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IN-SITU AND STAND-OFF DETECTION OF RADIONUCLIDES BY LASER SPECTROSCOPY

A feasibility study

RT/2022/2/ENEA

ITALIAN NATIONAL AGENCY FOR NEW TECHNOLOGIES,
ENERGY AND SUSTAINABLE ECONOMIC DEVELOPMENT

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Abstract

The Diagnostics and Metrology Laboratory (FSN-TECFIS-DIM) of the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA) applied for years laser photoacoustic spectroscopy (LPAS) to food safety (in-situ) and differential absorption lidar (DIAL) to explosive detection and environmental monitoring (stand-off). Taking into account the recent renewed interest in nuclear energy, from one hand, and the long-lasting public concern on nuclear safety and security, from the other one, a preliminary feasibility study on iodine detection by LPAS and DIAL has been carried out. Its results are promising for methyl iodide, a volatile form of radioiodine, and pave the way for the development of in-situ and stand-off laser sensors for nuclear security. The Laboratory for Methods and Techniques for Nuclear Security, Traceability and Monitoring (FSN-SICNUC-TNMT) applies gamma spectroscopy for monitoring mobile radionuclides in the environment and could use the LPAS and DIAL techniques to support the evaluation and the study of the concentration of relevant radionuclides for nuclear safety and security.

Key words: *Laser spectroscopy, Photoacoustic technique, Atmospheric lidar, Radioactive iodine, Radionuclide detection, Nuclear safety and security.*

Riassunto

Il Laboratorio Diagnostiche e Metrologia (FSN-TECFIS-DIM) dell'Agenzia Nazionale per le Nuove Tecnologie, l'Energia e lo Sviluppo Economico Sostenibile (ENEA) ha applicato da anni la spettroscopia laser fotoacustica (LPAS) alla sicurezza alimentare (in situ) e il lidar ad assorbimento differenziale (DIAL) alla rilevazione di esplosivi e al monitoraggio ambientale (a distanza). Tenendo conto del recente rinnovato interesse per l'energia nucleare, da un lato, e della perdurante preoccupazione dell'opinione pubblica sulla sicurezza e protezione nucleare, dall'altro, è stato condotto uno studio di fattibilità preliminare sulla rilevazione di iodio mediante LPAS e DIAL. I suoi risultati sono promettenti per lo ioduro di metile, una forma volatile di radioiodio, e aprono la strada allo sviluppo di sensori laser in situ e a distanza per la sicurezza nucleare. Il Laboratorio di Metodi e Tecniche per la Sicurezza Nucleare, il Monitoraggio e la Tracciabilità (FSN-SICNUC-TNMT) applica la spettroscopia gamma per il monitoraggio di radionuclidi mobili nell'ambiente e potrebbe utilizzare le tecniche LPAS e DIAL per supportare la valutazione e lo studio della concentrazione di radionuclidi rilevanti per la sicurezza e protezione nucleare.

Parole chiave: Spettroscopia laser, Tecnica fotoacustica, Lidar atmosferico, Iodio radioattivo, Rilevazione di radionuclidi, Sicurezza e protezione nucleare.

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1. Introduction

Severe nuclear incidents are characterized by the release in the atmosphere of a plurality of radionuclides that, at different degrees, are harmful to humans. Among them, radioactive ^{131}I is one of the most dangerous because it accumulates readily in the thyroid and with a radioactive decay half-life of about eight days. Once released, radioactive iodine may form a variety of different species and each with different transport properties in the environment. Notably, most of the airborne ^{131}I from the Chernobyl incident was detected in several locations in the form of organic iodine compounds and with methyl iodide (CH_3I) as one of the most abundant species. In addition to health problems related to thyroid absorption, breathing methyl iodine can cause pulmonary edema with the buildup of fluids in the lungs and may also damage kidneys. Skin contact can cause a rash and formation of blisters. It follows that measuring gaseous radioactive CH_3I release in nuclear plant incidents is critical to assess their severity, to plan graded response plans and to make quicker and better-informed decisions to protect workers in the nuclear site and people off-site nearby areas affected by radioactive plume deposition on the ground.

