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1. Executive Summary

DIRAC aims at developing an advanced and hand-portable sensor to be used on the field by Customs and Police officers in their daily fight against the production, trafficking, and street distribution of Amphetamine Type Stimulants (ATS) and precursors.

The heart of the sensor is made of a micro-GC column, and of a laser-based IR analyzer, that measures the absorption spectra of the vapours released by the GC and transiting through an IR hollow fiber. The sensor further integrates advanced solutions for sample collection, pre-concentration, and early detection of target compounds by a second, orthogonal detector based on Surface Ionization (SI).

The project led to the development of three prototypes, that show diverse and complementary sensing capabilities:

- The Identification (ID) Unit accepts liquid and solid traces collected on a swab, and recognizes with high specificity a wide range of targets, from precursors to ATS free bases and salts, as pure substances and as solutions, mixtures, and street samples. Data are processed by an Expert System, that compares the measured sample with a reference database (DB) of spectral and chromatographic patterns. If direct identification fails, the Expert System proceeds by searching for similarities between the unknown and classes of psychoactive substances defined within the DB. If no similarity can be established, the unknown is classified as a negative.
- The Vapour Detection Unit analyzes vapours pre-concentrated from the open air or from the headspace of a vessel, in search of volatile precursors. Since GC separation is here bypassed, response is faster, but less accurate in the case of vapour mixes.
- The Salt Detection Unit collects solid particles in an air flow, precipitates electrostatically preferentially those that, like ATS, have higher proton affinity, and uses SI detection to provide early warning in the presence of amine groups. This Unit is fast and extremely sensitive to ATS salts. It is however prone to false positives, and its results should be preferably confirmed by the ID Unit.

It is worth to note that the three sensing schemes described above could all be implemented within the same sensor, for example by adding a minimal number of switching valves and fluidic bypasses into the ID Unit.

The sensors were presented at an audience of end users in the course of a small-scale demo, that was held in one of the Customs' warehouses in the cargo area of the Brussels National Airport. The ID and the Vapour Detection Units were successfully tested with negatives and with a wide range of precursors and pre-precursors such as APAAN.

Interviews with end users and external experts show that the DIRAC sensor can fill an existing market gap, by enabling reliable detection and identification of precursors, particularly in the case of 'big traces' and 'dirty' environment, where IMS sensors are prone to saturate or give false alarms. Applications and scenarios that best match the performance characteristics of the sensor are those that were represented in the final demo, that is the (off-line) screening of goods in the cargo area of airports and harbors.

2. Main objectives and context

The DIRAC project was submitted and approved in reply to a FP7 call focused specifically on the detection of ATS precursors. The European Commission was asking for a sensor to be used on the field by Customs and Police officers in their daily fight against the production and trafficking of illicit drugs. The sensor, in particular, had to demonstrate hand-portability, and full functionality, from sampling to read out.

DIRAC proposed a sensor that exploits the combination of Gas Chromatography (GC), for chemical separation, and InfraRed Absorption Spectroscopy (IRAS), for chemical analysis. The proposal took into account the high false alarm rates reported for commercial field-sensors, and intended to exploit the well known superior specificity of GC-IRAS systems. In this context, of particular relevance appeared a few comparative studies published before the FP7 call, demonstrating that GC-IRAS (in its GC-FTIR implementation) performs even better than GC-MS in the case of amphetamines and precursors, and that very efficient Expert Systems can be designed based on IRAS spectra, suitable for the automatic identification of banned ATS, and for the classification of new 'designer' drugs.

Since GC-FTIR systems are only available as bench-top instrumentation for bulk analysis in the forensic lab, the first main objective for the DIRAC project was to design and develop an advanced GC-IRAS sensor suitable to meet: a) hand-portability; b) sensitivity to traces; c) ability to provide rapid, automatic, non controversial response, as necessary to support immediate decision-taking by the user.

To reach this objective, DIRAC proposed:

- The development of a palm-size GC module, based on silicon-micromachined capillary and valves, with fast elution times, minimized dead volumes, and efficient flow matching with the IR analyzer.
- The development of a very compact IRAS analyzer, wherein standard FTIR/light pipe set up is replaced by a broadly tunable Quantum Cascade Laser (QCL), an IR detector, and an IR hollow fiber for optical coupling. As vapours released by the GC transit through the hollow fiber, the system acquires absorption spectra by scanning the laser across its spectral tuning range. Since the hollow fiber works as a gas cell of very small volume, even trace amounts of the analyte can be detected, since they reach relatively high concentrations when vaporized into that cell.
- The development of an Expert System that compares spectra and elution times with a reference database to a) identify the targets; b) establish chemical similarities between an unknown and a set of predefined classes of psychoactive substances and precursors, to detect 'non-negatives'.

A second, main objective and challenge of the project was to make the sensor suitable for the widest possible range of applications, and, in particular, able to detect not only precursors as specified in the call, but also ATS. This objective was known to be very ambitious, in consideration of the many diverse forms and chemo-physical characteristics of the target compounds. For example, precursors are seized mostly as pure compounds, while ATS are generally mixed with excipients and adulterants, and often collected as solid

traces, together with much larger amounts of interfering material, ex. dust or skin particles. Also, many precursors are 'volatile' liquids, others are solids that easily sublime upon heating, while ATS are mostly non-volatile solids, that tend to decompose when thermally desorbed.

To address these problems, DIRAC proposed the development of advanced methods and hardware for sample collection, treatment and pre-concentration, and, in particular:

- The development of an advanced sampling module, that uses electro-static precipitation to collect, preferentially, solid particles with higher proton affinity (as those found in ATS samples).
- The development of two silicon-micromachined pre-concentration modules, both based on supramolecular receptors (cavitands), one addressing volatile precursors and ATS in free amine form (through extraction from the vapour phase), the other addressing non volatile ammonium salts (through extraction from the liquid phase).

The technical solutions indicated above were proposed as the building blocks of a sensor that, as a whole, was expected to feature:

- High specificity / Identification ability;
- Broad chemical range (ATS precursors, ATS as free amines and salts, possibly other drugs and additional compounds of interest in the security domain);
- Broad detection range (ideally from traces to bulk);
- Robustness (to recognize the target in the presence of interferents, solutions, mixes);
- Hand portability (the size of a hand-luggage, battery operatable);
- Ease of use (adaptable sampling tools, fully automated sensing process, simplified and non-ambiguous reporting);
- Ability to operate in two alternative sensing modes, to provide, respectively, 'early detection' (response in max 2 min, some false alarm accepted) and 'identification' (a bit longer response time accepted, if false alarms are minimized).

These features had already been drafted as targets in the proposal, and were then confirmed and refined as sensor requirements in the course of the first year of the project, after a few meetings and interviews organized with end users and external experts.

3. Main achievements and foreground

The project led to the development of three sensor prototypes, that were extensively tested, validated in the lab, and finally presented at an audience of end users in a small scale demo. The three prototypes are referred to as Identification (ID) Unit, Vapour Detection (VD) Unit, and Salt Detection (SD) Unit, and are described in paragraph 1. Paragraph 2 analyzes their performance characteristics. The three units are all built of (a sub-group of) the same few building blocks for sample collection, treatment, and analysis, arranged in different sequences; structure and operating principle of these building blocks are given in paragraphs 3÷7.

3.1. Sensor Prototypes

The Identification Unit consists of a hand-portable sensing head, plus a PC and a graphic front end for sensor control, data processing, and reporting.

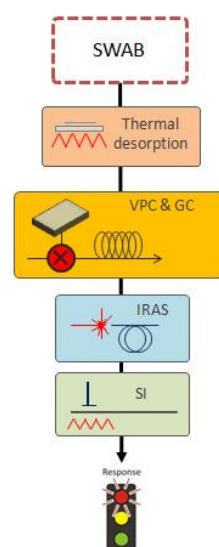


Fig. 1: Identification Unit. Left: the prototype in its aluminum hand-case. Right: sensing architecture.

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 Gas Chromatographic (GC) column, that separates and elutes the components of the mix in about 2-5 min, depending on chemical nature and volatility. 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 sent to an IRAS analyzer, essentially consisting of an InfraRed Hollow Fiber (HF) in an oven, an IR External Cavity Quantum Cascade Laser (EC-QCL), and a thermo-electrically cooled IR detector. IR radiation is guided from the source to the detector through the hollow core of the fiber, and attenuated at wavelengths corresponding to the roto-vibrational transitions of the vapours in transit in the fiber. High resolution absorption spectra are acquired by scanning the laser across its tuning range. 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.

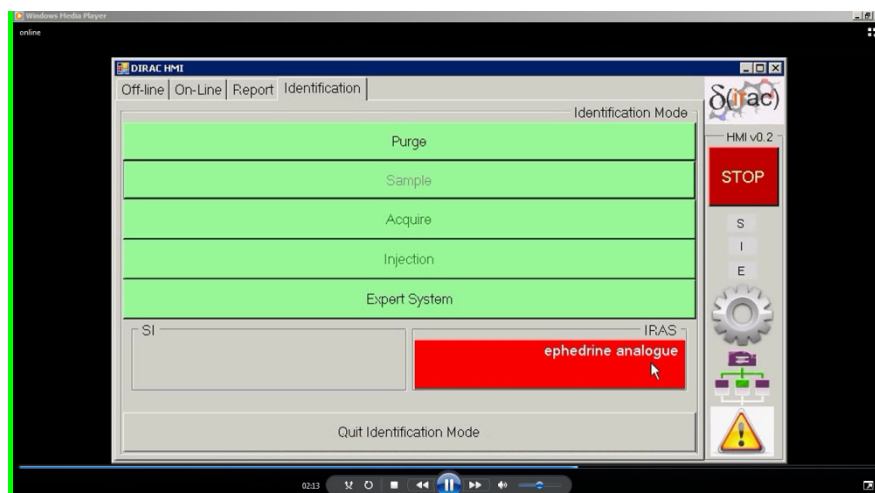


Fig. 2: Screen-shot of the DIRAC HMI during sample analysis and reporting.

The Vapour Detection Unit fits into an aluminum case identical to the ID Unit, and is driven by similar control sw and Expert System.

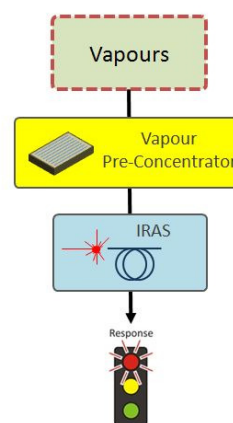


Fig. 3: Vapour Detection Unit. Left: the prototype in its aluminum hand-case. Right: sensing architecture.

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. 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 benzaldehyde, 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, solid particles are collected by a suction pump and Electro-Statically Precipitated (ESP) onto a ceramic plate. ESP precipitates preferentially particles with higher proton affinity, as is the case for ATS compounds that bring a free amine group.

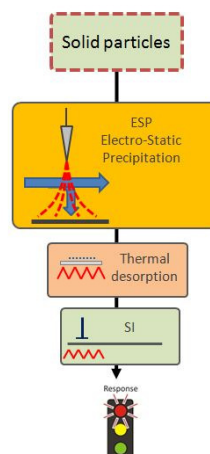
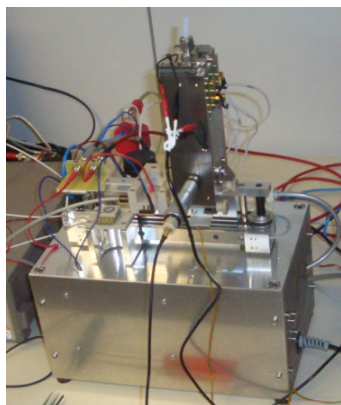


Fig. 4: Salt Detection Unit. Left: prototype. Right: sensing architecture.

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 (SI) 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.

3.2. Sensor performance

Unless otherwise specified, discussion will be focused on the Identification Unit, that is the prototype that was brought to the highest Technology Readiness Level in the course of the project. In this paragraph, performance will be analyzed with reference to a few specific requirements that were established in the course of meetings and interviews with end users.

Chemical range. The DIRAC project was proposed and approved in reply to a FP7 call that made specific reference to field-sensors of ATS precursors. A wider chemical range is however recommendable, as this would increase application and business opportunities. Indeed, the sensor was tested successfully with many different ATS precursors, pre-precursors and real drugs, of different nature and chemo-physical characteristics, such as:

- ATS precursors and pre-precursors with no amine group, such as BMK, benzaldehyde, safrole, isosafrole, piperonal, APAAN, PMK, ..
- ATS precursors with an amine group, such as ephedrine;
- Amphetamine and Methamphetamine, as free amines and as hydrochloric salts.

