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Ultra sensitive detection of chemical threats by atmospheric pressure chemical ionization mass spectrometry.

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Introduction

Karsa Oy is a startup company supported by the University of Helsinki, international industry partners and leading venture capital investors.

Based on proprietary technology originally developed for ultra-sensitive atmospheric research measurements, we have developed a molecular threat detector, the Tarkka TOF. It is based on selective, soft chemical ionization, high resolution time of flight mass spectrometry (TOF-MS) enabling the unambiguous detection of e.g. explosives and CWA molecules. The system is relatively low power and has been successfully used in field locations around the world.

In this poster, we present proof of concept detection of explosives hidden in electrical items and other workflows. The Tarkka TOF was coupled to an aluminum vacuum chamber that is connected to a scroll pump to produce vacuum and a compressor to pressurize the chamber with clean air. The chamber outlet is connected to the mass spectrometer inlet. The inlet is connected to a 3-way valve which guides the sample flow to the inlet during measurement cycle. The inlet consists of a reagent ion feed and an X-ray ion source. The walls of the chamber and the tubing from the chamber to the inlet are warmed to minimize samples sticking to them. Laptop computers prepared with traces of explosives in the battery compartment were sampled and we successfully detected nitro glycerin, TNT and even PETN and RDX in 30s or less.

Figure 1: Tarkka TOF consists of the high resolution (resolving power≈10000) time of flight mass spectrometer (TOF-MS), the atmospheric pressure interface (API) and the Chemical Ionization inlet. The dimensions are 148cm x 62cm x 48cm and weight is 110kg, and a separate pump rack.

Detection limits

To determine detection limits, we coupled an autosampler to the Tarkka TOF (see Figure 1). The samples we use are based on commercially available dissolved standards. Our autosampler (HTA, Italy) uses a modified firmware that allows us to automatically dilute the standards in 1:10 steps iteratively. Since the initial concentration of the standards is different, we normally repeat the dilution until we arrive at 100 femtogram / µl. 1 µl of the sample are injected into the system inlet using the autosampler.

The injected sample is evaporated in a proprietary vaporizer held at 200°C for most samples and fed to the ionization chamber, where the vapor interacts with the reagent ions. The resulting ions then enter the atmospheric pressure interface through a pinhole before being analyzed in our TOF-MS. For each threat a detection limit is estimated by plotting the recorded signal for the 1:10 dilutions. When the curve flattens, and the signals are not distinguishable from blank injections we report this as the detection limit in Table 1.

So far we can only share the detection of femtograms of the Sarin simulant Dimethyl methylphosphonate (DMMP) with the Tarkka TOF. Literature search suggests that real chemical warefare agents can be ionized and be detected with for example Ion Mobility Spectrometry. VX is considered non-volatile in C detection, but it's vapor pressure at 20C is 0.07 Pa [Buchanan et al, 1999] and is higher than the explosives TNT (0,0009 Pa [Ewing et al, 2013]), and much higher than PETN ($1x10^{-6}$ Pa, [Ewing et al, 2013]) and we therefore expect to detect trace amounts present e.g. even inside of devices.

Compound	Limit of detection	Compound	Limit of detection
TNR	<10 ng	TNT	<10 pg
UN	<1 ng	R-salt	<10 pg
Tetryl	<1 ng	NG	<1 pg
EGDN	<100 pg	RDX	<1 pg
1,3,5-TNB	<100 pg		
2,4-DNT	<100 pg		
ETN	<100 pg	Codein and paracetamol	From panacod headspace
HMTD	<10 pg	DMMP	<0.1 pg
PETN	<10 pg		
TATB*	<10 pg		

Table 1: List of threats detected, and corresponding detection limit. Highlighted in yellow the CWA simulant DMMP