Recently, it has been suggested to measure by laser spectroscopy methyl iodide for real-time monitoring of accidental releases of fission products [Chebbi 2020]. Indeed, methyl iodide, like many other organic compounds, has strong absorption lines in the infrared (IR) spectrum, making possible its detection both in-situ, by laser photoacoustic spectroscopy (LPAS) [Haisch 2012], and stand-off, by differential absorption lidar (DIAL) [Ismail 2015].

The Diagnostics and Metrology Laboratory (FSN-TECFIS-DIM) of the Italian National Agency for New Technologies, Energy and Sustainable Economic Development (ENEA) applied for years LPAS to food safety [Fiorani 2021a & 2021b] and DIAL to explosive detection [Fiorani 2013] and environmental monitoring [Fiorani 2015]. Having in mind that control authorities that routinely verify nuclear security will greatly benefit from portable and user-friendly systems, we undertook this preliminary feasibility study as a first step toward the development of field instruments.

2. State-of-the-art of radionuclide detection

Iodine has a fairly good fission yield (nearly 3%) and it is a dosimetrically significant radionuclide. Isotopes of iodine, notably ^{131}I, ^{135}I and ^{132}I (from the parent ^{132}Te), are produced and stay entrapped in considerable quantities in the fuel of nuclear reactors. Little amounts escape from fuel elements during normal operation but, due to retention in the fuel matrix and to the effective containment by the fuel cladding, the released quantities are very low and they are directly linked to cladding defects. Fuel elements are extracted from the reactor core at the end of their life cycle and they undergo chemical reprocessing to recover valuable materials such as uranium and plutonium. During reprocessing, removal of the cladding and dissolution of the fuel lead to the release of iodine (mainly the isotope ^{129}I) into gaseous and liquid wastes. Discharges of iodine resulting from reactor fault conditions can be relevant in quantity but are extremely rare. By using the retainment systems, the ^{131}I air concentrations are usually low in normal situations, far below the values measured after the Chernobyl and Fukushima accidents in 1987 and 2011, respectively. In the latter case, the concentration of ^{131}I reached 400 ppm 100 km from the nuclear power plant.

Another possible source of iodine radioisotopes releases could be an intentional nuclear test for military purposes. Since the signing of the Partial Test Ban Treaty in 1963 and before the Chernobyl accident, high values have been reported only once in northern Europe [Kauranen 1967]. The Comprehensive Nuclear-Test-Ban Treaty (CTBT) seeks to ban the nuclear arms race and proliferation by prohibiting nuclear test explosions in all environments. It has not yet entered into force as it awaits ratification by eight named nuclear-capable States. In the meantime, the Vienna-based Provisional Technical Secretariat (PTS) of the Comprehensive Nuclear-Test-Ban Treaty Organization (CTBTO) has been building and operating the International Monitoring System (IMS), a sensitive global verification system that aims to verify the treaty once it has entered into force. Out of 321 monitoring installations, 80 stations are designed for the detection of particulate radionuclides by measuring aerosol filters collected every 24 hours with gamma spectroscopy. The IMS aerosol systems have a minimum sample size of 12,000 m^3, such that, for a plume that covered the monitoring location for a full 24 hours, 1.2×10^5 fission debris atoms could be collected, leading to about 3600 ^{131}I atoms, being only a part as low as one-third of iodine in particulate forms [Aalseth 2009].

As ^{131}I decays in only 8 hours, it is a strong indicator of recent violations of CTBT, whereas ^{129}I, being long life, if dispersed in the atmosphere by nuclear weapons testing can still be

found at very low levels in the environment. In general, for forensic applications, concentrations of radioiodine above 20 ppb are regarded as significant.

Small amounts of ^{131}I can also occasionally occur in the vicinity of hospitals but in such cases, the air concentration is only a few $\mu Bq/m^3$ and is only locally detectable. Rarely, ^{131}I at very low levels is detected in large areas of northern Europe. In most cases, the sources of radioactive iodine detected during these events have not been traced.

