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*Original*

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## Development of miniaturised sensors for methane detection at trace levels for environmental monitoring applications

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### ABSTRACT

Methane (CH<sub>4</sub>) is the second most important greenhouse gas in the Earth's atmosphere. Anthropogenic emissions of CH<sub>4</sub> mainly come from the agricultural and energy sectors. The monitoring of CH<sub>4</sub> low-level emissions is fundamental to detect possible CH<sub>4</sub> leakages from industrial/energy plants, or from natural sources. The development and metrological characterisation of innovative sensors for detecting trace levels of CH<sub>4</sub> is challenging and promising. At INRiM a research activity on miniaturised sensors for CH<sub>4</sub> is ongoing, with support of Piemonte Orientale University "A. Avogadro" (UPO). The plasmonic amplification of the absorbance spectrum of CH<sub>4</sub> (surface-enhanced infra-red absorption - SEIRA) in the proximity of metallic microstructured components is exploited and different SEIRA platforms are under characterisation by means of Fourier transform infra-red spectroscopy. The experimental setup and some preliminary results concerning the development of gas-trapping porous organic frameworks are presented in this work.

### 1. Introduction

Methane (CH<sub>4</sub>) represents the second most important greenhouse gas in the Earth's atmosphere, after carbon dioxide (CO<sub>2</sub>), accounting for about 16 % of global emissions. Its concentration has increased by about two-and-a-half times from the pre-industrial age, reaching a value of 1927.35 ppb in September 2023 (global monthly mean) [1]. Anthropogenic emissions of CH<sub>4</sub> mainly come from the agricultural sector, responsible for around 1/4 of emissions, followed by the energy sector [2].

In 2021, in the framework of the EU Climate Law's target 2030, and as part of the proposals to deliver the European Green Deal, the European Union approved the "Methane Regulation" [3] aiming at the reduction of CH<sub>4</sub> emissions from the energy production sector. This represents the first-ever legislation of the EU to restrain CH<sub>4</sub> emissions in the energy sector.

In this framework, the monitoring of low-level CH<sub>4</sub> emissions is also fundamental to detect possible unwanted CH<sub>4</sub> leakages from industrial plants and faulty pipelines transporting natural gas, at concentrations close to ambient background levels or in ppb range which can sum up to tens of thousands of tons of emitted CH<sub>4</sub> per year if the leakage goes unnoticed [4]. The development and metrological characterisation of sensors for the detection of trace levels of CH<sub>4</sub> is of utmost importance both under the scientific and industrial points of view and the study of innovative sensors could be a promising approach. Other relevant areas of applications for low-concentration methane sensing devices include medical diagnosis of irritable bowel syndrome and similar conditions where traces of methane can be detected in the patient's breath [5] or efficiency control in chemical reactions such as plasmonic-driven conversion of CO<sub>2</sub> to hydrocarbons [6].

Many optical sensing technologies are based on the detection of infrared absorption bands of specific gas analytes, which can be filtered

for increased specificity. The optical gas sensing based on IR absorption is described by the Lambert-Beer law:

$$I = I_0 e^{-\alpha(c,\lambda)L}$$

where the intensity of the light incident on the gas medium is attenuated by an exponential factor depending on the absorption coefficient of the analyte and the optical path length. The IR absorption of gas analytes is typically associated with small cross sections entailing low absorbance intensities. To increase the absorbance and to be able to detect lower gas concentrations, the optical path length is often increased by using multipass cells which are often bulky and pose limitations in the transportation of the sensor.

Another approach to increase the absorbance of the gas medium in order to reach lower detection limits is by exploiting the physical phenomenon of surface-enhanced infrared absorption (SEIRA). SEIRA is a powerful analytical technique utilised in molecular spectroscopy to amplify the sensitivity of infrared spectroscopy for chemical, physical and biological sensing [7]. In SEIRA, molecules adsorbed on nano or microstructured metallic surfaces undergo significant enhancement in their infrared absorption signals, leading to improved detection limits and enhanced spectral resolution. This enhancement arises due to the localised surface plasmon resonance (LSPR) phenomenon, which intensifies the interaction between the incident infrared radiation and the molecular vibrations of the analyte. SEIRA enables the detection and characterisation of molecules with exceptional sensitivity, making it invaluable in various fields including materials science, catalysis, and biochemistry. In the field of gas sensing the development of SEIRA platforms is often limited by the volatility of the analyte, which cannot benefit from the electric field enhancement occurring in close proximity to metallic microstructures. Recently, some prototypes of SEIRA platforms for gas sensing have been proposed by introducing an "on-chip"

