unavoidable background count with associated noise.

NMT technology has to date been successfully interfaced with IMS, GC and Differential Mobility Spectrometry (DMS). This work suggests that NMT could replace widely-used detectors based on the Faraday cup in all of these devices if lower ion concentration measurements (and hence molecular concentrations) are required.

The Faraday cup sensor used in this comparison is typical for a GC detector. It may or may not be the most sensitive device of its kind. However, it is unlikely that more advanced electrometers can readily detect electric currents at the atto-ampere level as effectively as does ‘NMT’.

6. Conclusions

The NMT method, whereby ions are attached to tags, can provide a breakthrough in sensitivity by enabling a single ion to be detected. Experiments show a much greater sensitivity of NMT compared to a Faraday cup electrometer. Measurements equivalent to thirty atto-amps have been obtained. Therefore, NMT can be used as a high-sensitivity detector for GCs and other devices. It is anticipated that this new method of ion detection may improve results in a diverse range of applications including atmospheric science, medical diagnosis (e.g. for monitoring and diagnostics of early stages of lung cancer and other diseases) and detection of traces from illicit compounds.

Contributions

Michael Burton designed and performed the experiment. Boris Gorbunov performed the analysis and wrote the manuscript.

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Dr Brian Steer for help in tag preparation.

Competing Interests

Boris Gorbunov is a shareholder of Ancon Technologies. Michael Burton is an employee of Ancon Technologies.
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