All 37 isotopes of iodine chemically interact with the environment in the same manner (Figure 1): they can be easily dispersed in air, water or alcohol. Alternatively, they can recombine with other elements, entering the food chain. Iodine can also change directly from the solid state into the gas one. Due to this behavior, it is known as a very mobile radionuclide. In soil, however, it combines easily with organic materials and so it moves more slowly through the environment. All these forms tend to become airborne, attaching to the aerosols and being mobilized by the particulate air transport.

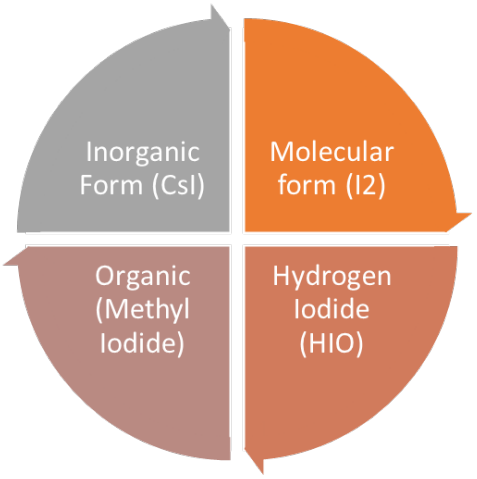


Figure 1. Chemical forms of iodine.

Monitoring of radioisotopes of iodine may be required for several reasons:

- in non-nuclear facilities, typically one radioisotope is used and it is evident which radioisotope is to be monitored,
- in nuclear plants, a range of iodine radioisotopes may be produced (Figure 2), with different half-lives and emissions, and workers need to be protected,
- iodine gets concentrated in the thyroid gland of the person exposed to it and delivers a radiation dose to the thyroid.

Iodine is generally trapped in a collection medium, like charcoal or zeolite, contained in a cartridge. Iodine cartridges are intended for the sampling of radioactive airborne iodine in either molecular (I_2) or organic (CH_3I) form.

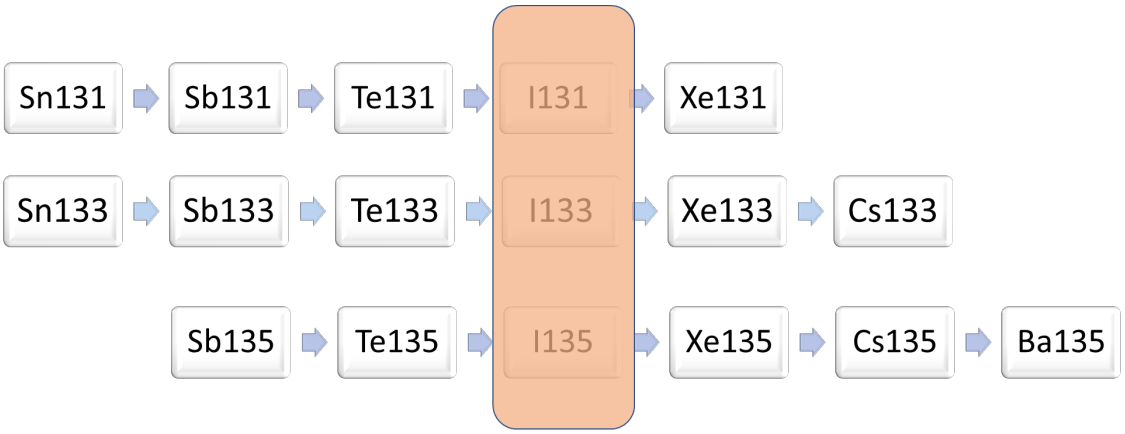
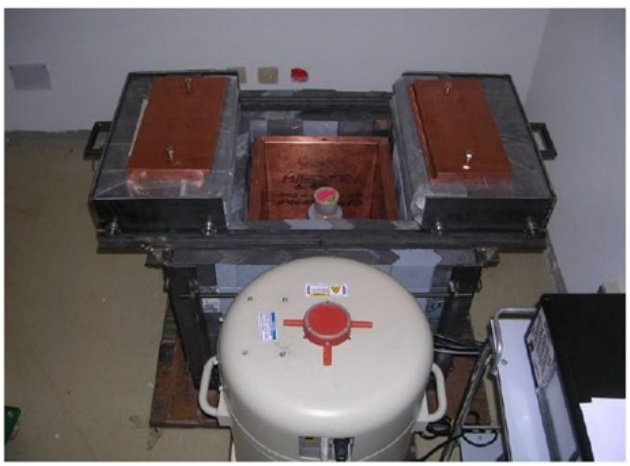


Figure 2. Decay chains of radioisotopes with half-lives longer than 1 second that are created in fission and/or are daughter products of radionuclides directly created in fission.

