Toward street detection of amphetamines

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A portable, advanced IR sensor in a hollow fiber matched to a silicon-micromachined fast gas chromatography column can analyze illegal stimulants and precursors with nanogram-level sensitivity.

It would be beneficial to detect amphetamine-type stimulants (ATS) and precursors not only in a forensic lab, but also via field sensors. These would be used by customs and law enforcement units in their daily fight against the trafficking and street distribution of illicit drugs. Such sensors would need to combine hand-portability, high sensitivity, fast response, low false alarm rates, and robustness, together with the ability to analyze substances with a range of different chemo-physical characteristics, and to establish chemical similarities between an unknown substance—potentially a new ATS molecule—and a known set of drugs banned or controlled by law.

Together, gas chromatography (GC) and IR absorption spectroscopy (IRAS) combine the chemical separation power of GC with the chemical identification ability associated with the analysis of molecular roto-vibrational transitions. GC-IRAS represents one of the most powerful techniques for the identification of amphetamines.[1] So far, however, GC-IRAS has been implemented essentially as bench-top instrumentation for forensic applications[2] and 'bulk' analysis.

With 'DIRAC' funding from the European Commission,[3] we are developing a GC-IRAS sensor that features hand-portability and fast response, together with the ability to analyze both bulk and traces, with nanogram-level sensitivity.[4] Sensitivity is greatly improved by matching the high radiation and spectral resolving power of a tunable external cavity-quantum cascade laser (EC-QCL),[5] with the very small interrogation volume ($\sim 70\mu$l) of an IR hollow fiber (HF).[6] The HF-IRAS module is efficiently coupled to a silicon-micro-machined (SMM) device that pre-concentrates the vapors of interest, and separates
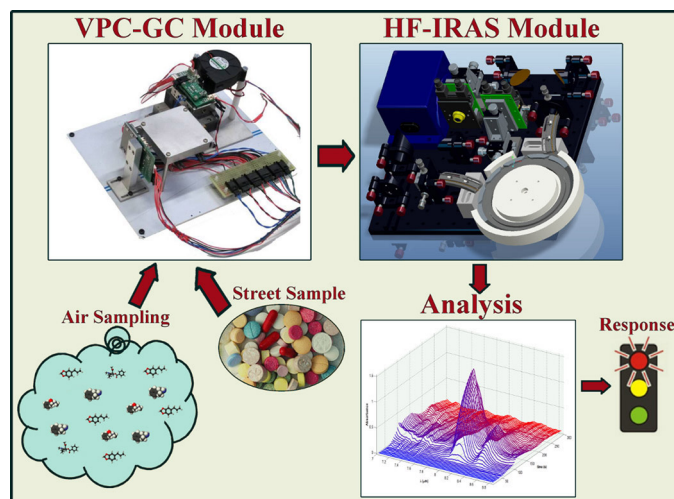

Figure 1. Sensor operational scheme. VPC–GC: Vapor phase preconcentrator gas chromatography. HF–IRAS: Hollow fiber infrared absorption spectroscopy.

vapor mixes with a short, fast, GC column with elution times of a few minutes.

The sensor treats and analyzes an unknown sample according to the general scheme shown in Figure 1. First, vapors are conveyed into an SMM vapor phase preconcentrator (VPC) by direct air sampling or by an external sampling unit that collects solid particles/liquids and releases thermally desorbed vapors into the VPC. The pre-concentration cartridge is filled with an innovative selective receptor[7] that retains our chemical targets. Next we heat the pre-concentration cartridge, which releases vapors into an SMM injection chip and fast GC column. The column separates the vapour mix into single-component chromatographic peaks that are fed into the HF-IRAS module. The IR radiation is guided through the hollow core of the fiber. Vapors entering the HF cause IR signal attenuation at wavelengths matching their roto-vibrational transitions. As vapors flow through the fiber, the laser scans its spectral tuning range, thus enabling the acquisition of an absorption spectrum.

We tested the system with ATS precursors, amphetamines, and mixes. Precursors without an amine group, such as safrole or piperonal can be easily vaporized and handled. Figure 2 shows the IR spectra measured for a 100ng sample of safrole. We estimate the limit of detection (LoD) as around 10ng or less.

