Publishable Summary

Project Objectives

DIRAC develops an advanced sensor system 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, to detect and recognize Amphetamine Type Stimulants (ATS) and precursors. The sensor further implements advanced methods for sample separation and treatment, that allow to analyse substances in different physical state and with pretty different chemical and physic-chemical characteristics (non aminic precursors, volatile amines, non volatile salts), as traces and bulk. The sensor essentially consists of a sampling unit, a very compact, hand-portable sensing head, and a processing/control unit on lap-top or palm-top PC (Fig. 1).

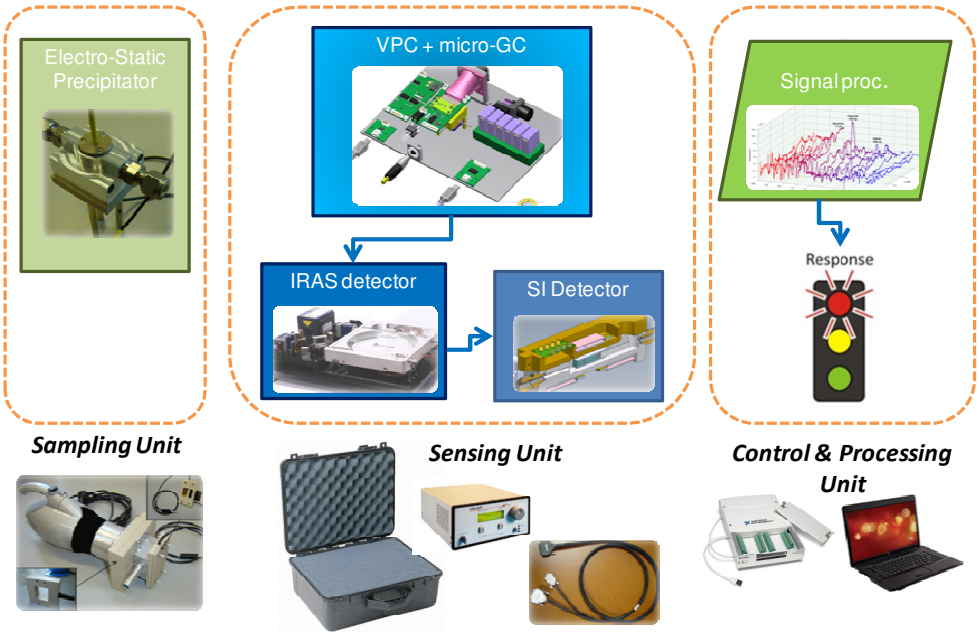


Fig. 1: *The DIRAC concept and architecture*

The sample flows from a sampler, to a pre-concentrator, to a separation column, to a HF-IRAS module, and, finally, to Surface ionization detectors.

The sampler consists of a vacuum-type particle sampler and an electrostatic precipitator. Particles with high proton affinity (as the aminic groups of ATSs) are charged by a proton shower and precipitated out of the air flow by an electric field. The protons are provided by a corona discharge.

The pre-concentrator extracts and pre-concentrates both volatile and non-volatile material. Volatile material is extracted by thermal desorption. Vapours are sent to a *vapour phase pre-concentrator (VPC)*, that consists of a silicon-micromachined packed column, functionalized with cavitands for selective trapping of aromatic groups. These groups are present in all our target chemicals. Upon heating, the pre-concentrator releases the vapours to the separation and analysis modules. The solid residual is then treated with a basic solution of methanol or water, to convert non-volatile amphetamine salts into volatile free amines. This conversion can follow different routes. In all the cases, the treatment ends up with the vaporization of free amines in an excess of solvent.

The separation module is a very compact device, that makes use of a FAST GC column on micro-machined silicon, and SU8 micro-valves for the injection loop. Working parameters (temperature, flows) and connections are adjusted to match the HF-IRAS module.

The HF-IRAS module essentially consists of an InfraRed Hollow Fiber in an oven, a Quantum Cascade Laser (QCL) IR source, 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. When vapours flow from GC into the fiber, they cause IR signal attenuation at wavelengths corresponding to their roto-vibrational transitions. As the laser scans its spectral tuning range, the system acquires high sensitivity absorption spectra. Downstream of the IRAS module, vapours are still available for analysis by orthogonal sensing techniques.

