First Year 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 very compact, hand-portable sensing head, and a processing/control unit on lap-top or palm-top PC (Fig. 1).

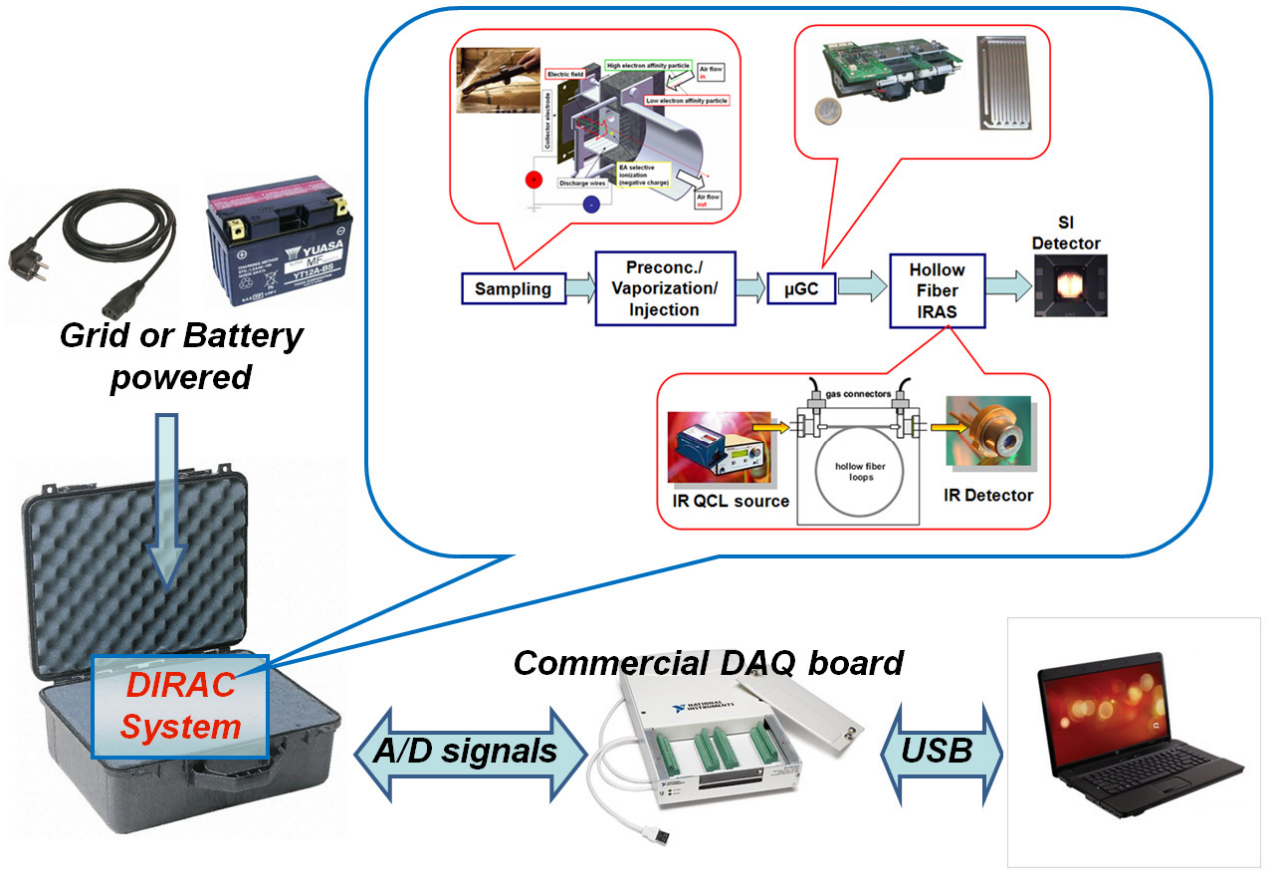


Fig. 1: *The DIRAC concept and architecture (to be finalized)*

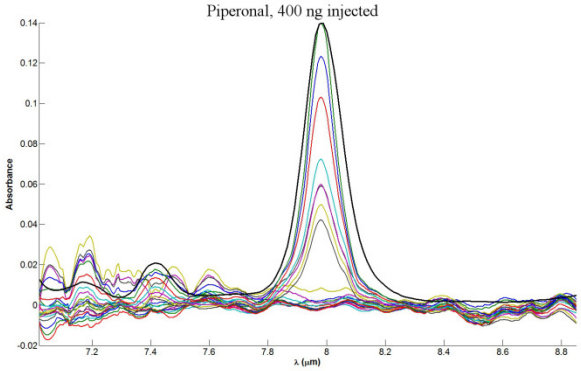
The sample flows from a sampler, to a pre-concentrator, to a separation column, to the HF-IRAS module, and, finally, to Surface ionization detectors.

The sampling module 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-concentration module extracts and pre-concentrates both volatile and non-volatile material. Volatile material is extracted by thermal desorption. Vapours are sent to the *vapour phase pre-concentrator*, 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 GC module is a very compact unit with a relatively short separation column on a micro-machined silicon chip. Working parameters (temperature, flows) must match the HF-IRAS module.
The HF-IRAS module essentially consists of an InfraRed Hollow Fiber in an oven, a Quantum Cascade Laser 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 strong sensitivity and selectivity towards aminic groups.

Main results achieved in the first year