In order to improve the collection efficiency, charcoal is generally impregnated with potassium iodide and tri-ethylene diamine (TEDA) to obtain collection efficiency close to 100%. On the other side, silver zeolite is more selective for iodine as it absorbs less noble gases than charcoal. These systems can sample iodine both in molecular and organic form as they are the most frequent species attached to airborne particles.

Once trapped, the activity of iodine is measured by counting the gamma emission of its decay by gamma spectrometry (Figure 3), either simultaneously (real-time measurement) or in a laboratory, if a cumulative sampling has been envisioned.

If only ^{131}I is intended to be measured, the detector used can be a sodium iodide crystal (NaI) that provides excellent efficiency but lower resolution. If also other isotopes should be measured, the best detector is High Purity Germanium (HPGe) which ensures better resolution, even if losing some efficiency [Nava 2013].



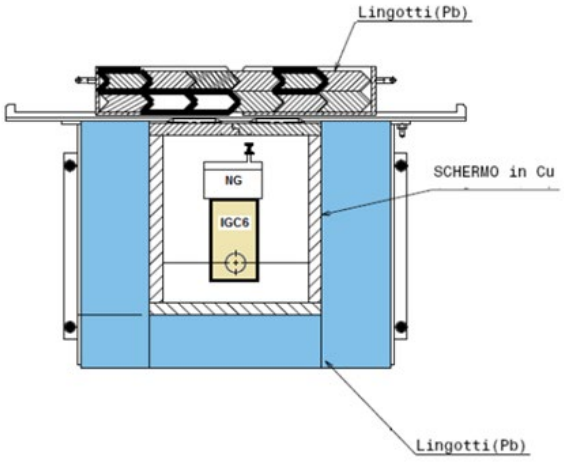


Figure 3. Low background system for gamma spectroscopy at the ENEA Noble Gas Laboratory (Brasimone Research Center, FSN-SICNUC-TNMT).

3. Methyl iodide absorption spectroscopy

The IR spectrum of methyl iodide is shown in Figure 4 [Linstrom 2022]. The most promising absorption lines are peaked at:

1. 885 cm^{-1} i.e. 11.30 μm,
2. 1259 cm^{-1} i.e. 7.94 μm,
3. 1409 cm^{-1} i.e. 7.10 μm,
4. 2981 cm^{-1} i.e. 3.35 μm.

Laser radiation at the first three peaks can be easily generated today by quantum cascade laser (QCL) [Faist 1994]. This solid-state source is compact, robust, tunable and has narrow linewidth. Its power is sufficient for in-situ measurements and can be modulated at acoustic frequencies for LPAS applications. In contrast, the first choice around 3 μm is a non-linear device like difference frequency mixing (DFM), optical parametric amplifier (OPA) and optical parametric oscillator (OPO) [Godard 2007]. The pulse duration and energy of those systems are highly suitable for DIAL technique, also in the case of long-distance stand-off detection.