The Surface Ionization detectors are miniaturized solid-state gas sensors that can feature excellent sensitivity and selectivity towards aminic groups.

An **Expert System** analyzes the data and tries to identify the unknown by direct comparison with a library of reference spectra and elution times. If identification fails, the Expert System tries to establish similarities with classes of psychoactive substances. If no similarity can be established, the unknown is classified as negative.

Main achievements to date

Analysis of solutions by GC/HF-IRAS coupling. The GC/HF-IRAS system has been tested with a wealth of samples, and, in particular, with methanol and ethyl-acetate solutions of amphetamines and precursors, as individual components and as mixtures (fig 2).

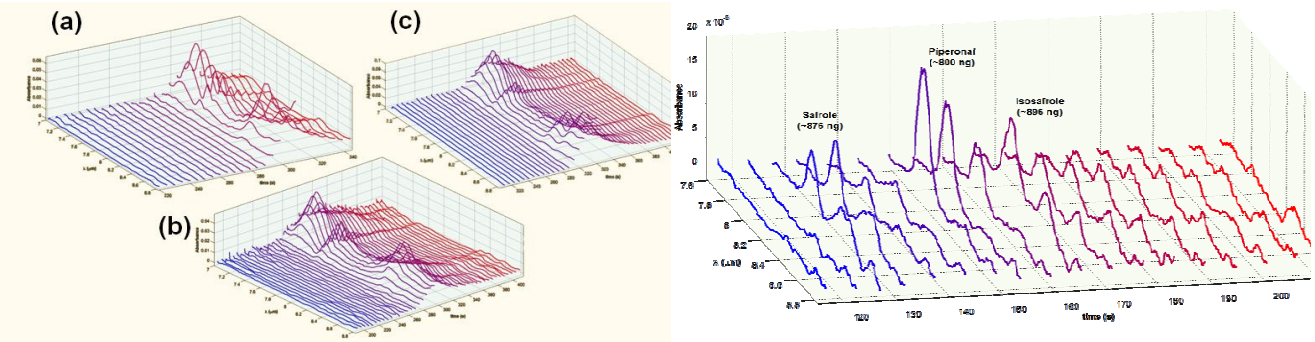


***Fig.2**: GC/HF-IRAS coupling tests. Left: Time evolution of IR spectra after injection of: a) Ephedrine 5 µg; b) Norephedrine 5 µg; c) Pseudoephedrine 5 µg. Right: The system is tested with a mix of Safrole, Piperonal, and Isosafrole (~ 800 ng each).*

The results demonstrate that the system is capable of analyzing all the compounds of interest, with Limits of Detection ranging from 10-20 ng, or better, for non-aminic precursors (safrole, piperonal, BMK,..) to 100-200 ng for amphetamines and aminic precursors (ephedrines). The lower sensitivity to amphetamines is partly explained by weaker absorption cross sections, and by the absence of narrow peaks in the IR range scanned by the QCL laser. However, the analysis of aminic compounds appears affected also by material losses along the fiber or at the gas-fiber connections (condensation at cold spots, or specific interactions at the surfaces). As such, it is expected that the ongoing hardware optimization will increase the sensitivity towards aminic targets.

Furthermore, it has been shown that when carrier gas flows in the GC and the hollow fiber are properly matched, and dead volumes at connections minimized, the HF-IRAS module can be coupled to a FAST GC column (fig. 3) . This allows to separate most of the samples of interest in less than 5 minutes.

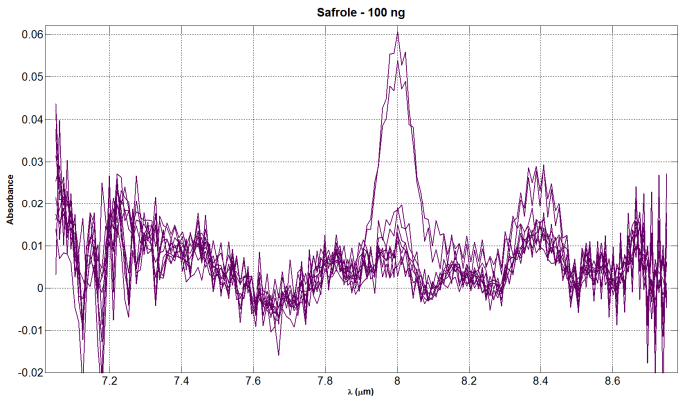


***Fig.3**: FAST GC/HF-IRAS coupling. IR spectra taken for a solution containing 100 ng safrole in methanol. 1 sccm He was used as carrier gas. The two safrole peaks at 8.0 and 8.4 μm appear about 180 s after the injection.*