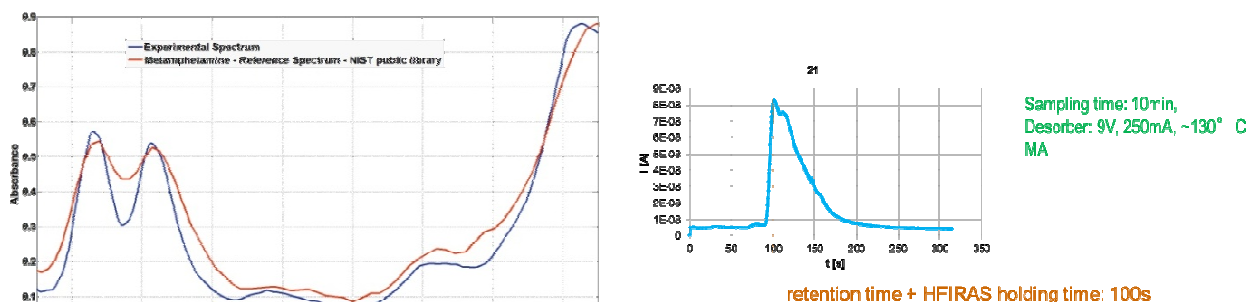


Fig. 5: Analysis of vapours thermally desorbed from a solid sample of MA·HCl. Left: HF-IRAS spectrum, compared to a MA spectrum from a reference database. Right: SI current plot measured at the output of the IR hollow fiber.

Since the sensor responds better to substances with ‘fair’ volatility, it was never tested with heavier natural drugs such as cocaine, or heroin. On the other hand, it is believed that the sensor would respond well to other substances of interest in the security domain, such as IED precursors and chemical agents, as long as a) the compound is stable enough upon thermal desorption; b) its IR fingerprints match the tuning range of the QCL.

Detection range. As with the chemical range, detection range should be as wide as possible, to cover, ideally, from real traces (nanograms) to bulk. The HF-IRAS analyzer demonstrated nanogram sensitivity when connected to a commercial injector and tested with precursors such as safrole or piperonal. Its sensitivity to other targets (ephedrines and amphetamines) was found 1-2 order of magnitude lower, because of weaker absorption coefficients in the spectral range covered by the laser. At the opposite, the SI detector showed sensitivities in the 10-100 pg range to amines, and orders of magnitude lower sensitivity to safrole and piperonal.

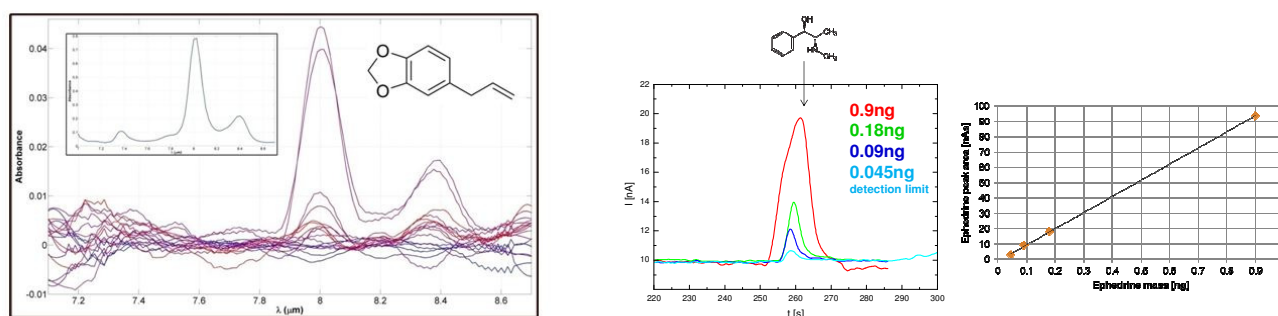


Fig. 6: Precursors analysis. Left: HF-IRAS spectra of 100 ng safrole, vaporized in a methanol solution (reference spectrum in inset). Right: SI current plot after injecting sub-nanogram amounts of ephedrine.

The sensitivity of the system as a whole is a bit lower than its detectors taken individually, essentially because of mass losses along the sensing chain. In very general terms, the system works at its best with ‘big traces’, that is with quantities in the range from hundreds nanograms to the hundreds micrograms. This range however changes with the nature and volatility of the analyte. In particular, its sensitivity is higher to precursors and lower to salts, because of the poor yield with which salts can be thermally converted into the

corresponding free base. Although not totally immune to saturation, the system is however much more resilient than commercial IMS sensors when tested with 'large' samples.

Selectivity. Strong classification/identification ability and minimized false alarm rates are of the greatest importance for use on the field. The HF-IRAS analyzer provides around 1 cm⁻¹ resolution spectra, that well match FTIR commercial databases. The sensor as a whole exploits synergies between GC, HF-IRAS, and SI modules, to deliver well defined and reproducible spectral and chromatographic patterns, that are the pillars for a successful recognition and identification process by a well designed and well trained Expert System. In a repeated sequence of tests held for the lab validation and the final demo, the Expert System was found capable to correctly distinguish positives from negatives, and correctly identify the nature of the positives. Although still preliminary, these results suggest a very strong selectivity potential.

Robustness. The sensor demonstrated ability to detect targets in the presence of potential interferences, as in the case of an ATS dispersed in a solid matrix of excipients and adulterants (a street sample), or in the case of a precursor in a solvent (APAAN in ethanol). Additionally, the sensor succeeded to separate analytes of similar chemical nature, as in the case of a mix of precursors.

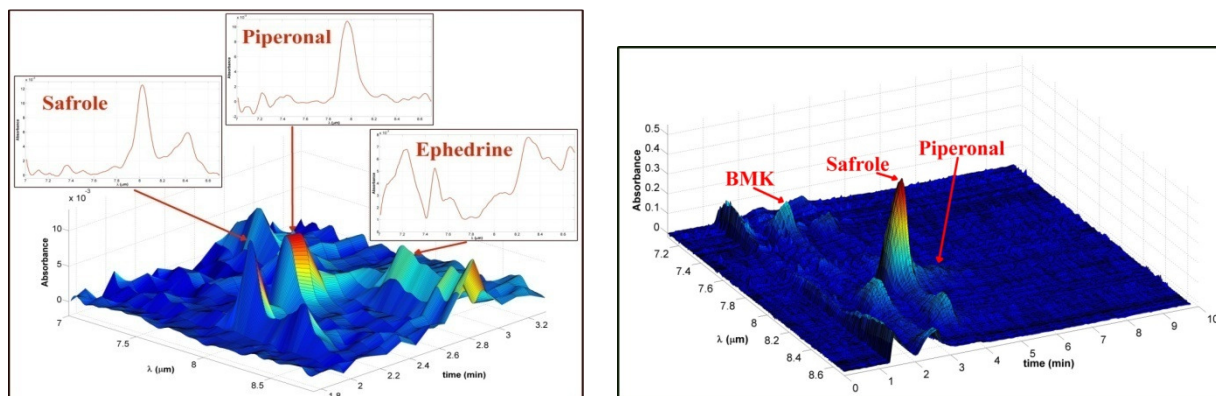
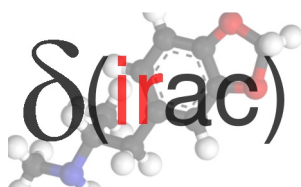


Fig. 7: Analysis of mixtures. Left: HF-IRAS spectra evolution after injecting a mix of safrole (600 ng), Piperonal (600 ng) and ephedrine (3 μg), vaporized from a methanol solution. Right: spectra evolution after injecting a mix of BMK, safrole, piperonal, and ephedrine, sampled from the headspace of a vessel at 70 °C. Ephedrine is undetected because of its low vapour pressure at 70 °C. Ephedrine appears however through its thermal degradation products (the first chromatographic peak after about 1 min).

Portability. The sensor fits into an aluminum case that matches the size of a hand-luggage according to air transportation criteria. With a weight of 15 Kg (case and accessories included), it is however a bit heavier than a hand-luggage. Power consumption of about 200 W (50% due to the QCL) makes the sensor compatible with battery operation.

Ease of sampling and use. The 'portfolio' of prototypes developed in DIRAC allows to collect samples in essentially any physical form.

The Salt Detection Unit uses a flexible pipe connected to a suction pump to 'sniff' solid particles, and an ESP to collect them onto a desorber plate.



The Vapour Detection Unit sniffs vapours from the air or from the headspace of vessels, and capture them into a cartridge filled with cavitands.

The Identification Unit accepts solid and liquid traces collected on a swab. Loading is made with the help of a docking station, that guides the sample plate with the swab on a vertical axis, to ease the coupling to the rest of the system. The ID Unit accepts also an 'external' thermal desorber, first loaded with solid particles by ESP, then transferred from the Salt Detection to the Identification Unit.

All these sampling modes could be easily integrated in a unique system. Once the sample is acquired, the operator presses a start button on a touch screen, and the HMI automatically drives the entire process, from thermal desorption, to pre-concentration, GC separation, signal acquisition, and analysis. At the end of the process, the system automatically generates both a synthetic and a detailed report. The synthetic report, in particular, just indicates if the sample is negative or positive, and, in the latter case, name of the molecule or of the class of similarity.

Detection modes and response time. The three prototypes provide diverse and complementary detection and identification capabilities. As already noticed, all these sensing capabilities could in principle be implemented in a unique system, by integrating a proper number of switching valves and fluidic bypasses.

The Salt Detection Unit collects and precipitates solid particle, and uses Surface Ionization to detect substances of interest. The entire process lasts less than two minutes, from collection, to sample transfer, thermal desorption, and sensing. With a sensitivity to amines that is orders of magnitude larger than to other molecules, this Unit can provide early warning in the presence of ATS salts. It is however prone to false positives, due for example to molecules with an amine group, other than ATSs.

The Vapour Detection Unit collects, pre-concentrates, and analyzes vapours by HF-IRAS. Sampling time is in the range of 30-60 s, while the response time of HF-IRAS is another 60 s, so that the entire process lasts about two minutes. The Unit is effective to detect and identify volatile precursors, if they are present as pure substances, while it is prone to false positives or false negatives in the case of vapour mixes.

The Identification Unit collects, desorbs, pre-concentrates, separates, and analyzes by HF-IRAS and SI, samples of different nature and form. The sensing scheme guarantees real identification capabilities, but the process is time consuming. GC is one of the bottle necks, with typical elution times of 2-3 min, that can raise up to 5 minutes for heavy molecules and 'large' samples. Sample collection and thermal desorption take additional minutes, and the process as a whole currently lasts about 8 minutes. The system processes spectra, elution times, and SI plots, and tries to match them to a reference database of target molecules. In case of positive identification, the system displays the name of the target molecule. If identification fails, the IR spectrum is further processed by a second routine, that verifies similarities with classes of banned or controlled substances (hallucinogenic, stimulant, ephedrine-like,...). In case of positive classification, the system displays the class. If classification fails, the system displays a negative.

3.3. Sampling methods and hw

As observed in a previous paragraph, DIRAC developed a portfolio of sampling tools that allow to collect samples in essentially any physical form. Liquid and solid traces can be

collected manually on a swab and loaded into the thermal desorber of the Identification Unit, while vapour traces can be sucked into the VPC of the Vapour Detection Unit. Furthermore, DIRAC explored a method for the selective collection of particles, based on Electro-Static Precipitation (ESP). ESP should separate proton affine particles from irrelevant particles, and is of special interest for the selective sampling of drug particles in salt form previous to their desorption and detection in the gas phase.

Research on ESP led to the development of a particles sampling station that can be coupled to either the SI detector of the Salt Detection Unit, or to the VPC/GC/IRAS analyzer of the Identification Unit.

3.3.1. Particles sampling station

In the particles sampling station developed by EADS, solid particles are collected by a suction pump and Electro-Statically Precipitated onto a ceramic plate. The plate is then moved on a rail car from a 'sampling' to a 'desorption' position. There, the sample is thermally desorbed, and vapours are released into the detector (SI or GC/IRAS). The process is controlled via a Graphic User Interface written in Labview.

Fig. 8: Particles sampling station (here connected to a SI detector). a): metal box with stepper motors and powers supplies; b) sample holder, movable along the x and z axes; c) ESP chamber; d): SI detector; e) PC and GUI to control the sampling and desorption processes; g) PC and sw to display SI signal plots.

