Publishable Summary

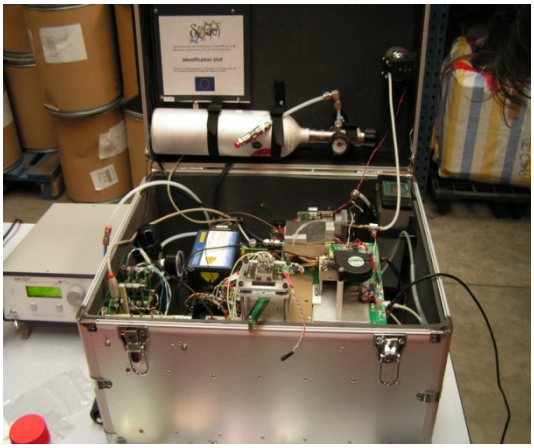
Overview

Detection of Amphetamine Type Stimulants (ATS), precursors, and derivatives, remains an open challenge if we move out of forensic labs, and consider field-sensors for daily use against the production, trafficking, and street distribution of illicit drugs. In DIRAC, an advanced sensor of ATS is developed, that combines *miniaturized Gas Chromatography* (GC) as its key chemical separation tool, and *Hollow-Fiber-based Infra Red Absorption Spectroscopy* (HF-IRAS) as its key analytical tool. GC-IRAS is, together with GC-Mass Spectrometry, the most powerful technique for the identification of amphetamines, particularly for its ability to reject false positives and to recognize designer drugs, that is establish chemical and pharmacological similarities between new substances and known drugs. While GC-IRAS is today available only as bench-top instrumentation for forensic labs and bulk analysis, DIRAC develops an advanced sensor that combines hand-portability –for field operation– with a wide detection range, from traces to bulk. Furthermore, the sensor integrates new solutions for sample collection, separation and treatment, that allow to analyse substances in different physical state and with different chemical characteristics.

Main achievements

Prototypes. The project led to the implementation of three prototypes, that will be referred to as Identification (ID) Unit, Vapour Detection (VD) Unit, and Salt Detection (SD) Unit, respectively.

The Identification Unit (Fig. 1) consists of a hand-portable sensing head, plus a processing & control unit on PC, and a graphic, user-friendly front end (HMI).



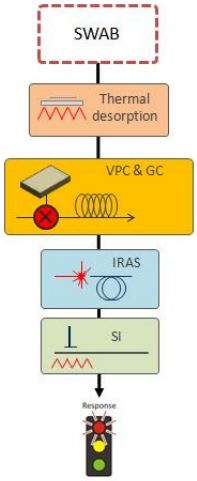


Fig. 1: Identification Unit. *Left: the prototype in its aluminum hand-case. Right: sensing architecture.*

Solid particles or liquid droplets are collected on a swab and loaded into the system. A *Vapour Pre-Concentrator* (VPC) extracts and pre-concentrates vapours thermally desorbed from the swab. The pre-concentration cartridge is functionalized with cavitands, designed to trap selectively molecules with an aromatic group (that is present in all our target compounds). Upon heating, the pre-concentrator releases the vapours into a *short FAST GC column* with elution time of the order of 2-4 min. VPC cartridge, GC column, and injection valves, are *all silicon micro-machined components* integrated on a single, very compact VPC/GC electro-mechanical platform. Out of the GC column, vapours are analyzed by a *HF-IRAS module,* essentially consisting of an InfraRed Hollow Fiber in an oven, an IR External Cavity Quantum Cascade Laser (EC-QCL), and a thermo-electrically cooled IR detector. IR radiation is guided through the hollow core of the fiber to couple the source

and the detector. Vapours in the fiber cause IR signal attenuation at wavelengths corresponding to their roto-vibrational transitions. As the laser scans its spectral tuning range (7.2÷8.6 µm), the system acquires high sensitivity absorption spectra. Downstream of the IRAS module, vapours are still available to be analyzed by a second, orthogonal *Surface Ionization (SI) detector*, that is a miniaturized, solid-state gas sensors, that features excellent sensitivity and selectivity against amines. Data are analyzed and fused by an *Expert System*, that compares the unknown sample with a reference database of IR spectra, elution times, and SI signals. If identification fails, the Expert System searches for similarities with classes of psychoactive substances. If no similarity can be established, the unknown is classified as negative.

The Vapour Detection Unit (Fig. 2) fits into an aluminum case identical to the ID Unit, and is driven by similar control sw and expert system.

Fig. 2: Vapour Detection Unit. *Left: the prototype in its aluminum hand-case. Right: sensing architecture.*

Unlike the ID unit, however, the VD unit collects its sample from the air, or from the headspace of a vessel, and bypasses GC to drive the vapours from the VPC directly into a HF-IRAS analyzer with tuning range 6.5 ÷ 7.5 µm. Compared to the ID Unit, the VD Unit is faster but less accurate. In real applications, it is recommended for detecting pure 'volatile' liquid precursors, such as safrole or BMK. Interestingly, the VD sensing scheme can be integrated in the ID Unit by adding a minimal number of switching valves and micro-fluidic bypasses.