Detection of target chemicals by HF-IRAS. An initial test vehicle of the DIRAC sensor was implemented, by coupling an evaporation chamber, a vapour-phase pre-concentrator, and a breadboard of the HF-IRAS module. This vehicle was tested with several target chemicals, as solids, liquids, vapours, and as water or methanol solutions. Experimental results show that the sensor is capable of analyzing a wealth of ATS precursors, with Limits of Detection in the 10s nanograms range, or better (Fig.2a). Furthermore, it is suitable to deal with vapours directly trapped from the headspace of a vessel (Fig. 2b). Finally, it is capable to treat and analyze ephedrine (or other aminic target) dissolved in an excess of methanol or water (Fig. 3). The latter result demonstrates the ability of the sensor to deal with non-volatile ammonium salts of ATSs, by treating the sample with a solvent and a base, to convert the salt into a free amine that can be easily vaporized.



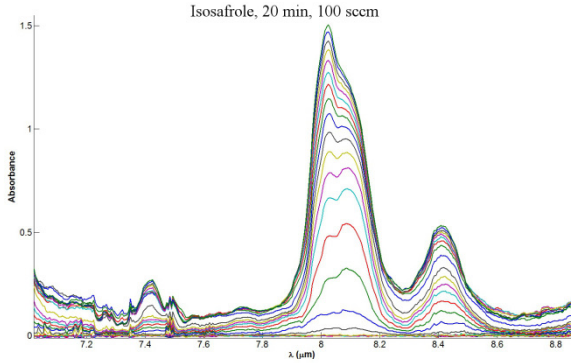


Fig. 2a *(left): IR absorption spectrum of Piperonal, vaporized from solid grains and injected in the IR Hollow Fiber. Reference spectrum in black (from NIST).* ***Fig. 2b*** *(right): IR Absorption spectrum of Isosafrole, sampled at RT from the headspace of a vessel containing a few µl of the substance. Vapours are trapped in the pre-concentrator by Quinoxaline cavitands (QxCav) and (upon heating) released to the HF. QxCav show very strong trap & release efficiency towards aromatic compounds.*