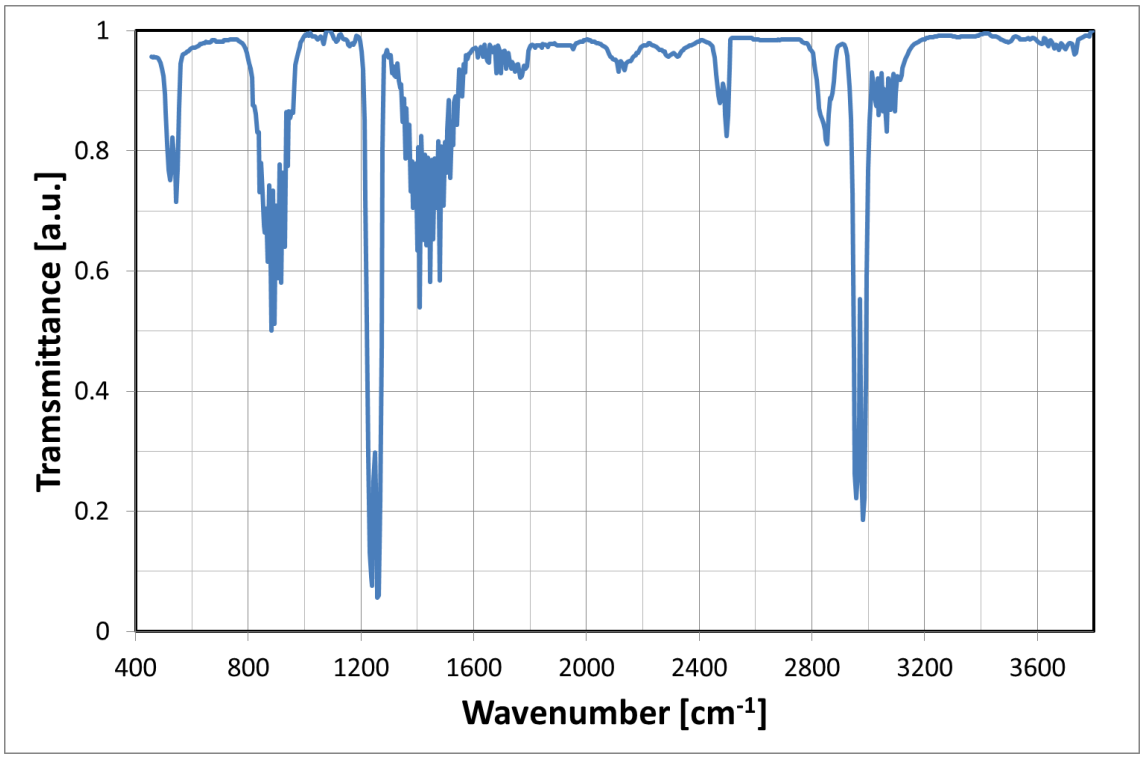


Figure 4. IR spectrum of methyl iodide.

4. In-situ detection of methyl iodide by laser photoacoustic spectroscopy

Recently, it has been suggested to measure methyl iodide by laser photoacoustic spectroscopy [Chebbi 2020]. The authors of that study developed two systems, the first one based on CO_2 laser and the second one on QCL, as described in Table 1.

Source	CO_2 laser	QCL
Power [mW]	200	2
Wavenumber [cm^{-1}]	893	957
Wavelength [µm]	11.20	10.45
Absorption strength (relative to 885 cm^{-1} i.e. 11.30 µm)	0.5	0.125
Limit of detection [ppm]	0.15	10,000

Table 1. Main characteristics of two systems for in-situ detection of methyl iodide by laser photoacoustic spectroscopy.

One of the difficulties encountered by the authors was that "QCL technology associated to this specific wavelength [11.30 µm] is not available on the market". Fortunately, the situation changed and FSN-TECFIS-DIM, in the framework of the application of LPAS to food safety, acquired a QCL emitting more than 100 mW at that wavelength, as shown in Figure 5.