In the Salt Detection Unit (Fig. 3), solid particles are collected by an air drawer and electro-statically precipitated onto a ceramic plate.

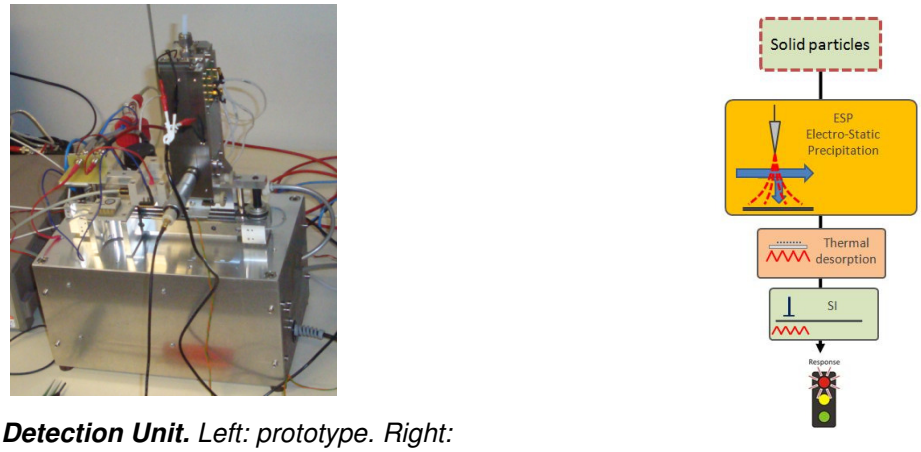


Fig. 3: Salt Detection Unit. *Left: prototype. Right: sensing architecture.*

The plate is then moved on a rail car from a 'sampling' to a 'desorption' position. There, the sample is heated up, and vapours are released and analyzed by a Surface Ionization detector. This Unit exploits the extreme sensitivity of SI detectors towards amines, to perform rapid screening of solid traces in search of ATS salts. The SD Unit, however, is prone to false positives, and has to be intended only as an early warning stage that triggers more accurate analysis by the ID Unit.

Experimental results. In the course of the project, the DIRAC sensor was tested extensively with a wide range of precursors in many different forms, either collected from the headspace of a vessel at room temperature, or thermally desorbed from pure solids and liquids, mixtures, or solutions of organic solvents. The IRAS analyzer is very sensitive to Safrole (Fig. 4, left), Piperonal, BMK, PMK, and other similar precursors, that feature strong absorption patterns in the spectral range of the QCL. For most of them, limits of detection LoD are estimated around a few nanograms. The IRAS analyzer is less sensitive to ATS and precursors with an amine group, partly because of their weaker absorption patterns, partly because of their tendency to stick to any cold spot before entering the fiber (so causing mass losses). The SI detector behaves at the opposite, with LoDs around 1 microgram for safrole, and tens of picograms for ephedrine and ATS. When tested with mixtures, the system demonstrates good ability to separate the substances and recognize the sample composition (Fig. 3, right).

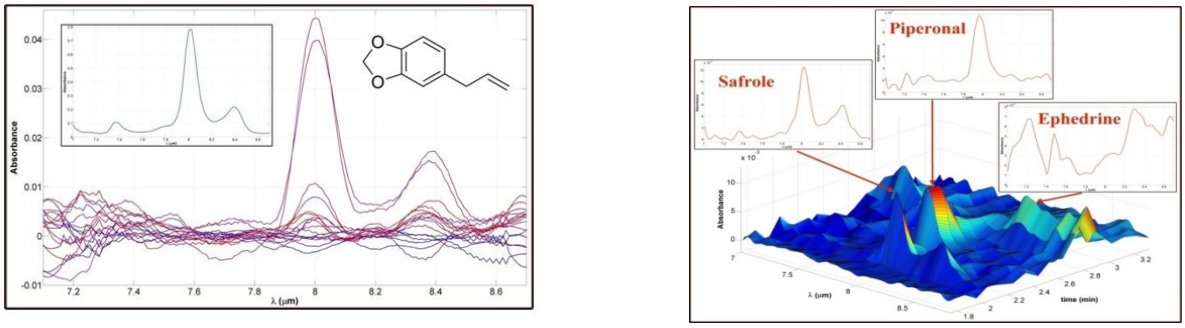


***Fig.4**: **Precursors analysis**. Left: HF-IRAS spectra of 100 ng safrole, vaporized in a methanol solution (reference spectrum in inset). Right: Analysis of mixture; HF-IRAS spectra evolution after injecting a mix of safrole (600 ng), Piperonal (600 ng) and ephedrine (3 µg), vaporized from a methanol solution.*

Later, the sensor was tested successfully also with Amphetamine and Methamphetamine (MA) hydrochlorides (Fig. 5), and with street samples containing MA plus additives. Detection of heavier molecules, like MDMA·HCl, was found more challenging, probably because of the lower volatility and of the stronger mass losses along the sensing chain.