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porous metal-organic frameworks (MOFs) layer for gas preconcentration and trapping near plasmonic microstructures [8]. These results pave the way for the development of miniaturised portable gas sensors with low power consumption. The employment of organic porous layers, an alternative to costly and often toxic MOF synthesis, is interesting to push the development of on-chip gas trapping and sensing. The present work discusses the development of SEIRA-based sensing devices for low concentrations of CH<sub>4</sub> using organic micro porous aromatic frameworks (mPAF) as trapping layers. The discussion focuses on the development of a finite element method (FEM) computational model to solve Maxwell's equations to evaluate the best geometry of the plasmonic microstructures and the following clean-room fabrication processes. Additionally, the work focuses on the development of strategies for on-chip growth of organic hyper cross-linked polymers with proven gas storage capabilities [9] as alternatives to MOFs. Fourier transform infra-red (FTIR) spectroscopy is also discussed for the characterization of the sensors' capabilities in laboratory-controlled conditions, including the design and realisation of an *ad hoc* gas cell for the experimental tests of amplification of the CH<sub>4</sub> peaks on SEIRA substrates.

## 2. Methods and procedures

### 2.1. Structure of the project

The project MetPlaSM ("Methane Plasmonic Sensing and Metrology") aims to design, realise and characterise sensing devices exploiting SEIRA to amplify CH<sub>4</sub> absorbance spectrum. The project is mainly articulated in the following tasks:

- 1) Modelisation and simulation of the amplification of the electromagnetic field in the proximity of micro and nano plasmonic structures, with different dimensions and critical sizes;
- 2) Fabrication of metallic nanostructures, (e.g. Au, Ag) by means of electronic lithography on substrates transparent to IR radiation;
- 3) Realisation of sensing elements with different geometries based on the results of the simulations and realisation of porous structures for the gas trapping close to the nanostructured material;
- 4) Characterisation of the amplification properties of the plasmonic nanostructures with test molecules;
- 5) Finally, realisation of a measurement setup, for the sensor characterisation at different CH<sub>4</sub> concentration levels, and definition of a calibration strategy under controlled humidity and temperature conditions.

### 2.2. Finite element method modelling

The realisation of a SEIRA substrate requires the precise engineering of an array of metallic microstructures whose reflection or transmission windows match the vibrational frequency of CH<sub>4</sub> IR absorption bands and are accompanied by the onset of an enhanced electric field. To obtain a prediction of the proper dimensional parameter of the metallic array to support plasmonic enhancement we used a finite element method simulation using the proprietary software COMSOL Multiphysics with RF module to solve Maxwell's equations at the interaction of the incident IR radiation with the substrate.

The simulation involved a two-dimensional periodic structure consisting of a unit cell with a single grating element. We considered an electromagnetic plane wave both normally incident and with a 45° angle of incidence to the surface. We varied the wavelength in the range between 3100 nm and 3800 nm with a particular focus on the value of 3318 nm corresponding to a vibrational frequency of CH<sub>4</sub>. Periodic boundary conditions were applied to the unit cell to extend the domain to an infinite periodic structure. The unit cell comprises a silicon or glass substrate, on which a gold stripe with a fixed height of 40 nm was deposited. Initially, the grating was immersed in air. We conducted a parametric sweep, varying the stripe's width in the range between 900 nm and 2200 nm, and the pitch of the cell in the range between 2.6 μm and 4.2 μm. Subsequently, we introduced a medium around the gold stripe with a refractive index of 1.326 and we then compared the grating

optical behaviour and the field distribution near the resonance structures.

The model has been validated with a transmittance measurement in the optical range (500–800 nm) using a home-built setup schematised in Fig. 1. The intensity of the radiation transmitted by the sample is used to calculate the transmittance and to compare it with the computational values, reported in Fig. 1c.