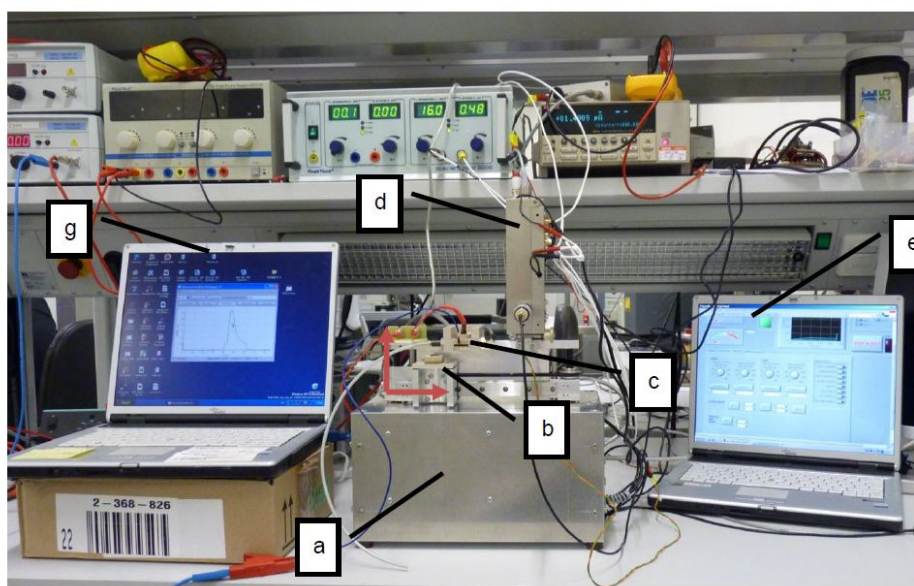
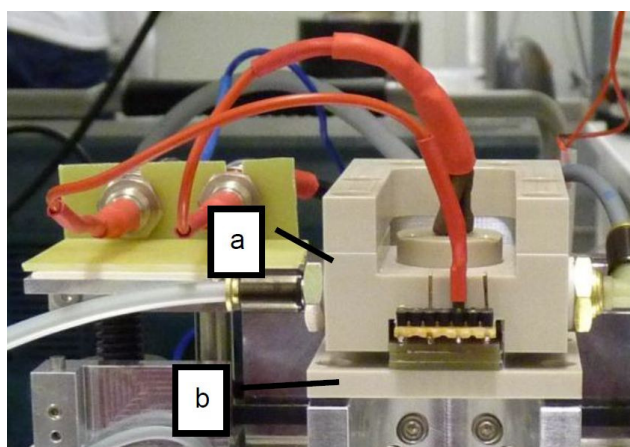


Fig. 9: ESP module. Sample holder (b) in sampling position closes the sampling chamber (a) and places the sampling/desorber plate under the needle electrodes (see text). In this position, air flows through the sampling chamber driven by a suction pump. A large potential difference is created by a high voltage power supply between sampling plate and needles, resulting in a corona discharge. According to the ESP principle proton affine particles should be preferentially sampled on the sampling plate.



3.3.2. ESP method and results

Operating principle. ESP requires a gas discharge, also known as plasma, that occurs whenever an intense electric field is strong enough to ionize the molecules and atoms between closely spaced electrodes. However, if the electric field is strongly non-uniform, for example between a sharp needle and a flat conductive surface, a corona discharge is formed, in which positive or negative ions predominate over most of the electrode gap. Since the electric field is much stronger in the region close to the needle, only there ions will be generated. Igniting a plasma in humid air creates various negative species, such as O_2^- and OH^- , as well as positive ions, mostly H_3O^+ . These are those ions which initiate the so called Atmospheric Pressure Chemical Ionization (APCI) process. Whether negative or positive ions predominate in the electrode gap, depends on the polarity of the needle electrode. In case a positive potential is applied, positive H_3O^+ ions predominate. These can transfer their charge to higher proton affinity molecules such as Ephedrine (drug detection).

Amine containing molecules like drug molecules and drug precursor molecules are characterized by very high proton affinity values. With the help of an electric field, trace amounts of target gas ions can therefore be separated from their surroundings. APCI is an established process and is used e.g. in ion mobility spectrometry analytics.

The idea within DIRAC was to apply the APCI process to target particles to separate analytically relevant drug residue from irrelevant dirt particles, and to apply the Corona field to accumulate the particles on a desorber plate for subsequent evaporation into the DIRAC gas detectors.

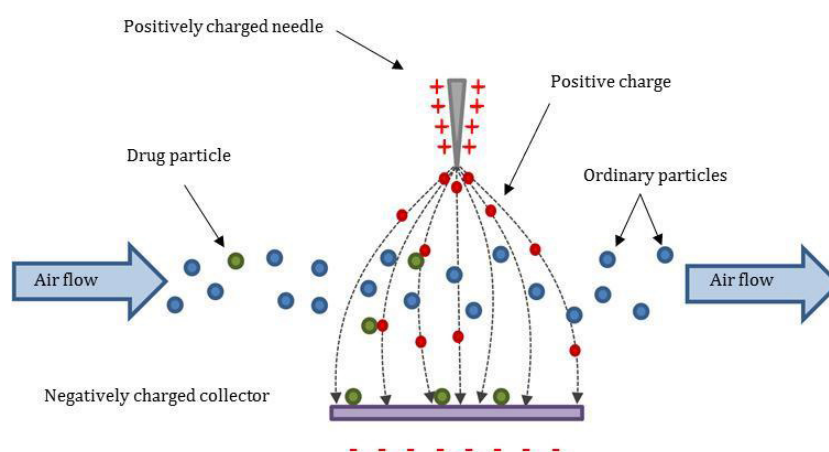


Fig. 10: Separation of amine-based narcotics in a positive corona discharge.

Desorber plates. Another characteristic of narcotic materials, besides their proton affinity, is that they are very sticky. This latter property can be used as a second sampling criterion. In experiments aimed at assessing these possibilities, two different kinds of desorber plates were used:

- Desorber plates without metallization on the front side. After reaching the collector surface, the electrically charged narcotic particles accumulate as long as the plasma is present. As the ion charge is not removed, the particles stick to the desorber plate by electrostatic forces. As the particle accumulation process causes

a build-up of positive charge, a counter-field is created, which causes the particle accumulation to saturate.

- Desorber plates with metallization on the front side. After reaching the collector surface, the electrically charged explosive particles lose their extra charge to the conductive collector plate. As the collected substances are also “chemically” sticky, they should accumulate on the collector surface without saturation as long as the plasma is present.

General experiment. The ESP process was investigated with different substances such as flour, saccharose, ephedrine and ephedrine hydrochloride. Flour and saccharose represent a meaningful set of interferents, since flour does contain an amine group as ATS, while saccharose does not. The substances were sucked into the sampler, and the sucked particles in the air stream passed the Corona discharge region where proton affine particles can be charged and collected on the desorber plate, while the airstream is guided to the exhaust. The sampling yield of each substance was determined by balancing the initial weight and the output weight. Before starting the tests, all substances were brought into powder form by using a porcelain mortar. Tests were provided with and without Corona discharge and with different desorber plates.

The relative humidity (r.h.) in the lab was enhanced to 45% with the help of a bubbler bypass. In connection with these tests, the desorber plates were automatically transferred to the desorption position and the respective yields were evaporated into a SI detector.

Measurement results. The full process chain of the standalone detection unit consisting of sucking in particles, collecting particles, desorbing particles and detecting in the gas phase was found to work.

Using the desorber plate without metallization it was found that in case of proton affine particles (ephedrine, ephedrine-HCl) less particles could be sampled compared to non-proton affine particles (saccharose). An explanation is that the increasing electrostatic charging decelerates the accumulation. Desorber plates with metallization seem to improve the yield of ephedrine and ephedrine-HCl.

A positive discrimination of the amine containing particles (flour, ephedrine and ephedrine/HCl) compared to the non-amine containing particles like saccharose is not visible. The respective yield is with all substances round about the same.

However, when the Corona discharge process is not in operation during the suction process, no particles at all are sampled on the desorber plate but are carried away by the air stream.

The most likely explanation would be the formation of an ‘ionic wind’ caused by the Corona discharge. Regardless of the nature of the corona discharge, the generated ions repeatedly collide with the surrounding air molecules, transferring kinetic energy, but retaining their electric charges. As a result, a massive amount of air molecules are pushed by a handful of ions towards the collector plate. Due to the formation of an “ionic wind” through the Corona discharge, the transfer of charges from the generated ions to the drug particles is severely hindered.

Conclusions and outlook. The results showed that corona discharges can effectively concentrate particles from an air flow through electrostatic separation to a collector plate,

but cannot select drug particles from others. The electrostatic sorting of particles in proton affine particles and remaining particles needs to be improved by a redesign of the corona discharge unit. In particular, it was found out that the directions of the electric field and the airstream must be antipodal in order to avoid that neutral particles are carried over by the so called “ionic wind” produced by the electric field and get sampled together with the charged particles. Furthermore, experiments suggest that separation yield could take advantage of adhesion forces and of the stickiness of drug particles.

3.4. Pre-concentration and separation methods and hw

With reference to the chemo-physical characteristics of the analytes, DIRAC had to deal with two very different classes of molecules: volatile compounds, such as most of the ATS precursors, and non-volatile ammonium salts, such as the ATS that are commonly found in street samples. This determined the need of defining and developing two complementary sensing strategies, that will be referred to as ‘the liquid route’ and ‘the vapour route’, respectively. Both routes make use of cavitands for pre-concentrating the analyte. Cavitands, defined as synthetic organic compounds with enforced cavities of molecular dimensions, are versatile molecular receptors, whose complexation ability can be tuned by the appropriate choice of the bridging groups delimiting the pre-organized cavity

In the liquid route, the sample is dissolved in water or other polar solvent, and ammonium salts are selectively captured by cavitands grafted on a silicon surface immersed in the liquid. The capturing event is transduced into an electric signal to provide detection.

In the vapour route, the sample is thermally desorbed, and vapours are first pre-concentrated by cavitands packed into a column, then separated by a fast GC capillary column, and eventually analyzed by IRAS and SI detectors.

3.4.1. Liquid phase pre-concentration and detection

TetraPhosphonate cavitands (Tiiii) were the receptors used for liquid-phase pre-concentration and detection. In Tiiii, the presence of four P=O groups oriented toward the cavity allows the selective complexation of ammonium ions via synergistic H-bonding, cation-dipole and CH- π interactions. The recognition properties of phosphonate cavitands toward ammonium salts have been assessed in the solid, in solution, and in the gas phase.

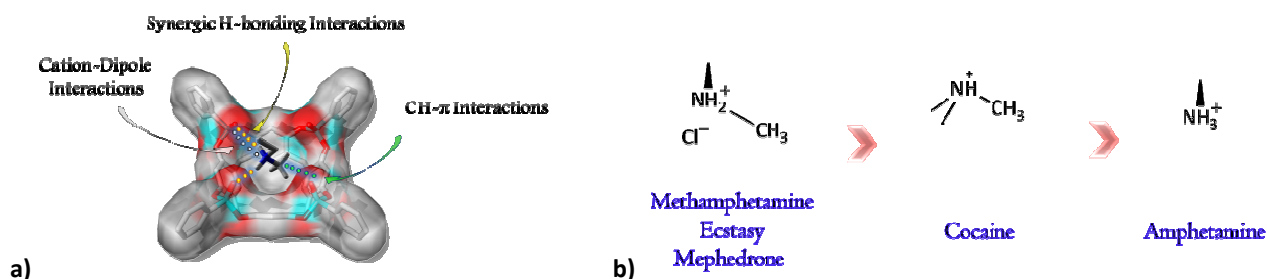


Fig. 11: Tiiii cavitands. a): Interactions involved in the ammonium salts complexation; b): Selectivity Scale toward ATS in methanol.

The selectivity toward Amphetamine Type Precursor (ATS) in methanol follows the order secondary amines (like methamphetamine and ecstasy hydrochloride), tertiary (cocaine hydrochloride), and finally primary amines (amphetamine hydrochloride). In water, the

selectivity scale remains unchanged, but the gap between secondary and tertiary amines increases.

Based on this experimental evidence, a **supramolecular nanomechanical sensor** was developed by INSTM, suitable for the direct, label-free screening of methamphetamines and related designer drugs *in water*. Tiii cavitands are grafted on the top face of a silicon microcantilever (MC), which has its bottom face passivated with a 1-dodecene layer.

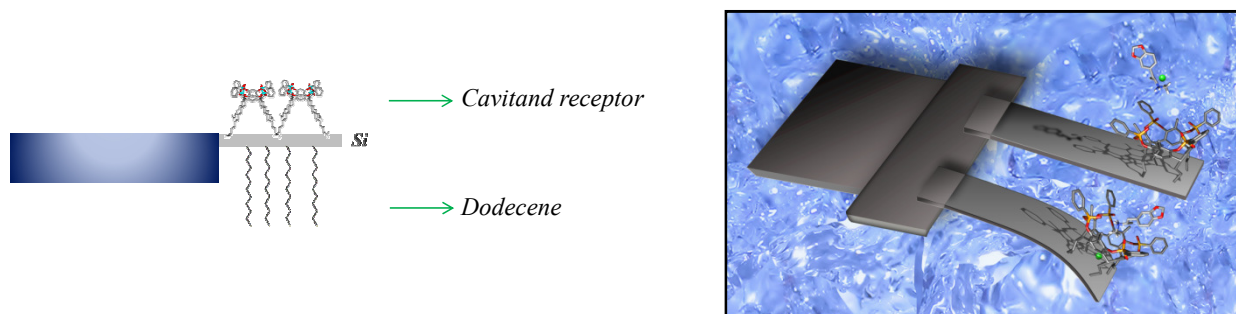


Fig. 12: INSTM Supramolecular nanomechanical sensor.

In this device, the energy of the molecular recognition between the cavitand host and the drug guest is harnessed to bend the cantilever. Experiments were conducted by means of a commercial platform which is equipped with a microfluidic system to handle liquid delivery to the sensor, and multiple lasers for simultaneous optical measurement of the deflection of an array of eight MCs.