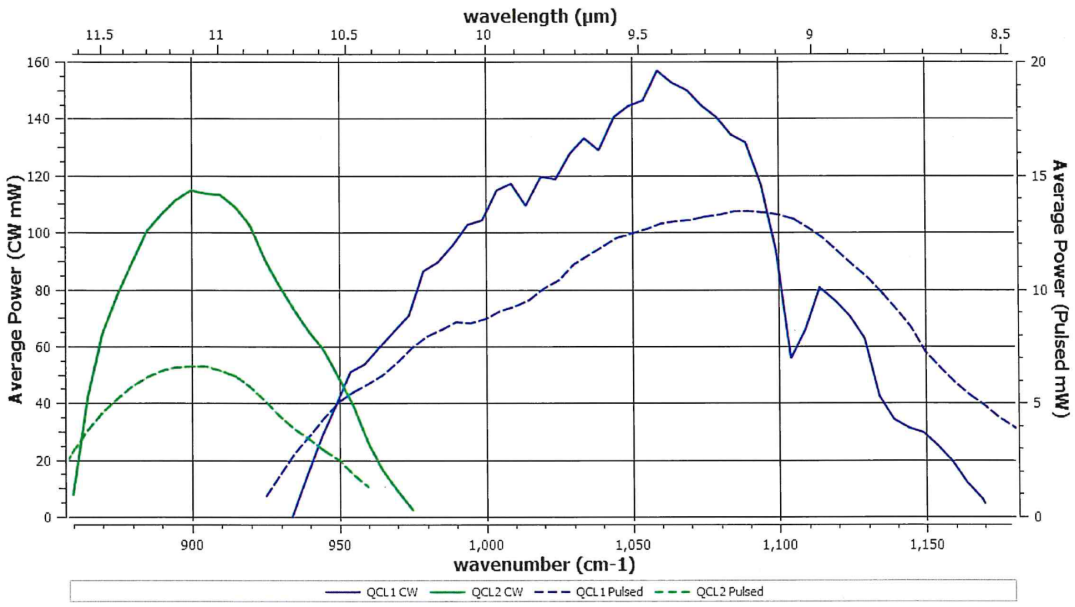


Figure 5. Emission spectrum of a QCL available at Frascati Research Center, FSN-TECFIS-DIM.

A QCL emitting more than 350 mW at 7.94 μm − where methyl iodide absorbs even strongly (Figure 4) − is also available at FSN-TECFIS-DIM, but this wavelength has been discarded by the authors for possible interference with the absorption of water vapor. Nevertheless, this point requires further study because it can not be excluded that the spectral purity of our laser source could allow the disentanglement of methyl iodide and water vapor. In a nutshell, although up to now LPAS has been applied at FSN-TECFIS-DIM to liquid and solid samples [Fiorani 2021a], it can be reasonably expected in the short-medium term to use this technique in the real-time and in-situ detection of methyl iodide vapors, hoping to develop in the medium-long term portable and battery-operated prototypes, as it already happened for food safety (Figure 6).