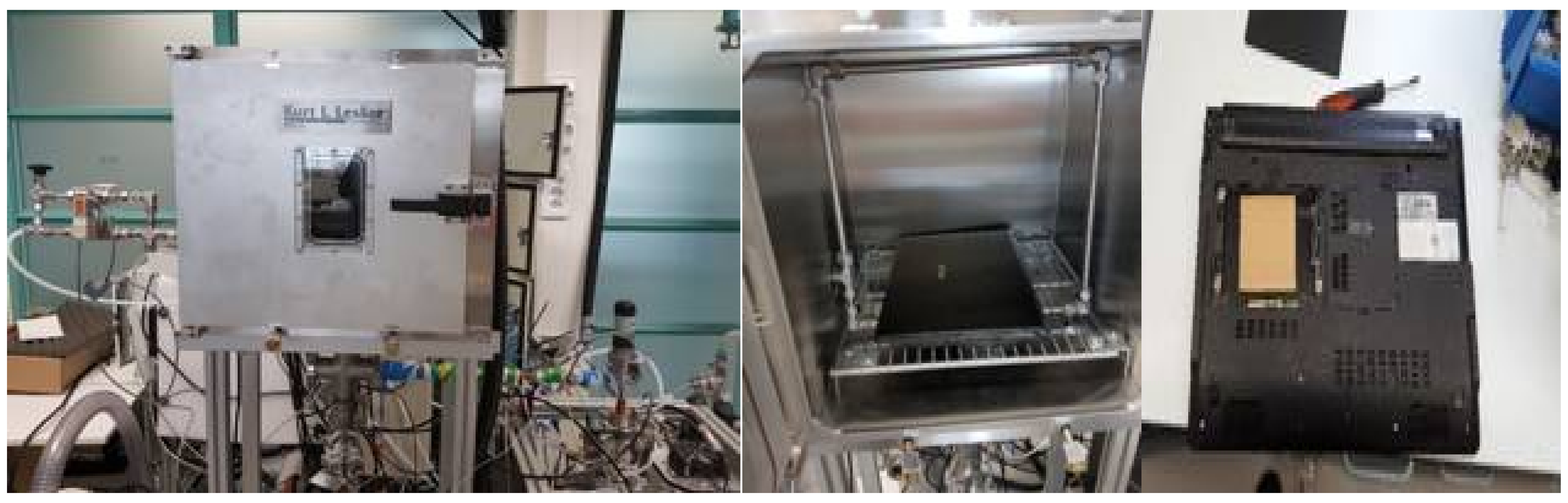

Figure 2: (left) Proof of concept system consisting of a vacuum chamber, pressurization system and CI inlet to Tarkka TOF. (middle) Laptop in the sample chamber. (right) simulated explosives threat (Explosives deposited on cardboard or aluminum foil) placed inside laptop for detection

Detection of hidden Explosives

We measured the sample foils inserted in laptops and detected all of the samples. The signal of the explosives, especially for RDX, is so high that it is probable that there have been particles detached from the substrate. This can be due to the characteristics of the aluminium foil as a substrate, it might move and crinkle during the pressurization of the chamber and this might initiate detachment of particles. After the target sample measurements, the sample got contaminated and the blank measurements had significantly higher signal due to carry over (Fig. 3). The NG is the most volatile compound of the three and its background signal got lower relatively quickly but TNT and RDX are less volatile and their background signal remained high for a longer period.

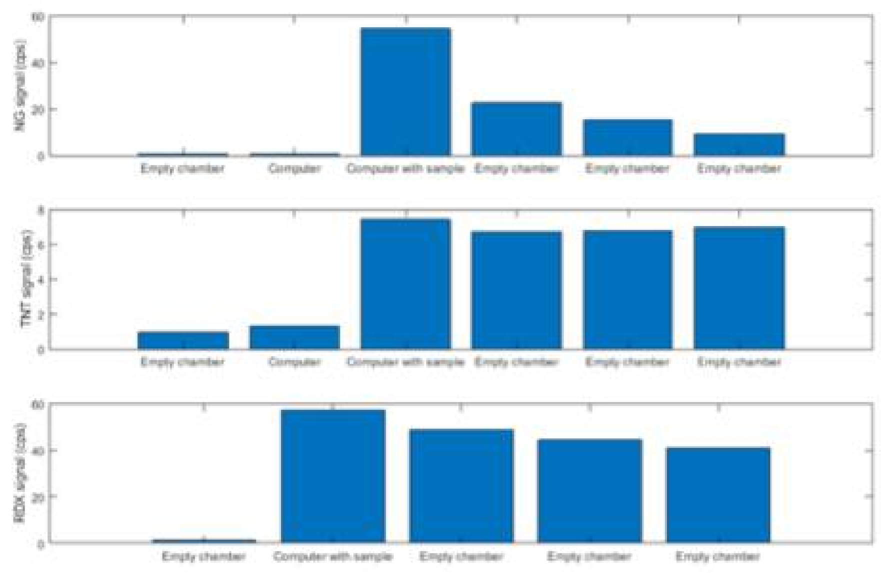

Figure 3: The signals of NG, TNT and RDX in 30 s measurement periods with blank measurements before and after the sample measurement.