The sensor was tested with water solutions of illicit drugs (amphetamine, MDMA, cocaine hydrochlorides), excipients, mixes of illicit drugs and excipients that mimic a street sample, and a real street sample containing 3-fluoromethamphetamine (3-FMA). Experiments demonstrate high sensitivity and selectivity against the whole class of methamphetamine drugs, independently of the type of residue attached to the $^+\text{NH}_2\text{-CH}_3$ moiety, and suggest that the sensor could be used for the detection of illicit and designer ATS in wastewaters and biological fluids such as saliva, urine and blood plasma, at very low concentration of about 10^{-6}M (best detection conditions at 10^{-4}M).

3.4.2. Vapour phase pre-concentration and GC separation

Tetraquinoxaline cavitands (QxCav) were the candidate material initially selected for pre-concentrating both ATS and precursors from the vapour phase. This choice originated from the known ability of QxCav to confine within their cavity an aromatic group, that is present in all our target compounds. QxCav were packed as a fine mesh within a silicon micro-machined VPC cartridge. The cartridge was operated at room temperature to suck the air and pre-concentrate the vapours, then heated up at $300\text{ }^\circ\text{C}$ to release the vapours into the separation and analysis modules. QxCav were found to pre-concentrate efficiently volatile precursors such as safrole, BMK, PMK, but showed scarce affinity towards targets with an amine group (ATS, ephedrine). This led, in the second phase of the project, to test additional cartridges packed with a fine mesh of TENAX, that is a commercial broad-range pre-concentration material. During the lab validation and the final demo, a QxCav

cartridge was used in the Vapour Detection Unit, and a TENAX cartridge in the Identification Unit.

After initial tests as a stand-alone module, the Vapour Phase Concentrator was later developed together with a FAST GC separator as a unique and highly integrated platform, with a footprint of 205 x 160 mm, and a maximum height of 120 mm. This platform is referred to as the 'VPC/GC supermodule'.

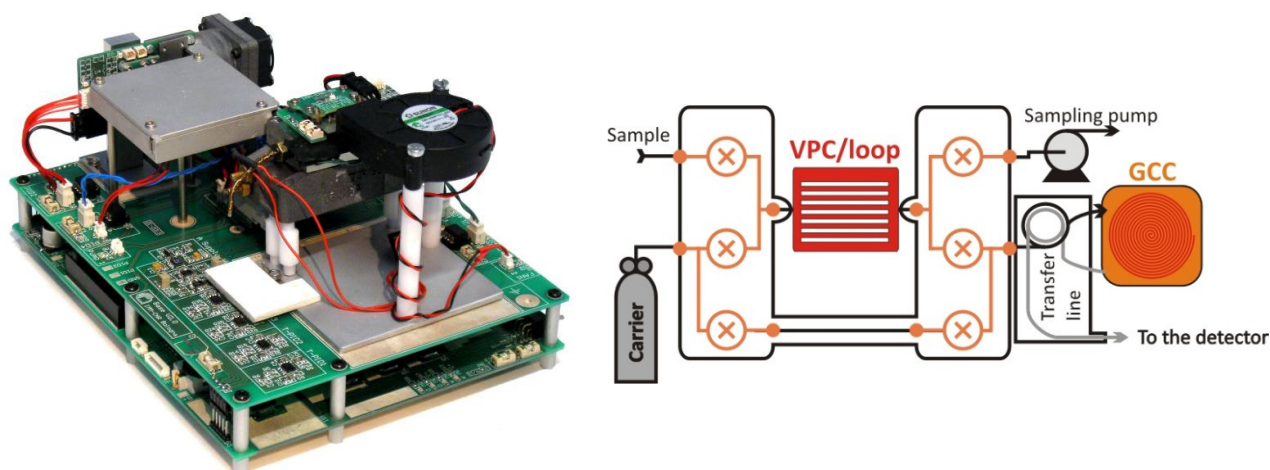


Fig. 13: CNR-IMM VPC/GC super-module. Left: hardware. Right: fluidic scheme.

The VPC/GC supermodule essentially consists of:

- An injector assembly, based on:
 - 6 externally actuated membrane valves, integrated in 2 MEMS chips;
 - a VPC cartridge, which acts as GC injection loop.
- Fluidic interconnections between the valves, the VPC, the sample inlet, the sampling pump, and the GC column. These interconnections are partially implemented at chip level inside the injector chips (orange colour in the above figure), and partially inside a metallic interconnection block.
- The GC separation column, which separates the single components injected from the VPC.
- A transfer line, enabling to control the temperature of the interconnections between the injector assembly, the GC column and the detector, which is not part of this assembly.

All the critical components of this assembly (VPC cartridge, injection loop, and GC column) are silicon-micromachined chips as shown in the next figures. The injection loop, in particular, is made of two chips the size of an euro-cent, each based on three pneumatically actuated MEMS SU-8 membrane valves with ultra-low-volume switching capabilities, that withstand the max operating temperature of the system (150 °C).

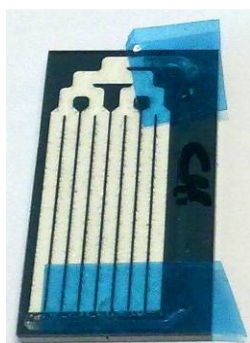


Fig. 14: CNR-IMM Pre-concentration cartridge. Left: the chip. Right: the column packed with a QxCav mesh (by INSTM).

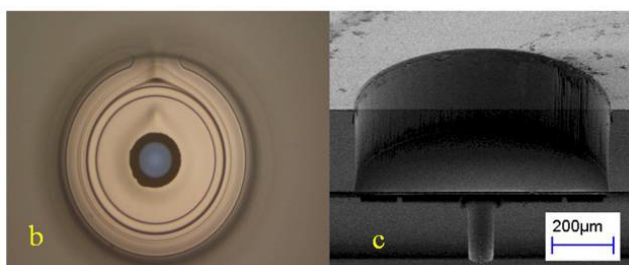
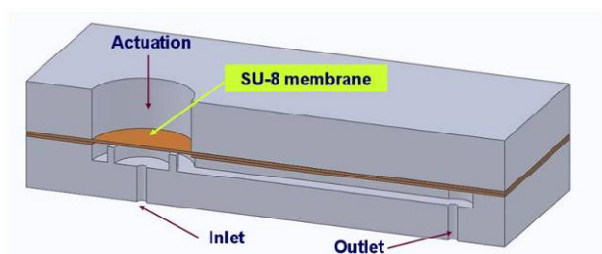


Fig. 15: CNR-IMM Micro-valve with SU8 membrane. Left: scheme; b): optical plan; c): SEM image.

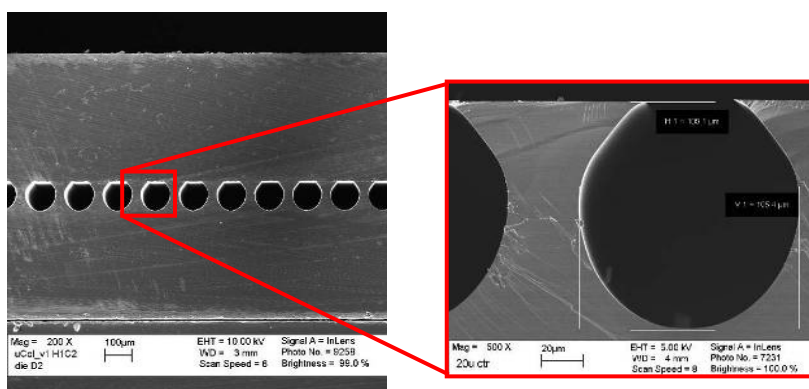
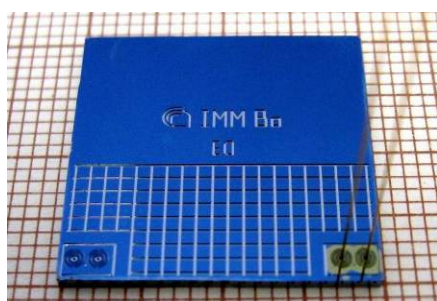


Fig. 16: CNR-IMM MEMS FAST-GC column 2 m x 0.1 mm on a chip. Left: photograph; right: SEM micrographs.

3.5. HF-IRAS analyzers

In DIRAC, the HF-IRAS analyzers essentially consist of an InfraRed Hollow Fiber (HF) connected to the output of the GC column, an IR External Cavity Quantum Cascade Laser (EC-QCL), and a thermo-electrically cooled IR detector. IR radiation is guided from the source to the detector through the hollow core of the fiber, and attenuated at wavelengths corresponding to the roto-vibrational transitions of the vapours. High resolution absorption spectra are acquired by scanning the laser across its tuning range.

The project delivered two HF-IRAS analyzers, that were independently developed by FRAUNHOFER IPM and by CREO. This, in turn, allowed to fabricate and demonstrate the two sensor prototypes that, in previous paragraphs, have been referred to as the

Identification Unit and the Vapour Detection Unit. The two HF-IRAS modules make use of similar components and major sub-assemblies, adopt similar solutions for optical and micro-fluidic connections, and show comparable performance characteristics and limits. At the same time, the two modules are complementary, in that they cover complementary regions of the IR spectrum.

- The FRAUNHOFER IPM module covers the spectral range $6.5\div 7.5\ \mu\text{m}$. This range contains the most important and intense fingerprints of ATS, and may enable classification of a new designer drug, not present in the database (see discussion about the Expert System).
- The CREO module covers the spectral range $7.2\div 8.6\ \mu\text{m}$. In this range, ATS fingerprints are less intense and less specific, but easier to detect, because they are not so heavily affected by the absorption bands of water vapour.

The final assignation of the IPM module to the Vapour Detection Unit, and of the CREO module to the ID Unit, was essentially based on logistic rather than technical reasons.



Fig. 17: HF-IRAS analyzers. Left: FRAUNHOFER IPM module, used in the Vapour Detection Unit; right: CREO module, used in the Identification Unit.

Fig. 18: FRAUNHOFER IPM module. Optical path in the open air is minimized to reduce absorption due to water vapour. Commercial electronics is mounted on the front side of the base plate.

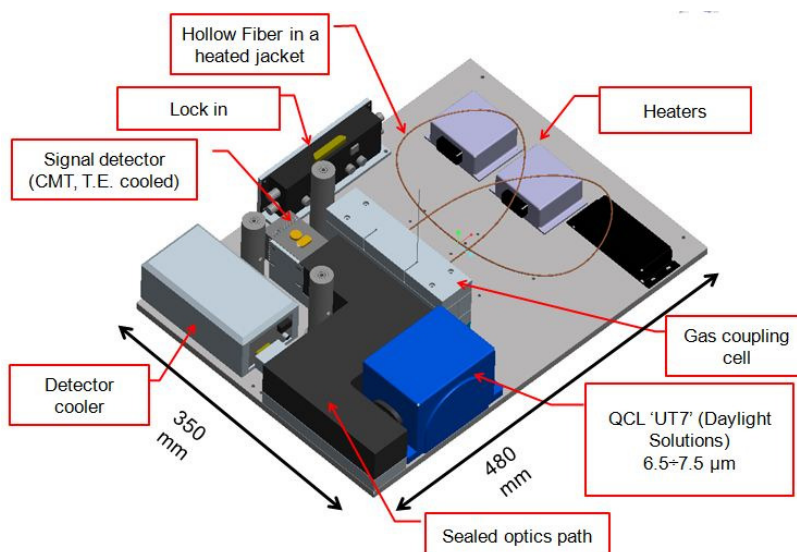
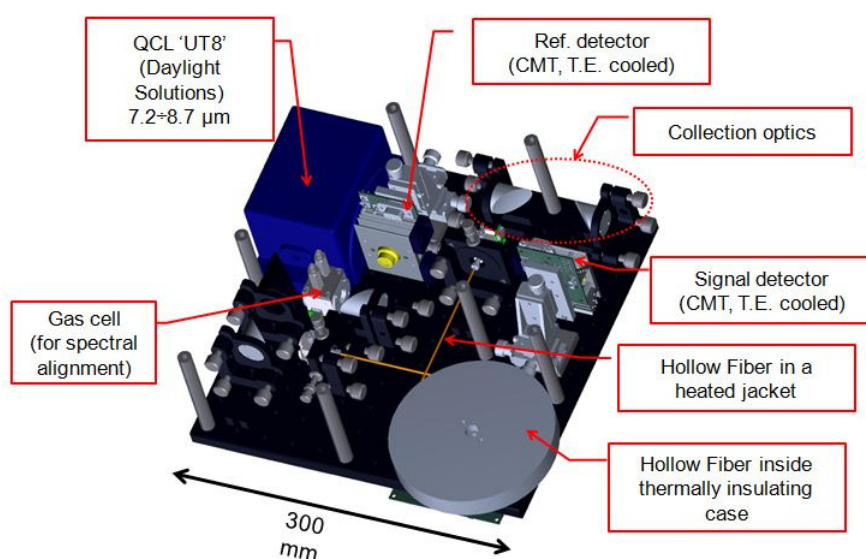


Fig. 19: CREO module: 3D drawing. Reference detector and gas cell allow to align the spectra and mitigate the jitter of the source. Customized electronics is mounted on the back side of the base plate.