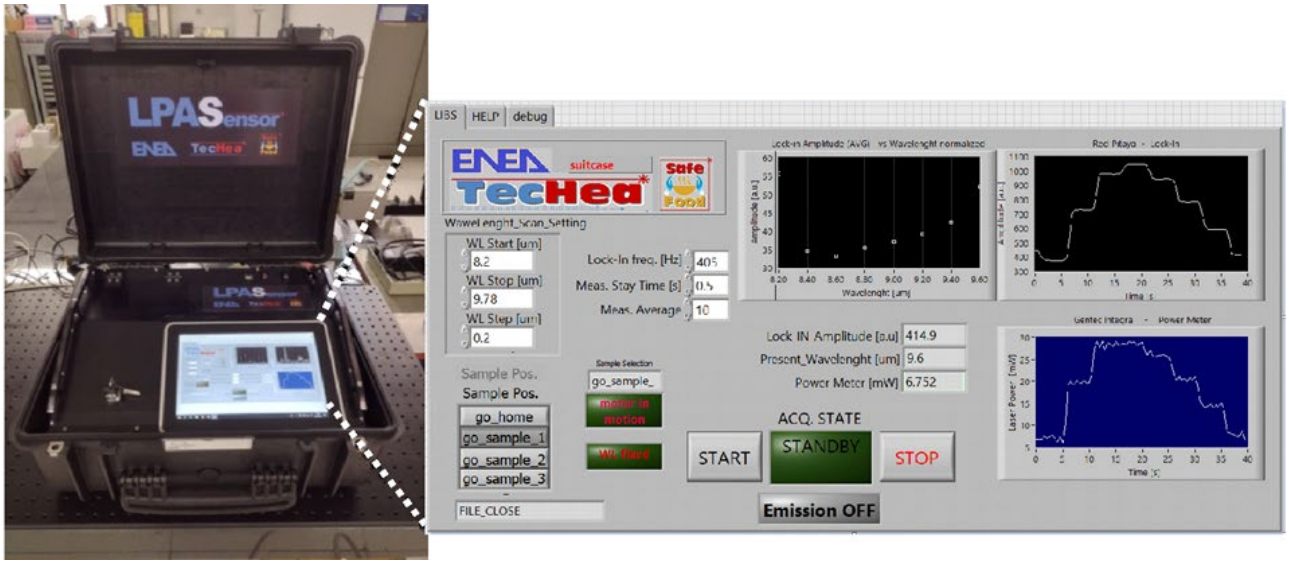


Figure 6. Portable and battery-operated LPAS sensor for food safety available at Frascati Research Center, FSN-TECFIS-DIM (patented [Fiorani 2021b]).

5. Stand-off detection of methyl iodide by differential absorption lidar

As already mentioned, DIAL − due to its requirement of long-distance ranging − relies on laser pulses characterized by high energy and short duration. Unfortunately, present sources in the "fingerprint region" (500 − 1500 cm^{-1}), including QCLs, are not suitable for this application and the methyl iodide absorption at 2981 cm^{-1} (3.35 μm) has to be selected, where, as noted earlier, a non-linear device − like DFM, OPA and OPO − is the first choice. In the last decade, FSN-TECFIS-DIM applied non-linear devices to explosive detection [Fiorani 2013] and environmental monitoring [Fiorani 2015] by DIAL.

The most interesting case is explosive detection because the OPO-based DIAL system transmitted exactly at 3−4 μm, where methyl iodide strongly absorbs. In that case, the target molecule was acetone, a well-known improvised explosive device (IED) precursor (Figure 7). Three field campaigns were carried out in Frascati (2013), Pratica di Mare (2014) and Grindsjön (2014). The limit of detection was 100 ppm at 50 m.

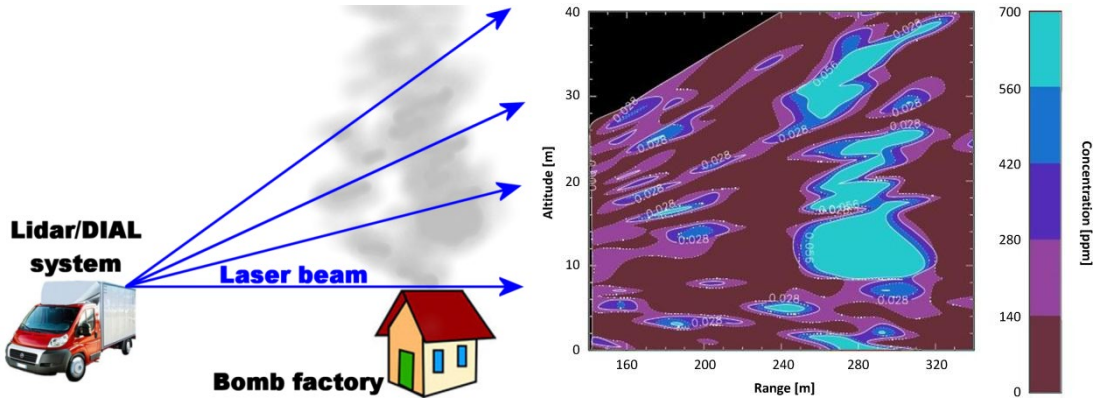


Figure 7. Principle of operation of the OPO-based DIAL for explosive detection. The system was on board a minivan firing an invisible laser beam towards the "bomb factory" (left), thus allowing the concentration of explosive and/or precursor compounds in its neighborhood to be retrieved (right). The laser beam scanned the plume at different elevations. The plume range is retrieved from the lidar (light detection and ranging) principle.

As far as environmental monitoring is concerned, a DFM/OPA-based DIAL transmitted at 2 μm and detected CO_2 in volcanic plumes (Figure 8). Three field campaigns were carried out in Pozzuoli Solfatara (2014), Stromboli Island (2015) and Mount Etna (2016).