Chemical targets with an amine group, such as ephedrines and amphetamines, are more difficult to analyze for two reasons. First, their absorption spectra lack the sharp peaks of safrole in the spectral range of our QCL. Second, they tend to stick at cold spots along the sensing chain, which translates into broadening and attenuation of chromatographic peaks. In the case of ephedrine, we estimated the LoD as around 130ng, one order of magnitude higher than for safrole.

In a real application, the sample might contain chemical targets mixed with interferents of different nature. Furthermore, the analysis of ATS salts—the usual form in which ATS are trafficked—might require some chemical treatment to deprotonate the ammonium salt and enable vaporization as a free amine. To test the performance against mixes, we started with mixes of different precursors. In fact, as precursors are chemically similar, their separation is already a challenging and meaningful objective. A mix of precursors—safrole, piperonal, and ephedrine—was evaporated and injected directly into the system (see Figure 3). The results show that the substances are well visible and resolved.

In conclusion, our sensor is already capable of analyzing ATS and precursors, as pure compounds and mixes, by sampling the air or by thermally desorbing liquids, solids, and solutions. LoDs are around 10ng for many precursors, and 10 times larger for targets containing an amine. As the lower sensitivity to amines is partly due to recondensations at fluidic joints, LoDs will im-

Figure 3. IR absorption spectra after the injection of a mix of safrole (∼600ng), piperonal (∼600ng) and Ephedrine (∼3μg). Inset: 2D sections corresponding to the transit of the specified substances.

prove once 'cold spots' are eliminated. While these results are exciting, the work ahead is still important. We need to assemble the hardware inside a suitable portable case, and conditions and procedures must be optimized. In addition, we need to implement an expert system to identify chemical targets and classify designer drugs. Last but not least, the system must be tested in the field.

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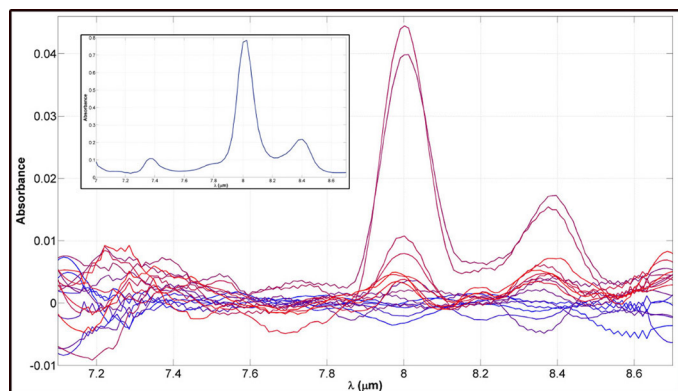and
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Figure 2. Infrared (IR) absorption spectra after the injection of 100ng safrole in methanol. Inset: A reference spectrum from the National Institute of Standards and Technology public database.[8]
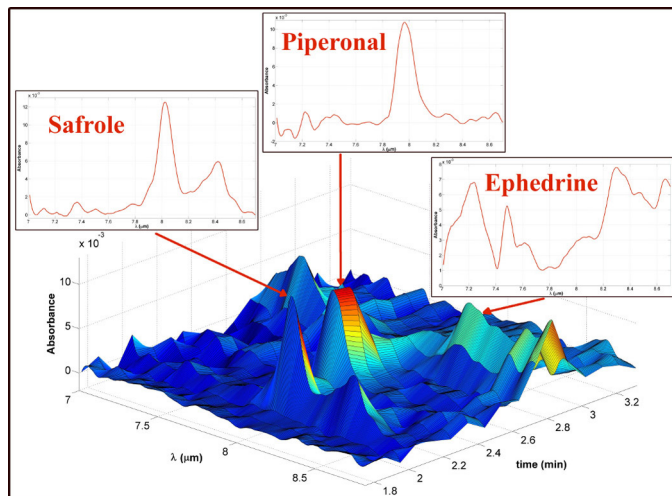
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