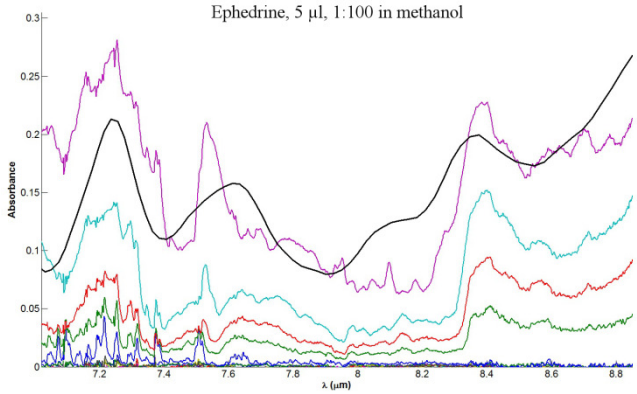


Fig. 3: *IR Absorption spectrum of Ephedrine. Reference spectrum in black (from NIST). Ephedrine was vaporized in a solution 1:100 of methanol. The pre-concentrator selectively trapped and (upon heating) released the analyte. No evidence of the presence of solvent in the measure. This experiment simulates the procedure that must be followed to deal with non-volatile salts: the salt is treated with methanol and a base, and converted into a free amine. The amine (and the solvent) can be easily vaporized and injected into the sensor.*

Particles collection and separation by Electro-Static Precipitation. Substitute amine particles (L-arginine, tris, urea) were tested in a large precipitator breadboard, along with ephedrine (a target amine) and ephedrine hydrochloride (which should not behave entirely as an amine). Initially the precipitator was operated at ambient conditions, without adding humidity. Since there is always a certain amount of humidity present in the air, this type of operation corresponds to a low humidity Electro-Static Precipitation (ESP) -as opposed to a completely dry one-. As a result, a mass yield of 1-4% was obtained. This yield was significantly higher than the reference yield without an electric field (0%), but also significantly lower than comparison experiments in the negative mode with high electron affinity particles (TiO_2, 44%).
Next, the experiment was repeated with added humidity from a synthetic air stream through a water bubbler, resulting in a relative humidity of approximately 76%. The yield was significantly improved with the wet ESP, up to a maximum of ≈ 10%. It is very important to note that this preliminary study cannot be used for quantitative analysis to assess how well the final precipitator will perform, since it was not performed with hardware specific to this task. It is expected that the specifically designed precipitator with feature higher yields. However, the preliminary study indicates that the approach is feasible in principle and that adding artificial humidity to the ambient air potentially improves the yield significantly. Furthermore, it was shown that ephedrine hydrochloride could be precipitated, although at a lesser yield than the amine species.

SI detectors as drug sensors. Tests and procedures were implemented to assess the sensitivity and selectivity of Surface Ionization (SI) detectors towards ATS drugs and aminic precursors. SI gas sensing tests were performed using Fe_2O_3 as sensing material. The reason for choosing Fe_2O_3 is that it shows a very high selectivity towards amines as

compared to other hydrocarbons. Target gases were Ephedrine (EP), Ephedrine Hydro-Chloride (EPCl), MDMA (Ecstasy), while interfering gases were methanol and water. These measurements were performed at a substrate temperature of 300°C, which is comparable to normally employed operation temperatures of metal oxide gas sensors. This surprisingly low operation temperature for SI we assume is due to the Fe_2O_3 sensing material.

Measurement curves of the targets MDMA, EP, EPCl and the interfering substances DBA, methanol and water have been recorded. While MDMA, EP, EPCl and DBA are detectable in ppb concentrations, water does not produce any response at a concentration of 2000ppm; a methanol response could only be observed at concentrations larger than about 200ppm. These results demonstrates that SI process selects amine containing targets from non-amine containing interferents with orders of magnitude higher sensitivity. However for discrimination of different amines e.g. drugs and pharmaceuticals further analytics are necessary.

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 will be designed to operate at different processing rates, to provide 'detection' or 'identification' of illicit drugs and precursors. In the *detection mode*, the sensor should deliver (in about 2 minutes) an early warning in the presence of substances with functional groups similar to ATSs or precursors, and classify the substance as Negative, Precursor, Illicit Substance, or Non-Negative (that is a substance with strong chemical affinities to ATSs or Precursors). In the *identification mode*, a refined analysis (and a few minutes longer wait) should allow to identify correctly the target chemical 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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