### 2.3. Fabrication of metallic microstructures and realisation of the sensing elements

As discussed, the plasmonic amplification of the absorbance spectrum of CH<sub>4</sub> happens in the proximity of a metallic micro or nano-structured component located on transparent substrates and with different geometries engineered to match the vibrational frequency of the gaseous analyte infrared absorption peak.

In order to enhance the selectivity and the sensitivity of sensors based on this phenomenon, and to reach concentrations below 100 μmol/mol and hypothetically down to 5–10 μmol/mol, the model-driven fabrication of the microstructures is required. Since the FTIR setup, discussed in detail in Section 2.4, has a radiation beam with a diameter of approximately 1 cm, which cannot be focalised, it is necessary to extend the microstructure array across a minimum area of 1 cm<sup>2</sup>. This poses a constraint in the realisation of the metallic microstructure for which direct-writing laser lithography offers a versatile solution. This patterning method is analogous to optical lithography and has a limiting resolution of about 900 nm, but no mask is required, allowing to test multiple designs of the plasmonic surfaces. A negative pattern is lithographed on a photoresist layer spun on a glass substrate

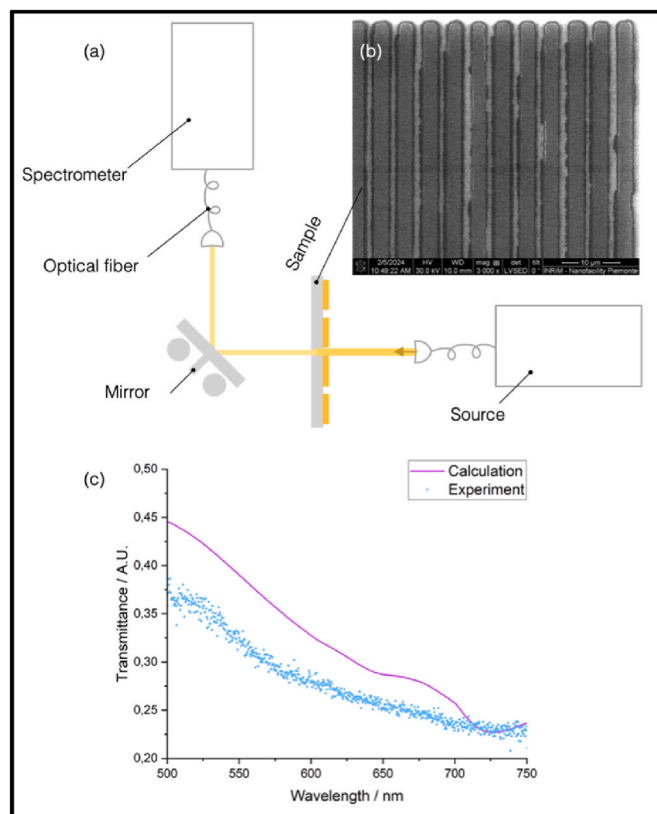


Fig. 1. (a) Schematic representation of the optical setup for the transmittance measurement in the wavelength range from 500 nm to 800 nm. (b) Low-vacuum SEM image of the array of gold microstrips on a glass substrate used for the model validation. (c) Plot of the calculated (light-blue dots) and experimental (purple solid line) transmittance spectrum showing a good agreement.

(Corning glass) coated with a 5 nm Ti and 40 nm Au layer. The pattern is then transferred to the metallic layer by using Ar ion plasma at 300 W. The final array of microstructures is characterised by scanning electron microscopy (SEM) to verify the dimensional and morphological features. The SEM imaging is performed under low-vacuum mode, with a residual pressure of 0.8 mbar, because the glass substrate is insulating. Several lithographic patterns are being tested depending on the electric field modelling results.

In parallel, the on-chip integration of fabrication also requires optimization. Two strategies are under study to encapsulate the sensitive elements in porous environments aiming at keeping the CH<sub>4</sub> in close contact with the metal microstructures [9]. The first framework is ZIF-8, a zeolitic imidazolate framework, commercially available at Merck as Basolite Z1200. This is being deposited on gold-coated substrates by previously functionalising the surface with a thiophenol self-assembled monolayer (SAM) to build active sites for the MOF crystals to nucleate. ZIF-8 has previously been reported as a good solution for CH<sub>4</sub> or CO<sub>2</sub> preconcentration near plasmonic microstructures [10]. A second framework is mPAF, also referred to as hyper cross-linked polymer, being synthesised directly on the gold-coated chips. These polymers have been previously tested for gas storage applications as pressed powders [9], so developing a strategy for on-chip growth is essential. The first polymeric layers have been grown on gold as shown in Fig. 2. Several synthesis tests are running and different microstructured elements are being developed for testing in laboratory conditions, and to select the most suitable for integration in a portable device for CH<sub>4</sub> emission monitoring at low concentration levels.