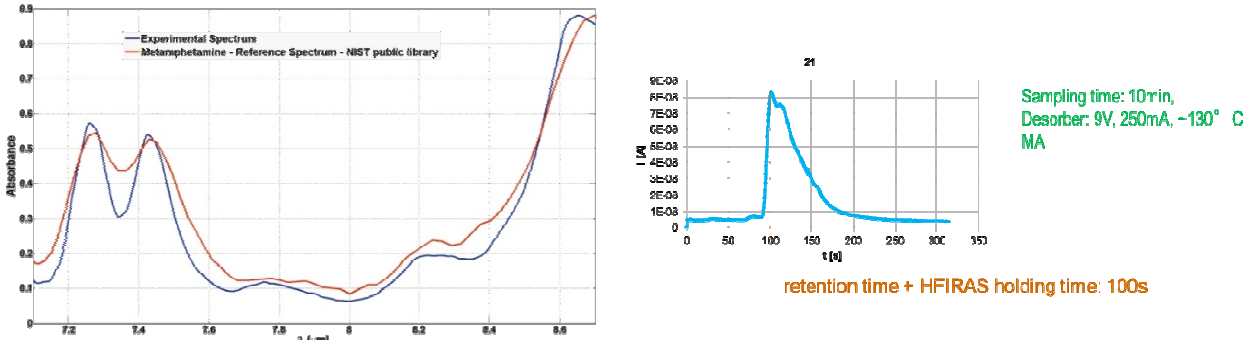


***Fig.5**: Analysis of vapours thermally desorbed from a solid sample of MA·HCl. Left: HF-IRAS spectrum, compared to a MA spectrum from a reference database. Right: SI current plot measured at the output of the IR hollow fiber.*

Final demo. The demo was held in the cargo area of the Brussels National Airport, in one of the Customs warehouses where seized goods are kept in stock . It was attended by a number of end users from Customs and Police departments across Europe. The Vapour Detection Unit was tested first, with vapour traces collected from the headspace of vials. Demonstration was carried out with samples of pure volatile precursors, and of negatives. Later, the Identification Unit was the tested with liquid traces collected on a swab. Demonstration included tests with precursors dissolved in a solvent and potential interferent. All the positives were correctly identified. Negatives were correctly rejected. Two of the photos taken at the event are shown below. Additional photos can be downloaded at this link: http://www.fp7-dirac.eu/allegati/1dirac-final-demo-images.pdf

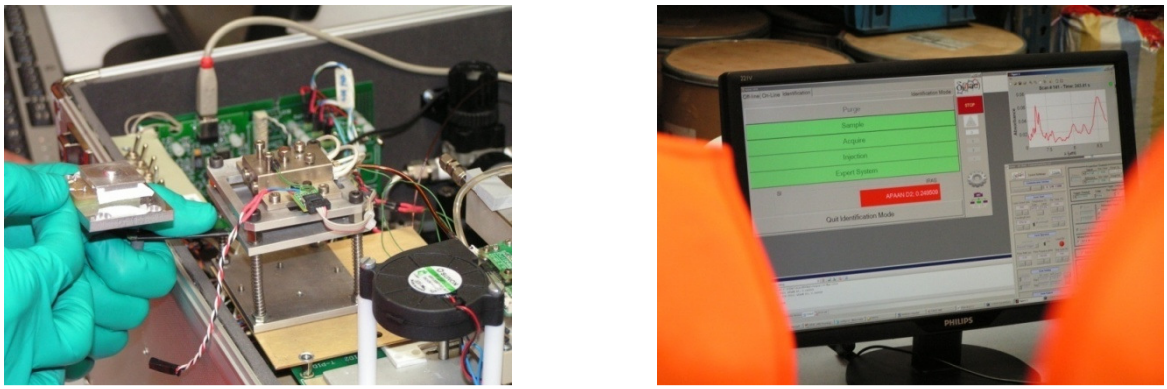


Fig. 6: DIRAC demonstration. *Left: liquid traces of precursor in ethanol, collected on a swab, are loaded into the thermal desorber. Right: the system correctly identifies the target.*

Impact

The impact potential of the DIRAC sensor was discussed extensively with end users in the course of meetings and interviews. The market of illicit drug sensors is currently dominated by systems based on Ion Mobility Spectrometry (IMS). IMS sensors are extremely effective to detect traces of illicit drugs (with limits of detection better than 1 ng), but they quickly saturate in the presence of 'big traces' (from µg to mg), particularly in 'dirty' environments, as is often the case when goods are controlled at the borders. Also, IMS instruments are prone to fail in detecting precursors . For the detection of precursors, other instruments have been proposed, based on Raman spectroscopy. Raman sensors, however, can be used only with bulk samples, and not with 'big' or real traces. Also, they are prone to fail if the substance fluoresces, or if it is dissolved in a masking solvent. In synthesis, end users seem to agree that the DIRAC sensor can fill an existing performance gap by enabling reliable detection and identification of precursors, particularly in the case of 'big traces' and not pure substances. Applications and scenarios that best match the performance characteristics of the sensor are those that were represented in the final demo of the project, namely the (off-line) screening of goods in the cargo area of airports and harbors.

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