3.5.1. Critical components and subassemblies

IR hollow fibers and working temperature. Both modules make use of commercial IR hollow fibers by Polymicro Technologies, with an inner diameter of 300 μm and a length \approx 1 m. The hollow fiber consists of a silica capillary that is internally covered by an optical double layer of Silver/Silver Iodide, and externally protected by an acrylate coat. On demand, the acrylate coat can be replaced by a polyimide coat. This allows to raise a bit the working temperature, from 120-130 $^{\circ}\text{C}$ to $> 150^{\circ}\text{C}$. At about 170 $^{\circ}\text{C}$, Silver Iodide softens and the optical coating collapses. As a matter of fact, the systems were never operated continuously at temperatures in excess of 150 $^{\circ}\text{C}$. This temperature constraint

may limit the ability to deal with low volatility or sticky molecules, and is the main reason why the sensors were never tested with heroin or cocaine.

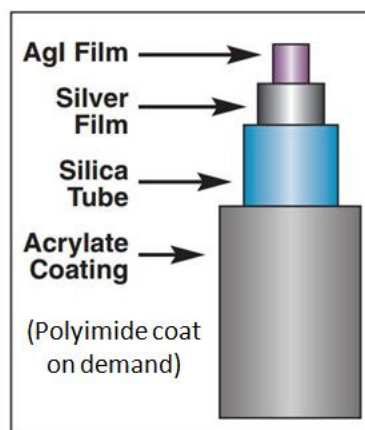


Fig. 20: Commercial IR hollow fiber (Polymicro Technologies).

Laser sources and spectral repeatability. The two modules make use of commercial EC-QCL of similar design, that is the models 'UberTuner UT7' (6.5÷7.5 μm) and 'UberTuner UT8' (7.2÷8.6 μm), both by Daylight Solutions, the US company. UT7 and UT8 are uncooled pulsed laser sources, that operate at 100 KHz and up to 5% duty cycle, with peak power of a few hundreds mW, and 1-2% peak to peak repeatability.

To scan their tuning range, these lasers can be operated in two alternative modes, that is in a 'continuous scanning mode' (the diffraction grating is moved continuously from one end point to another), or in a 'step-and-scan mode' (the grating is moved in a sequence of predetermined step, and stands still while the signal is acquired). The step-and-scan mode ensures higher repeatability, but, with an acquisition rate estimated around 1 spectrum /min, is too slow to match the dynamics of the DIRAC sensor.

DIRAC therefore adopted the continuous scanning mode, that allowed to acquire spectra at a rate of about 0.5 Hz, that is fast enough to track a tight sequence of chromatographic peaks outcoming from the GC. Experiments, however, evidenced that the Signal to Noise Ratio (SNR) of the system is greatly conditioned by the mechanical noise of the moving grating. Scanning rate is neither perfectly constant during a single scan, nor perfectly reproducible from one scan to the next. If a sequence of scans is plotted on the same graph, jitter can be visually estimated in the range of several nanometres. Jitter translates into noise in an absorbance spectrum (that is calculated as $\log [S(t_0)/S(t)]$, and therefore requires alignment of spectra taken at time t and t_0). Noise becomes stronger in the presence of rapid variations $\Delta S/\Delta \lambda$ or vertical 'steps' along the plot. Such steps can be due to the absorption lines of water vapour or other contaminant along the optical path, but also to the spectral response characteristics of the fiber itself.

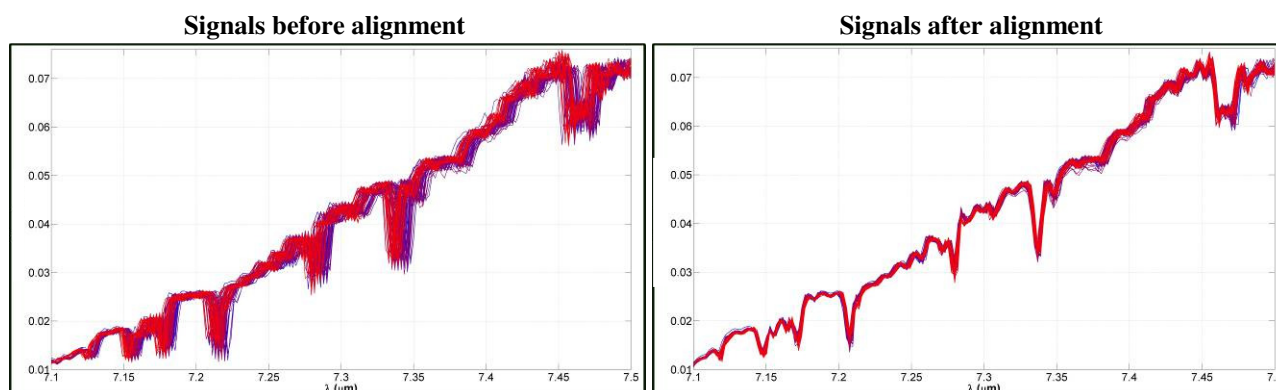


Fig. 21: spectral jitter and spectral alignment. Alignment procedure described in the text.

The problem can be mitigated if clearly recognizable spectral patterns are used as ‘flags’ to align the plots. A procedure was developed that uses as flags the absorption patterns of a vapour mix, that is placed inside a sealed optical cell along the path to a reference detector. A mix of water vapour, methane, and ammonia, appears particularly effective to align the spectra in the wavelength range from 7 to 8.5 micron, that is the range covered by the UT8 laser. This procedure improved SNR by a factor 5÷10 in the range 7.1 ÷ 7.5 micron, that is heavily affected by water vapour.

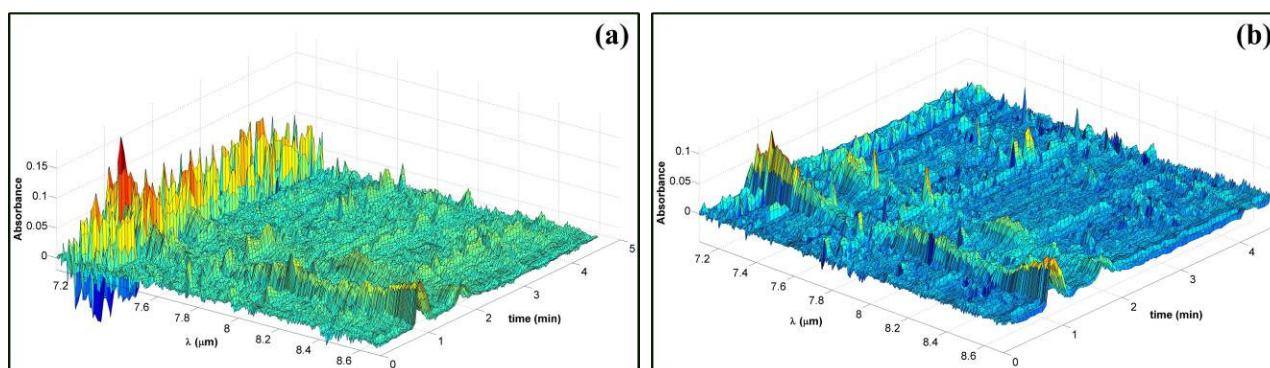


Fig. 22: spectral alignment and detection of BMK. The two pictures show a sequence of absorption spectra taken after injecting a sample of BMK vapour. In a), the laser jitter and the water vapour s heavily mask the BMK absorption band around 7.2 μm . The same band appears clearly visible in b) after spectral alignment.

Fluidic connections and system maintenance. Important efforts were spent in the development and testing of the optical and fluidic connections at the inlet and outlet of the hollow fiber. This led to an ‘optimized’ fluidic design that now features:

- Reduced flow losses (estimated <10% across the module at a working flow of 0.5 sccm);
- Minimized dead volumes ($\approx 10 \mu\text{l}$, corresponding to 10% of the inner volume of the fiber);
- Fast thermalization and reduced heat losses, through flexible heating jackets;

- Standard nut & ferule connections, that make replacement of the hollow fiber almost as easy as a GC silica column.

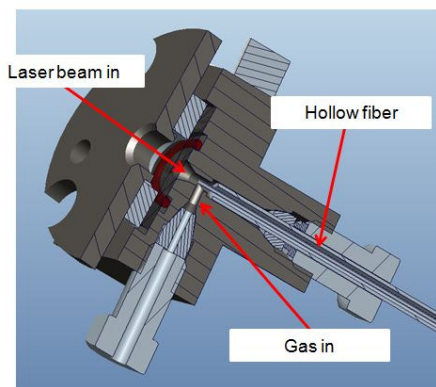


Fig. 23: coupling cell at the interface between GC and the hollow fiber.

3.6. SI detector

Surface Ionization (SI) detectors are conceptually very simple and inexpensive devices, comparable only to conventional metal oxide gas sensors, but featuring a very much higher sensitivity and selectivity to amine-containing drugs. Within DIRAC, such devices were studied in the form of single sensor devices as well as in the form of building blocks of increasingly more sophisticated detector and detector-sampling systems:

- Stand-alone SI detectors (EADS)
- SI detectors coupled to a particle sampler as in the Salt Detection Unit
- SI detectors coupled to IR analyzers as in the Identification Unit
- SI detectors coupled to pre-concentration and GC modules

The first part of this paragraph deals with the architecture and intrinsic performance of stand-alone SI detectors; the second is concerned with the functioning of SI detectors within more sophisticated detector and sampler-detector combinations.

3.6.1. Stand-alone SI detectors

In order to avoid running early on into MEMS technology problems, most of the SI detection experiments were performed on a macroscopic version of SI detector (**Fig. 24**). A ceramic heater substrate carries a Fe_2O_3 ion emitting film on its front surface and a screen-printed Pt heater meander together with a Pt temperature sensor on its back surface. Ion extraction is provided by a flat-plate counter electrode positioned at a distance of about 1mm above the emitter surface. For carrying out sensing tests these sensors were mounted inside a heatable stainless steel test chamber. This test chamber carries gas inlet and outlet ports that allow analyte vapours to be guided through the air gap formed by the ceramic heater substrate and the metallic counter electrode. In order to allow for well-controlled electrical fields inside the ionization device, the position of the counter electrode is adjustable by an external micrometer screw. During operation the test chamber was heated to about 80 °C to avoid condensation of the very sticky analyte vapours.

In order to assess the sensing properties of such SI detectors, a series of gas measurements was performed. In these experiments, a Fe_2O_3 ion emitter was used and heated to different operation temperatures and exposed to different target and interfering gas concentrations (ephedrine, ephedrine:HCl, MDMA, dibutylamine, ethene, methanol and water vapour). Arrhenius plots (**Fig. 25, left**) demonstrate the very high intrinsic selectivity towards amine-containing substances as compared to other hydrocarbon species. Remarkable is also the very high selectivity with regard to water and methanol vapours, two very common solvents for amine-containing drugs. The reason for this high selectivity is that amines can be very easily ionized due to their very low free-space ionization energy of about 7.5eV (**Fig. 25, right**). Once adsorbed on a high-workfunction solid surface, the ionization energy is largely reduced due to the fact that just enough energy needs to be imparted to an adsorbate to move one of its valence electrons to the lowest-lying free electron states inside the solid. In the case of amines, this amount is in the order of 1eV only. This amount of energy can be easily supplied by the thermal reservoir formed by the ion emitting film. As the free-space ionization energies of most interfering molecules are much larger (ethene~11.5eV; water~12.6eV), the detection of these latter species is exponentially suppressed.

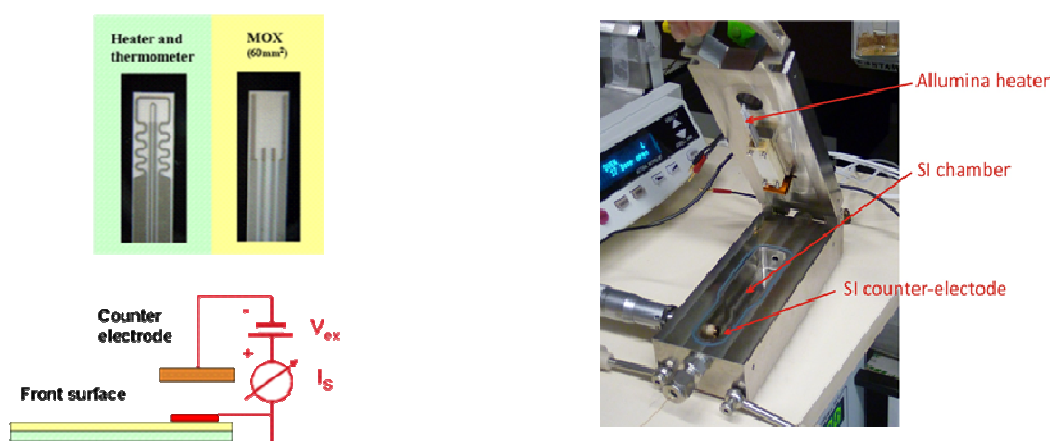
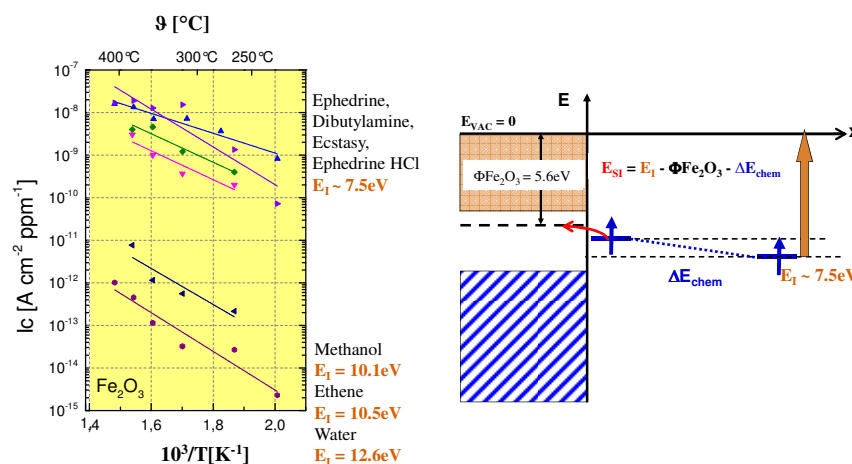


Fig. 24. Ceramic sensor in a parallel plate capacitor arrangement with the Au counter electrode to provide an almost homogeneous electrical extraction field.