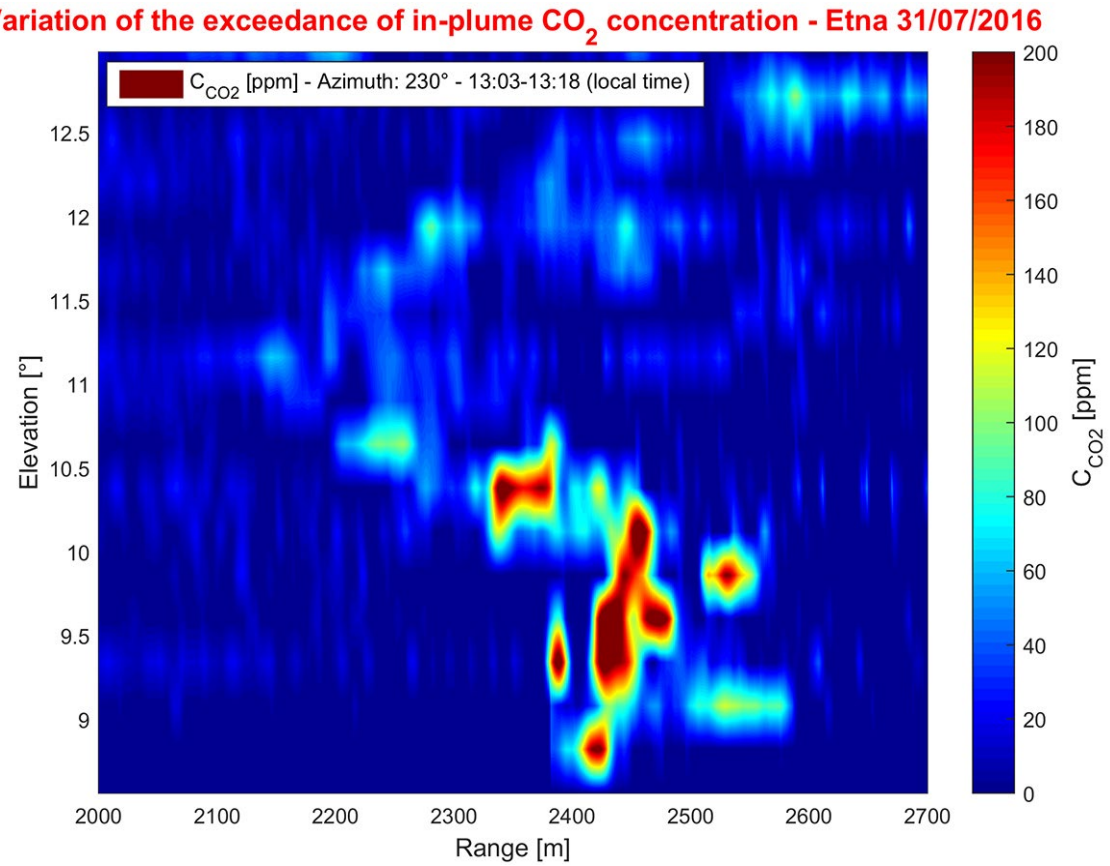


Figure 8. CO_2 concentration above the natural background level in the volcanic plume of Mount Etna measured by DIAL.

6. Conclusions

The experience gained at FSN-TECFIS-DIM in LPAS and DIAL indicates that both in-situ and stand-off detection of methyl iodide is feasible, although the limit of detection of the remote technique could be too high, at least for forensic applications. In-situ measurement of iodine by LPAS seems more promising also because DIAL systems are still heavy, bulky, complex and expensive.

Coupling total iodine measurements by both gamma spectroscopy and LPAS will allow better characterization of anomalous detections of iodine in the environment, for nuclear safety and security purposes.

Nevertheless, feasible does not mean easy. In order to reach this goal in the short-medium term, the following milestones should be achieved:

- Spectroscopic study of methyl iodide and possible interferents from existing databases (if any).
- Measurement of the absorption spectrum of methyl iodide and, if necessary, of the relevant interferents.
- Development of a photoacoustic cell for vapors.
- Realization of a laboratory prototype of an LPAS sensor for in-situ measurement of methyl iodide.
- Simultaneous measurements by in situ gamma spectroscopy and LPAS sensor and intercomparison of the results.

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