Analysis of vapour precursors by VPC/IRAS coupling. Experiments have shown that, when the HF-IRAS module is coupled to the Vapour phase Pre-Concentrator (VPC), the system is effective to analyze vapour precursors in the head-space of a vessel. Vapours are trapped in the VPC by Quinoxaline cavitands (QxCav), and, upon heating, delivered to the HF-IRAS module. QxCav show very strong trap & release efficiency towards aromatic groups as those present in all ATS precursors. In the case of Isosafrole (fig. 4) it was estimated that a fraction of a minute pre-concentration is enough to enable HF-IRAS analysis and identification.

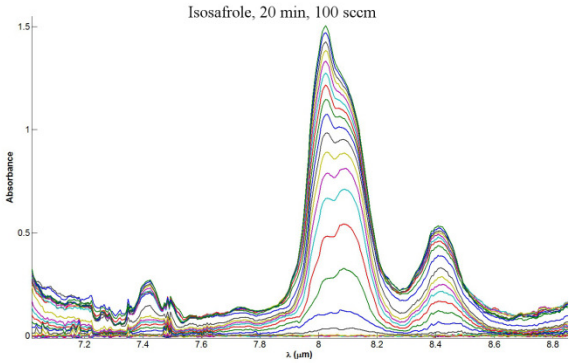
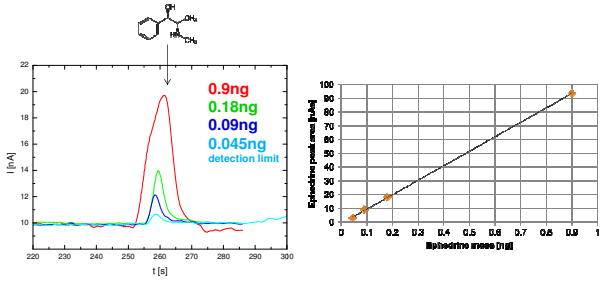


***Fig.4:** IR Absorption spectrum of Isosafrole, sampled at RT from the headspace of a vessel containing a few μl of the substance. Vapours are trapped in the pre-concentrator by Quinoxaline cavitands (QxCav) and (upon heating) released to the IR Hollow Fiber. QxCav show very strong trap & release efficiency towards aromatic compounds.*

Analysis of aminic compounds by GC/SI coupling. A major breakthrough in the project is the outcome of a joint measurement campaign on the coupling of GC and SI used as detector. This experiment has allowed to prove the feasibility, the straightforwardness and robustness of the GC/SI coupling, and to investigate in detail the selectivity and the extremely low detection limit of the SI detector towards amines.
Results can be resumed in:

- GC/SI is feasible, easy and robust
- SI detection limit is way below the ng threshold, in the order of 45 pg
- SI detector selectivity towards amines with respect non-aminic compounds > 10^5



These results confirm that the SI detector is an excellent alternative detector to the IRAS module, especially for the aminic compounds where the IRAS detector may lack in sensitivity.

Potential Impact

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 intends to implement an advanced sensor that combines hand-portability –for field operation– together with the ability to analyse both bulk and trace material. Furthermore, to match the requirement of a fast response, the sensor is being developed to operate at different processing rates, to provide 'detection' or 'identification' of illicit drugs and precursors. In the *detection mode*, the sensor will be capable of analyzing vapours and solid particles, to deliver an early warning for the presence of precursors and salts of amphetamines, respectively. In the *identification mode*, a refined analysis (and a few minutes longer wait) will allow to treat complex samples and identify correctly the target chemicals present in the sample.

As such, the DIRAC sensor has the potential to become a very valuable tool that customs officers and law enforcement units use in their daily fight against the production, trafficking and street distribution of illicit drugs. At a basic level, it is expected that the DIRAC system will be used on the basis of previous intelligence gathered by end-users. On another hand, it will enable end-users to collect data that, colligated with other information, could also provide new intelligence on the transit of ATS illicit drugs or their precursors.

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