#### 2.4. Measurement setup with an ad hoc gas cell for FTIR characterisation of the substrates

The FTIR spectrometer used is a Thermo Scientific Nicolet iS50, operating in the mid-IR range (400-4000 cm<sup>-1</sup>) and equipped with a mercury cadmium telluride (MCT) detector, refrigerated with liquid nitrogen, to enhance sensitivity.

The FTIR, shown in Fig. 3, is located in a glove box flushed with pure nitrogen (purity grade 6.0), to isolate it from the laboratory environment.

In Fig. 3 (right side), the gas cell realised at INRiM for the analysis of the enhancement of the CH<sub>4</sub> signal during the interaction with the metallic nanostructured components is shown.

This cell was realised in aluminium and was conceived with two sapphire windows transparent to the IR radiation, to allow the IR beam to pass through the cell and interact with the sample. A sample holder allows to alternatively analyse the blank or the sample and the samples can be mounted by removing the upper cover of the measurement cell. By mounting the cell on a slit it is possible to scan the sample surface or perform a rough alignment with the patterned microstructures. In Fig. 4, a schematic representation of the measurement cell is shown, with a sample located on the optical path of the IR radiation inside the FTIR spectrometer.

The CH<sub>4</sub> signal enhancement is monitored by focusing on the CH<sub>4</sub> peak at 3.318 μm (3014 cm<sup>-1</sup>) shown in Fig. 5.

The environmental conditions inside the glove box (temperature, relative humidity) are monitored during the measurement sequence by means of calibrated dataloggers (DeltaOhm, Italy) located inside the glovebox, to avoid interferences to the CH<sub>4</sub> absorption peaks, and to allow better measurement repeatability and reproducibility, for the subsequent calibration phase.

### 3. Conclusions

In the present paper, the realisation and preliminary tests for the realisation of miniaturised “on-chip” sensors for the gas monitoring field, to be applied to CH<sub>4</sub> detection at low and trace levels, were presented. The preliminary computational modelling phase for the