Fig. 25. Left: Temperature dependence of SI currents as normalized to gas/vapour concentration and emitter area; right: energetics involved in producing target gas ions at a heated Fe_2O_3 surface and in free space.



3.6.2. Detector-sampler combinations

A first set-up (**Fig. 26, a**) employed a single SI gas sensor facing directly a desorber pad that contains small amounts of collected drug residue (1mg). This desorber pad can be heated from below by forming a mechanical contact with a pre-heated metal rod ($T \sim 180^{\circ}\text{C}$) to produce a short flash of vapour that directly impacts into the air gap of the SI detector.

A second detector alternative (**Fig. 26, b**) is a combination of a gas chromatography (GC) capillary column placed in front of a SI detector. In order to provide a good coupling between the GC column and the SI detector, the GC column output was directly fed into the air gap between the emitter and collector electrodes of the SI detector. In this second case, the solid drug residue was first dissolved in methanol to obtain a liquid solution and the solution was then injected into the GC column using a syringe injector. Whereas the first system architecture was realized and tested at EADS, the second combination was assembled and tested in a bilateral test campaign of CNR and EADS at the CNR premises in Bologna.

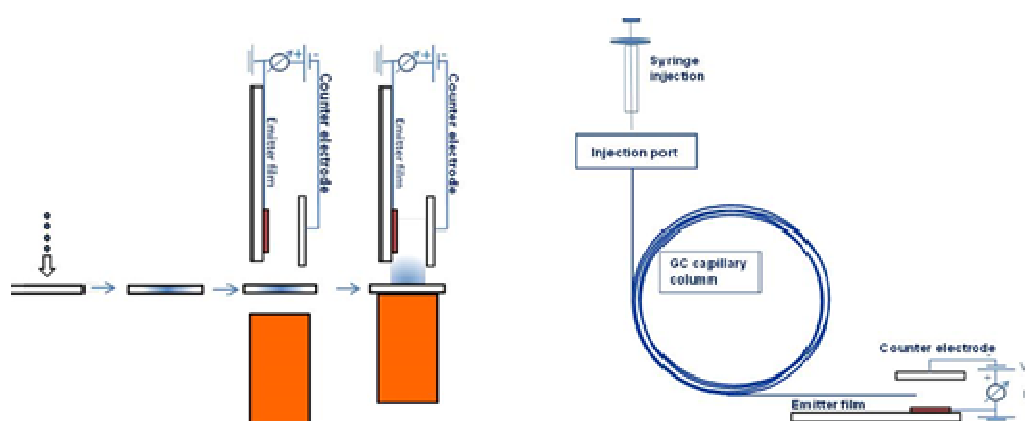


Fig. 26: Desorber-SI and GC-SI detector combinations. (a, left) flash evaporation and SI detection of a drug sample collected on a desorber pad. Flash desorption of the collected substance is initiated by pressing a pre-heated metal rod onto the bottom side of the desorber pad; (b, right) GC-SI detector combination. A liquid solution containing a dissolved drug sample is fed into a GC column using a syringe injector; the transmitted vapours are then fed into the air gap between the emitter and collector electrodes of a SI detector.

In the case of the desorber-SI combination, a hot air plume is generated whenever a flash evaporation event was triggered by contacting the hot rod with the collector pad carrying the different sample substances (**Fig. 27**).

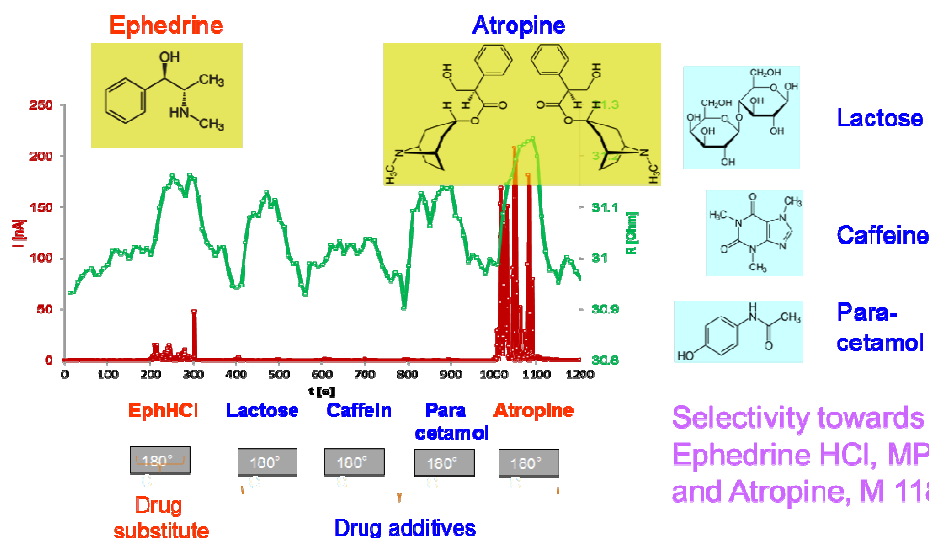


Fig. 27: SI currents (red curve) in response to a drug substitute and various pharmaceutical and filler materials (~1mg each). The SI emitter was a thin film of Fe_2O_3 heated to 310 °C. The green curve shows the variation of the emitter temperature as the different substances were flash evaporated into the SI detector.

The occurrence of such plumes is revealed from the changes in the resistance of the back-surface Pt thermometer. As expected, a SI response was only observed when the drug surrogate EphHCl was evaporated. The filler materials lactose, caffeine and paracetamol, in contrast, did not produce any SI response at all. The reason is that lactose does not contain any amine functional groups, while caffeine and paracetamol only contain amino groups incorporated into heterocycles. A huge SI response, however, was observed upon evaporating atropine. Atropine is a legal pharmaceutical substance, also containing an amine functional group, which explains its detectability. In all cases the response and recovery times of the SI detector were very short - in the order of seconds - limited only by the dynamics of the flash evaporation events.

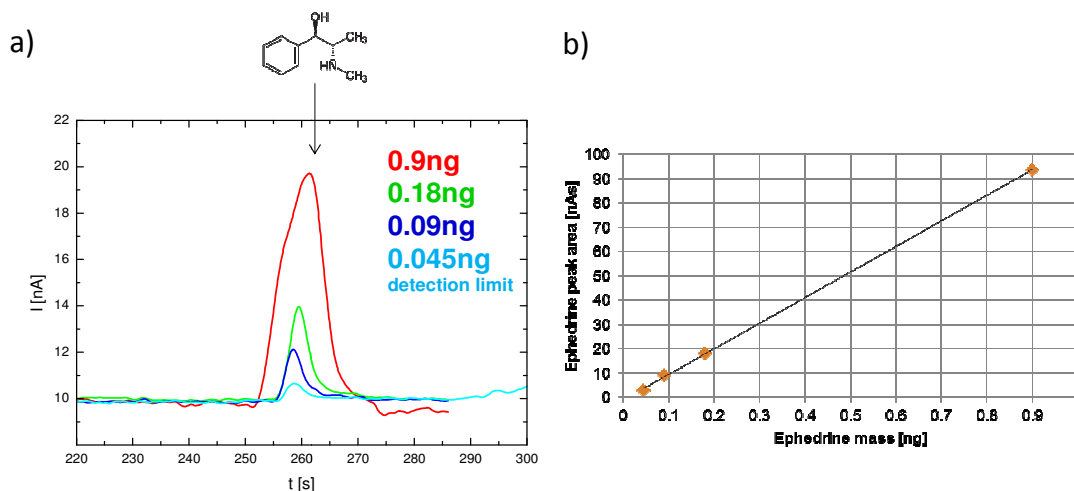


Fig. 28. (a, left) Ionization currents as a function of retention time at decreasingly lower ephedrine injections; (b, right) integrated ephedrine peak area versus injected ephedrine mass. The SI detector operation temperature was 490 °C.

These first experiments showed the excellent group selectivity to amine-containing substances, but they also demonstrated that additional selectivity is required to attain the selectivity to illicit drugs that is demanded by end-user requirements. This additional selectivity could be easily attained by operating the SI detector downstream to a GC column. In these latter experiments, the analyte was dissolved in methanol and injected into the split/splitless injector region of the GC columns. Ephedrine now turns up at a definite retention time (**Fig. 28, a**). In order to determine the minimum detectable amount of ephedrine, increasingly smaller amounts of ephedrine were injected. It was found (**Fig. 28, b**) that the height of SI signal scales linearly with the injected amount, which enables true concentration measurements. Minimum detectable concentrations turned out to be lower than 45picograms of ephedrine, which is comparable to IMS sensitivities.

3.7. Expert System

The expert system is an artificial intelligence application screening for ATS and their main precursors. It performs an automated general unknown analysis by using an identification module and a detection module.

The **identification module** is designed to perform an advanced library search, in order to identify accurately the individual identity when the tested compound is one of the substances included in the database. The reference spectral database contains a number of 169 compounds, including stimulant and hallucinogenic / psychedelic amphetamines (analogues, homologues and derivatives), sympathomimetic stimulants such as ephedrines, the main ATS precursors, narcotics and other compounds of forensic interest.

The **detection module** performs a pattern recognition process, in order to assign efficiently the class identity of the tested compound even when its reference spectrum is not present in the spectral library. PCA was used for reducing the dimensionality of the spectral data, i.e. to perform the selection of the most relevant IR absorptions and to eliminate both redundant spectral information and noise from the input database. This approach allows the multivariate analysis of the data based on pattern recognition techniques.

The detection module is able to assign the class identity of a compound according to the main types of biological activity of the ATS modeled as positives: stimulant amphetamine analogues (amphetamine analogues, class code M), hallucinogenic amphetamine analogues (3,4-methylenedioxyamphetamine analogues, class code T), psychedelic amphetamine analogue (2,5-dimethoxyamphetamine analogues, class code P) and psychedelic hallucinogenic amphetamine analogue (3,4,5-trimethoxyamphetamines, class code TMAs). Ephedrine analogues are also often abused for their stimulant pharmacological effect, as their molecular structures are very similar to stimulant amphetamines M. For the same reason, they are frequently used as precursors in the clandestine production of ATS. In consequence, the class of ephedrine analogues has also been modeled as a class of positives(class code E). The rest of the precursors cannot be modeled as a class of compounds, due to the important differences in their molecular structures. Consequently, if their individual identity cannot be assigned by the identification

module, they are classified by the detection module as “negatives” (class code N), meaning that they are *not* ATS compounds.

Two versions of the expert systems have been developed, one for the spectral window specific to the FRAUNHOFER IPM IR analyzer (6.5÷7.5 μm), and one for spectral domain in which the CREO analyzer operates (7.2÷8.6 μm). Both expert systems have been built as *Matlab 2012a* applications and converted to standalone executables.

The system (flowchart in **Fig. 29**) first calculates the integrated absorbance of the spectrum of the unknown (tested) compound, in order to eliminate the (background) spectra recorded at moments when no sample is present in the chromatographic column. If the integrated absorbance of the unknown is smaller than a predefined threshold, the system indicates that the recorded spectrum corresponds to “noise” and stops. If the spectrum has a larger integrated absorbance, it is then analyzed by the **identification module**. For this purpose, the spectrum is first normalized, and then preprocessed with a feature weight that acts as a selective amplifier.