Alternative CWA detection workflows

The Tarkka TOF selective chemical ionization platform can be operated for direct, online measurements of threat molecules down to the parts per quadrillion range. A second workflow offered by Tarkka TOF is to collect vapours and particles on filters with a handheld sampler, and the filter cartridges can be inserted for desorption and analysis. The Tarkka TOF also offers an injection port for manual or autosampler injections of liquid samples or for headspace from solid samples. The system is much simpler than traditional GC or LC setups and offers sensitivities similar to or exceeding traditional methods due to the selective nature of the chemical ionization.

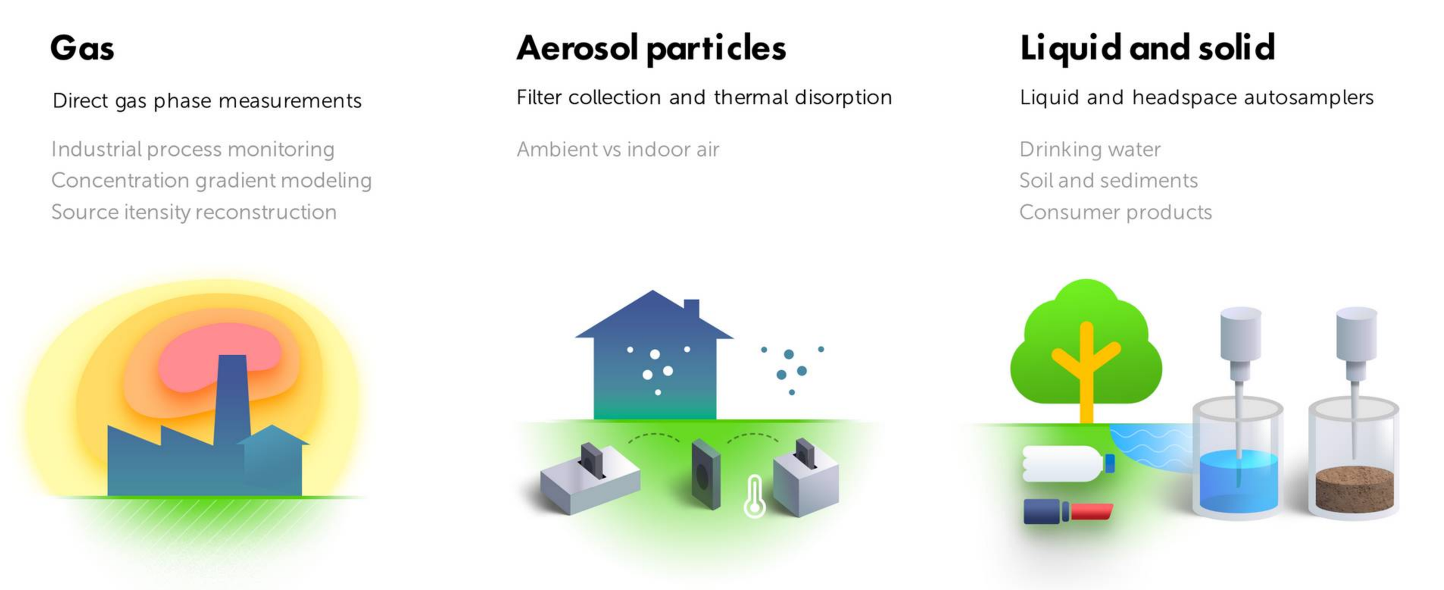

Figure 4: The Tarkka TOF allows the direct, online analysis of threat molecules, collection of vapours and particles on filters and subsequent desorption, and analysis of liquid samples.

Conclusion

The Tarkka TOF is an ultra-sensitive molecular analysis platform suited to detect threats online, in real time, or from filters, or dissolved in liquids. Our method is able to measure explosives (NG, TNT, RDX) hidden inside electronics such as laptops. We believe that CWA with similar vapour pressures as TNT or RDX, such as VX could also be detected with this method. In addition, Tarkka TOF platform offers other workflows for gas phase or liquid samples that are simpler than current GC or LC based setups.

Acknowledgments

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