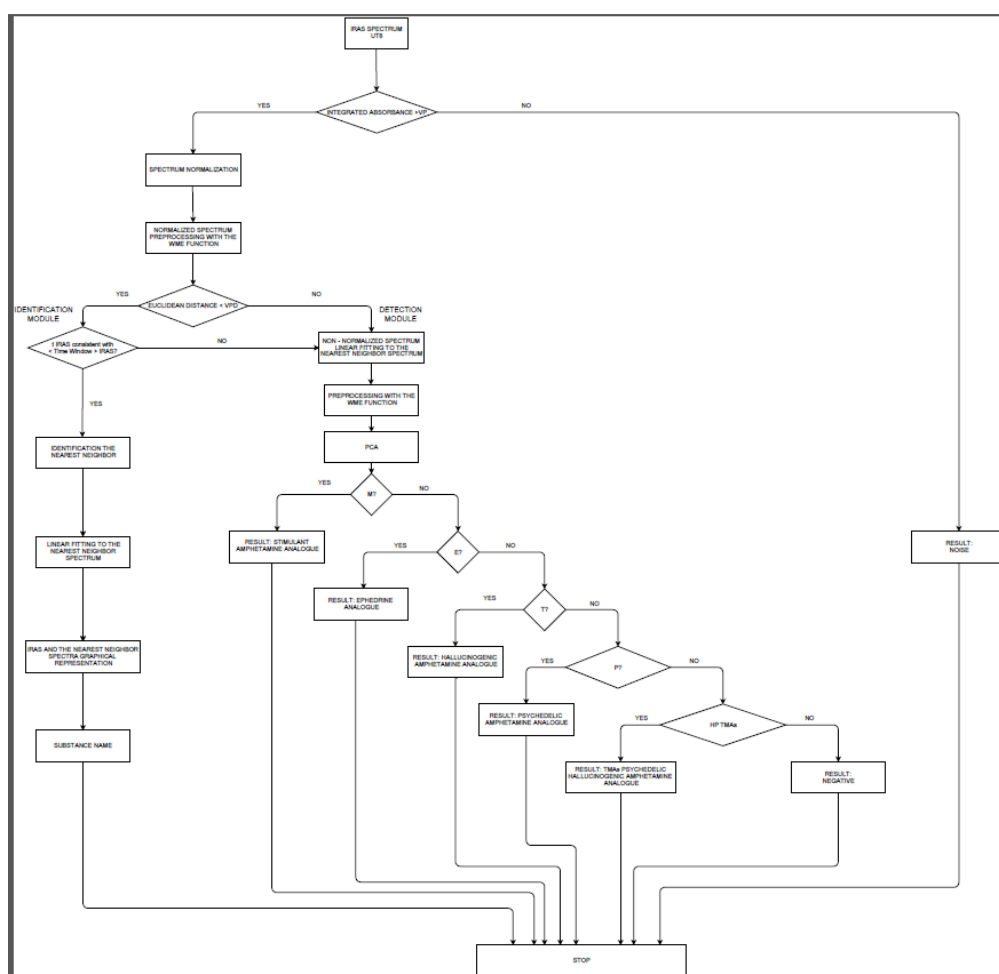


Fig. 29: Flow chart of the expert system built for the UT8 spectral window.

The Euclidian distance between the preprocessed normalized spectrum of the unknown and each spectrum included in the database (for which the known spectra have been processed in the same way as the unknown) is calculated and the best match is identified.

The Euclidian distance obtained for the best match is compared with a predefined threshold. This procedure is performed in order to detect the situations when the best match is significantly different from the tested IRAS spectrum, situation which appears when the spectrum of the unknown is not present in the database. If the distance is smaller than the threshold, the elution time t_{IRAS} is compared with known time windows obtained for the reference compounds. If the elution time belongs to one of these time windows, then the system identifies the unknown.

The tested spectrum is linearly fitted to the best match spectrum in order to compensate for differences in concentrations. Both spectra are then displayed graphically for a last visual inspection. This step is very useful especially in the case when the spectrum of the unknown is not present in the database. The user can more easily identify the cases of false identifications by comparing the spectrum of the unknown and of the best match. The identification process ends by indicating the name (*individual identity*) of the best match and the Euclidean distance between the spectrum of the tested compound and the spectrum of the best match.

If the Euclidian distance is larger than the predefined threshold, or if the elution time does not belong to any of the known time windows, it means that most probably the unknown substance is not present in the reference database. In this situation, the spectrum of the unknown is subjected to the **detection module** of the expert system, which assigns the *class identity* of the compound. The detection module operates as follows: the normalized spectrum is first preprocessed with the selective amplifier and then it is subjected to Principal Component Analysis (PCA). Its associated (PC2, PC1) scores are compared with those of the positive compounds forming the cluster of stimulant amphetamines (i.e. amphetamine analogues, class code M). If the associated point on the PC2 vs. PC1 score plot belongs to this cluster, then the detection system assigns this class identity to the tested spectrum. If not, the same procedure is then applied for the clusters formed by ephedrines (class code E), hallucinogenic amphetamines (i.e. 3,4-methylenedioxyamphetamine analogues, class code T), and psychedelic amphetamines (i.e. 2,5-dimethoxyamphetamine analogues, class code P) or psychedelic hallucinogenic amphetamines (i.e. TMAs, class code TMAs). If the tested spectrum belongs to one of the clusters, then the detection system displays the class identity of the compound and the process ends.

If it does not belong to any of these clusters, then the detection systems assigns to the unknown the class identity of "negative". We should emphasize that the detection module assigns the class identity "negative" to *any* non-amphetamine substance. In other words, the ATS precursors are correctly classified if they are assigned the class identity of "negative".

4. Impact Potential

4.1. Interactions with end users

The Impact Potential of the DIRAC sensor was analyzed with end users in the course of meetings and interviews organized at the start and at the end of the project.

A first meeting, held in September, 2010, was attended by representatives of:

- the Swiss Customs;
- the Belgian Federal Police;
- the German Federal Criminal Police (BKA).

Later in the course of the same year, a questionnaire about end users' needs and existing market gaps was circulated through Police and Customs departments across Europe. The questionnaire was answered by:

- the Customs Office of the Vienna airport, Austria;
- the Belgian Customs Investigation Group, Anti-Drugs (GAD) team;
- the Belgian Federal Judiciary Police Antwerp, Section Drugs;
- the Bulgarian Customs Agency, Sofia Airport Customs;
- the Malta Customs Enforcement Unit of the Malta Customs Department;
- the Swiss Customs Administration, Headquarters, Narcotic & Exploitation Unit, Bern.

The indications given at the meeting and the written replies to the questionnaire, were the base to formulate the key requirements of the DIRAC sensor prototype. These requirements are listed in the section 'Main Objectives and Project Context' of this Report.

A second meeting with the end users, held in October, 2013, was attended by representatives of:

- the Belgian Customs;
- the Swiss Customs;
- the Finnish Police.

Results of lab validation were presented to the audience together with general sensor characteristics and modes of use. The discussion that followed was centered around the following question: '*Does DIRAC fill any existing technical gap in the market of field-sensors used to detect illicit and controlled substances?*'

4.2. Does DIRAC fill any existing performance gap?

The question can be answered by looking at the market, that is currently dominated by the Ionscan (Smith Detection), and by other similar sensors based on Ion Mobility Spectrometry (IMS).

IMS sensors are extremely sensitive to banned ATS (with limits of detection better than 1 ng), but often fail to detect precursors. Also, they quickly saturate in the presence of 'big

traces' (from μg to mg), and experience high false alarm rates in 'dirty' and heavily contaminated environments (the typical situation in which goods are inspected).

For the detection of precursors, field-sensors other than IMS are today available, mostly based on Raman spectroscopy (for example TruScan, by Thermo Scientific). Raman sensors, however, lack the sensitivity to analyze real and even 'big' traces. Also, they are prone to fail if the substance fluoresces, or in the case of mixes. Indeed, examples are reported of precursors smuggled in liquid solutions, in which the solvent masks the Raman fingerprints of the target.

When compared with the field-sensors available today, the DIRAC sensor appears particularly attractive as it features:

- strong specificity to both ATS and precursors;
- ability to treat mixes and solutions (robustness);
- wide sensing range, centered in the 'big traces' domain, combined with a good resilience to contamination and poisoning.

These features make the sensor useful to Police officers in applications such as:

- rapid on site analysis of waste left on unauthorized ground, to determine if the waste is coming from a clandestine lab;
- rapid on site analysis of chemicals found in a clandestine lab after a raid, to determine what are the synthetic drugs produced;
- on site analysis of fumes outcoming of a (suspected) clandestine lab (or bomb factory).

In general, however, DIRAC better matches the needs of the Customs, particularly for the (off-line) screening of goods in transit through airports and harbors.

As a practical example, the Belgian Customs suggested that the sensor could find application in the cargo area of the Brussels National Airport, to control goods, and, in particular, to control the content of plastic or cardboard 'drums' of weight 20-50 Kg. Tons of precursors (and, today, especially APAAN) transit every year through the airport, smuggled in those drums. Control should possibly be completed without opening the drum. Since the lid and the external surface of the drum are generally heavily contaminated by big traces of the substance, these big traces could be collected on a swab and analyzed by the DIRAC sensor.

4.3. The DIRAC demo

Following the suggestion from representatives of the Belgian Customs, 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 (Belgium, Switzerland, Finland).

The Vapour Detection and the Identification Unit were set on two nearby desks (**Fig. 30**).



Fig. 30: DIRAC prototypes prepared for the final demo. Vapour Detection Unit on the left, Identification Unit on the right.

The Vapour Detection Unit was tested first, with vapour traces sampled from the headspace of small vials. Demonstration was carried out with samples of BMK, safrole, PMK, and negatives.

The Identification Unit was tested second, with liquid traces collected on a swab and thermally desorbed. The first sample was pure safrole, while the second was a solution of APAAN in ethanol.

All the positives were correctly identified. Negatives were correctly rejected.



Fig. 31: APAAN smuggled in a cardboard drum. The white powder is packed into two plastic bags (one inside the other). Particles are swabbed from the external bag.

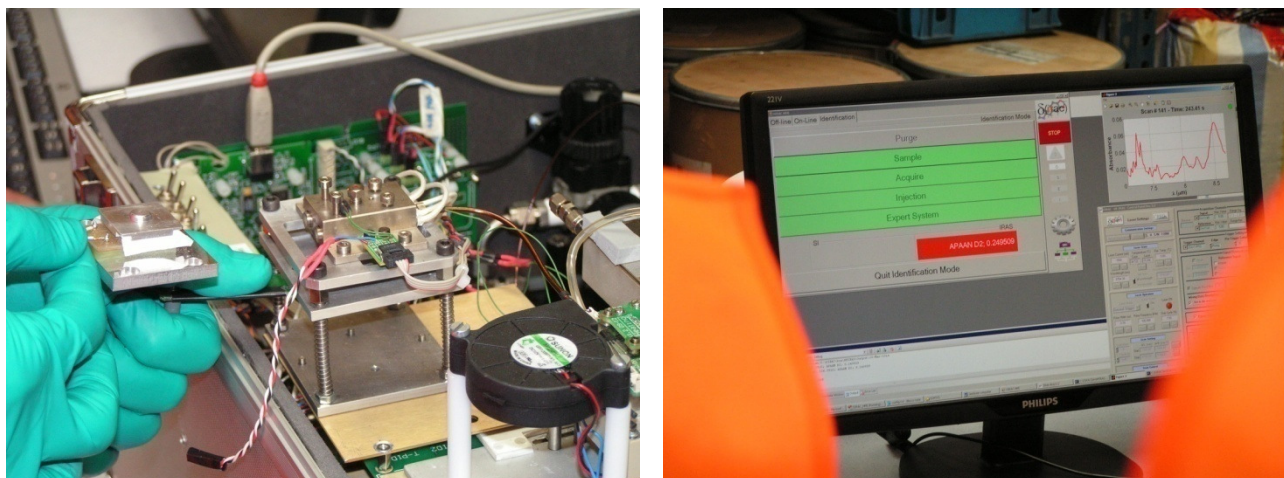


Fig. 32: DIRAC demonstration. Left: liquid traces of APAAN in ethanol, collected on a swab, are loaded into the thermal desorber; right: the system correctly recognizes the presence of APAAN in the sample.

Some of the photos taken at the event are shown in this report. Additional photos are available at this link: <http://www.fp7-dirac.eu/allegati/1dirac-final-demo-images.pdf>.

4.4. The way ahead

Despite its very promising performance characteristics, the DIRAC sensor is not yet mature for industrial prototyping and commercialization. New R&D activities appear necessary particularly to: a) expand detection and chemical range (to make it fit for a wider range of targets and applications), and, b) reduce size, power needs, response time (of outmost importance in any field-application).

This paragraph draws a few R&D axes along which the DIRAC sensor could evolve in the next 3 years from its current version 1.0, to a new version 2.0, with substantially enhanced sensing capabilities.

4.4.1. Improved sensing strategy, architecture, and design

Self-limiting sampling. Today, the sensor is resilient, but not immune to saturation and poisoning. A non-specific vapour-mass detector could be used as feed-back to the sampling cycle, to enable a self-limiting sampling strategy. When the vapour mass released into the VPC exceeds a threshold, the self-limiting system redirects vapours to exhausts, so avoiding to saturate and poison the VPC and the rest of the system. This would allow to extend the detection range upwards, from big traces to 'bulk'.

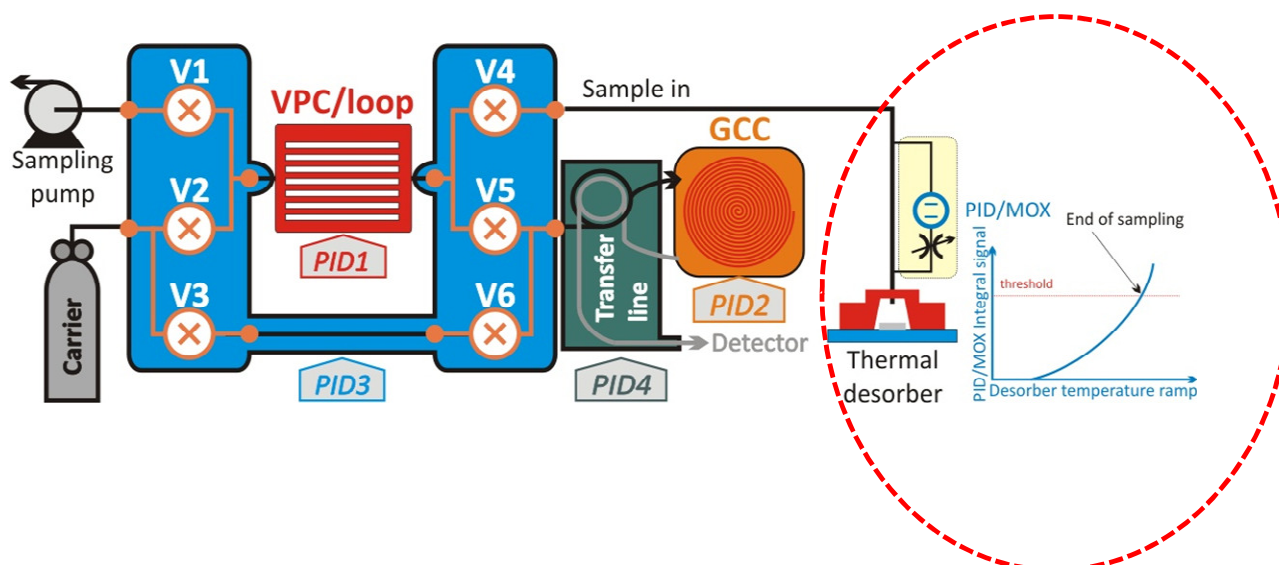


Fig. 33: DIRAC evolution and the self-limiting sampling strategy. Self limiting sampling would avoid saturation and poisoning of the VPC, so enabling analysis of 'larger' samples.

SI relocation and optimization. At the outlet of the GC column, the sample could be split and sent simultaneously to IRAS and SI, so avoiding delays and losses between the two detectors, improving sensitivity of the SI, and easing interpretation of results. Redesign of the SI detector, with miniaturized geometries and reduced dead-volumes, would allow easier integration into the sensing chain.

IRAS in the condensed phase. Downstream of the hollow fiber, the eluted peaks are still available for analysis. First, they could be condensed as separate thin film spots on an IR transparent rotating disk. Next, an IR beam from the laser source could be redirected onto the spot (through a second hollow fiber, for example), to acquire a second IR spectrum, this time in the condensed phase. Integration time could be as long as necessary for a verification and confirmation of the HF-IRAS result. Also, the analysis could take advantage of localized surface plasmons (Surface Enhanced IR Absorption Spectroscopy SEIRA) to increase sensitivity by orders of magnitude.

Re-design of critical components. Improved design of the GC column would allow to decrease substantially carrier gas flow and consumption (for field operation), reduce elution time, improve separation ability and flow matching with the IR analyzer. Cryogenic focusing would increase sensitivity.

4.4.2. Use of new components and sub-assemblies available off the shelf

Laser source. The laser is currently the dominating source of noise of the IR analyzer, with noise levels of around 0.01 absorbance units. As discussed in the section 'Main achievements and foreground' of this report, noise is dominated by the poor repeatability of the spectral scan. Additionally, the laser is expensive and relatively cumbersome, as it consists of a laser head plus an external control unit of the size of a shoebox. DIRAC 2.0 could take advantage of new QCL sources now available off the shelf. These new sources

have a wavelength repositioning speed that is fast enough to enable more accurate 'step and scan' operation. This is expected to improve substantially spectral repeatability and limits of detection. Furthermore, the new sources are more cost effective and compact, and cover a much larger tuning range (so improving detection and identification skills). In the near future, the advent of QCL dies integrated on a chip could further abate size and costs.

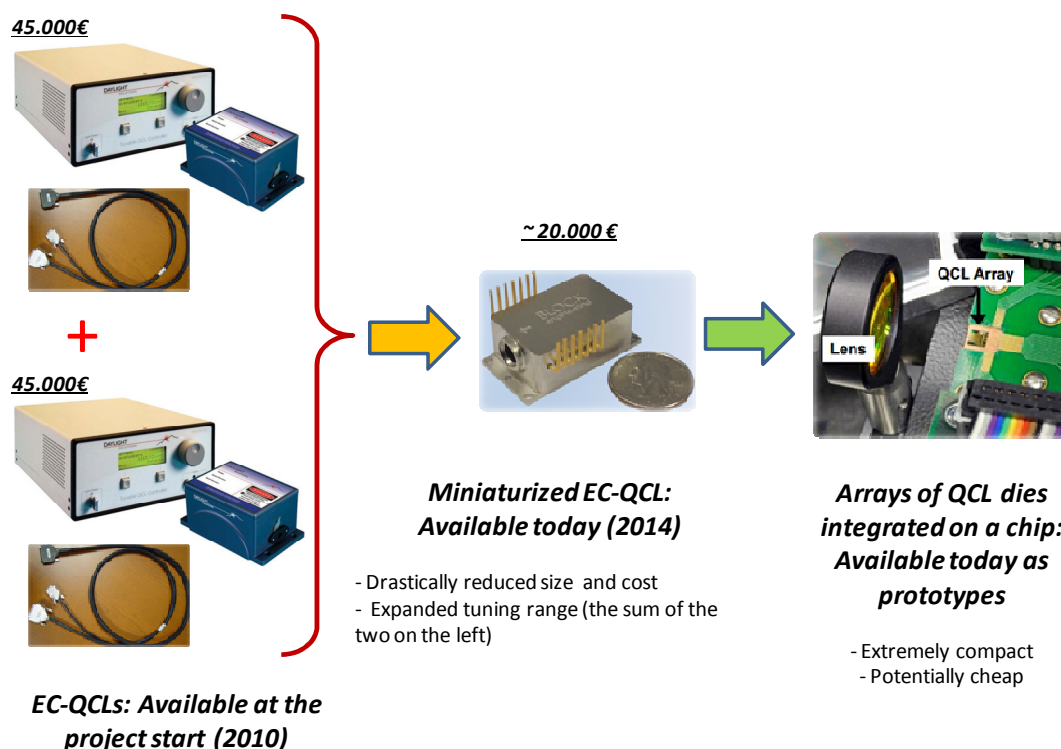


Fig. 34: DIRAC and the progress in QCL technology.

Thermal and fluidic components. Homemade thermal and fluidic components (as those used for thermal desorption) could be replaced by COTS used in GC instrumentation and readapted. This would guarantee tighter sealing, reduced mass losses, and increased sensitivity and chemical range.

4.4.3. New materials and microdevices

New coating materials for Hollow Fibers. Currently, the inner surface of the fiber is coated with a double layer of silver and silver iodide (to improve optical throughput). Since silver iodide softens at about 170°C, the fiber cannot be operated safely at temperatures in excess of 150°C. Silver iodide could be replaced by other, temperature resistant and IR transparent materials, to operate the fiber at temperatures up to 250-300°C. This would allow to treat heavier and sticky molecules, such as MDMA, cocaine, and heroin.

Microdevices for a highly integrated DIRAC sensor. Hollow Fibers could be replaced by Substrate Integrated Hollow Waveguides SIHWG, fabricated by silicon micromachining technology. The SIHWG chip would be extremely compact and easy to heat and control in

temperature. The next step would be to optically couple the SIHWG to second chip with an array of QCL dies (in replacement of the 'bulky' EC-QCL). As a final step, we envision a highly integrated system, with all its main sub-assemblies (VPC, GC, SIHWG-IRAS, SI) fabricated on silicon chips and assembled on a unique and extremely compact platform.

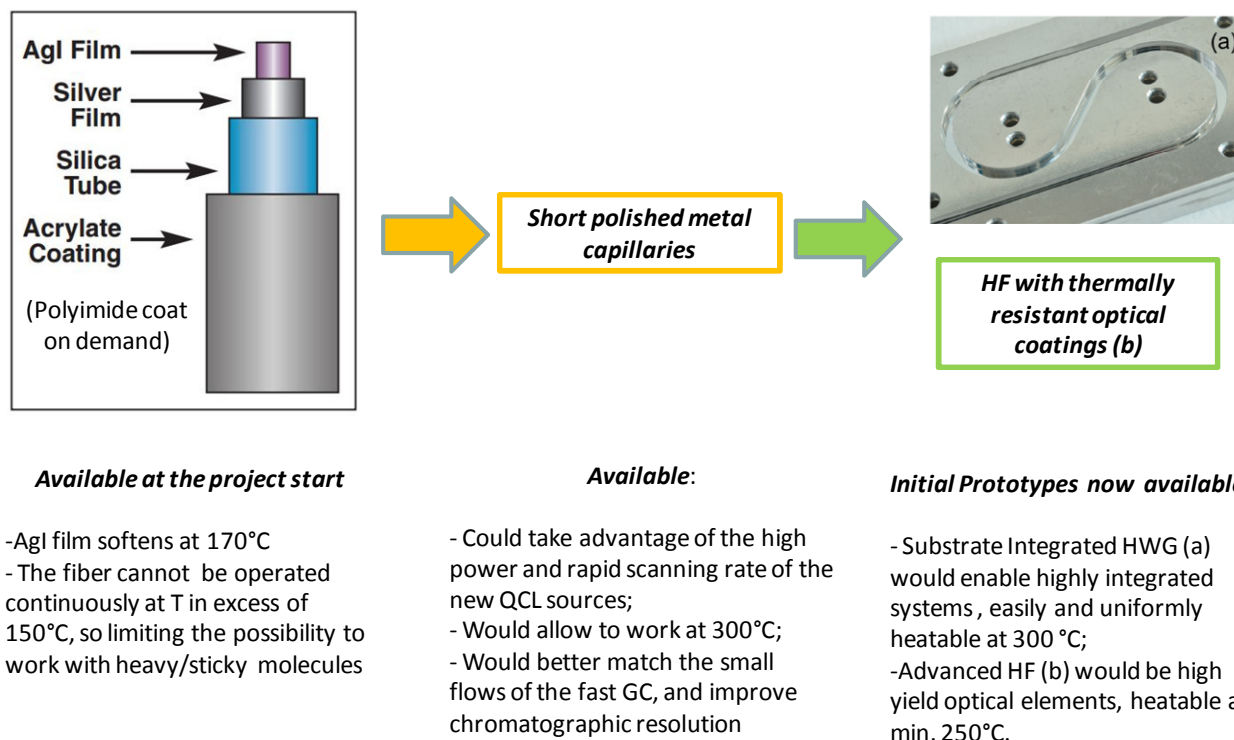


Fig. 35: DIRAC and the progress in IR hollow wave guiding

4.5. Conclusions

At a large extent, the DIRAC sensor meets the objectives and requirements that were fixed with the end users at the project start. Its performance characteristics seem to fill an existing gap in the market, by enabling reliable detection and identification of a wide range of target substances, particularly in the case of 'big traces', in 'dirty' environments, and in the presence of potential interferents and mixes. 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.

Many lessons have been learned in the course of the project, and new technologies and critical components have become available in the meantime. This progress allows to envision a possible rapid evolution of the DIRAC sensor, from its current version 1.0, to a new version 2.0, with superior sensing capabilities. In particular, we envision a new DIRAC sensor of drastically reduced size, weight and power consumption, wider chemical range (including non –ATS drugs and explosives), and able to analyze from real traces to bulk samples with unique identification skills.

5. Contacts

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FRAUNHOFER Fraunhofer Institute for Physical Measurement Techniques IPM http://www.ipm.fraunhofer.de/ PoC: armin.lambrecht@ipm.fraunhofer.de johannes.herbst@ipm.fraunhofer.de		Development of the second IR analyzer
CNR IMM Centro nazionale Ricerche Istituto per la Microelettronica e Microsistemi http://www.bo.imm.cnr.it PoC: cardinali@bo.imm.cnr.it zampolli@bo.imm.cnr.it		Development of the micro-fabricated VPC and GC modules
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<p>NBI National Bureau of Investigation http://www.poliisi.fi/ PoC: laura.aalberg@poliisi.fi</p>		<p><i>Review of target chemicals; support to the definition of sensing procedures</i></p>
<p>NICC Nationaal Instituut voor Criminalistiek en Criminologie http://www.nicc.fgov.be/ PoC: Filip.VanDurme@just.fgov.be</p>		<p><i>Review of end users' needs and final assessment of system performance; link between the consortium and the end users</i></p>
<p>INSTM Consorzio Interuniversitario nazionale per la Scienza e Tecnologia dei Materiali http://www.instm.it/ PoC: enrico.dalcanale@unipr.it</p>		<p><i>Development of the methods and materials for vapour and liquid phase pre-concentration</i></p>