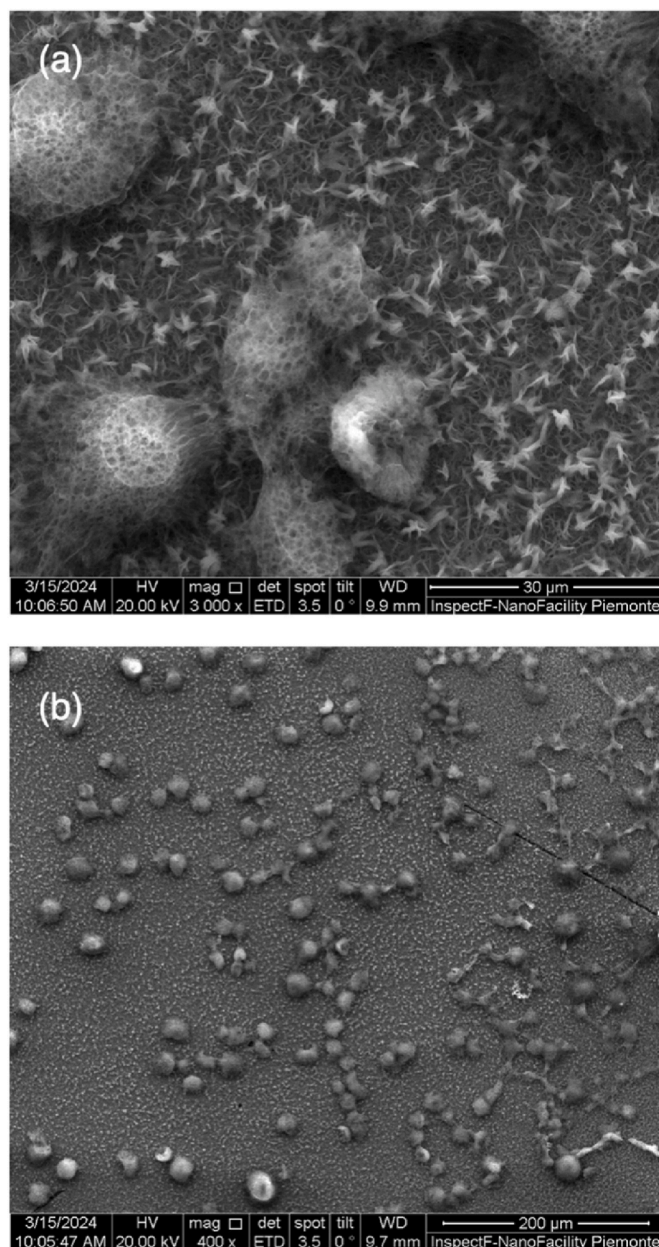


Fig. 2. (a) mPAF layer synthesised on a gold coated substrate. Two different porous structures are visible. (b) Low magnification SEM image of the same polymeric sample showing the homogeneous growth over a large area.

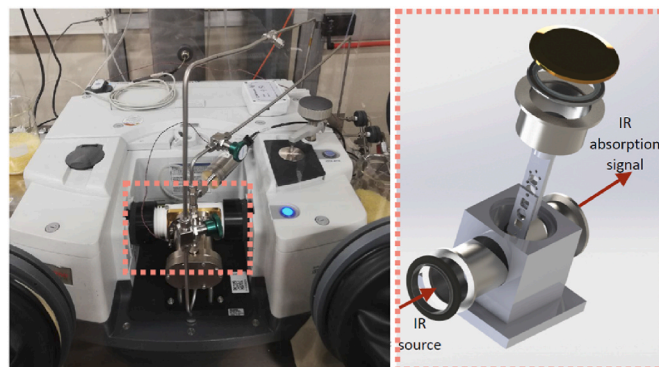


Fig. 3. The FTIR setup at INRiM (left side) and the gas cell (right side).

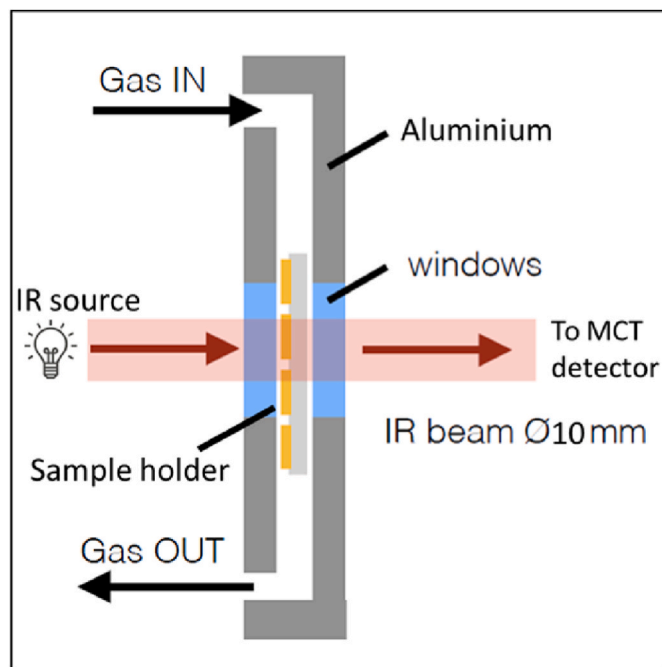


Fig. 4. Schematic representation of the measurement cell, with the sample located on the optical path of the FTIR spectrometer.

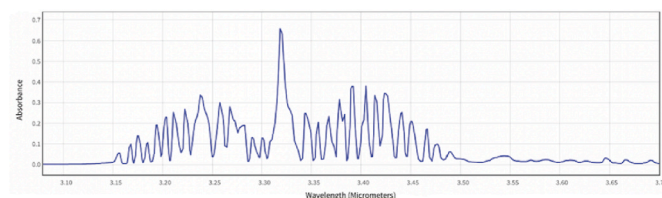


Fig. 5. CH<sub>4</sub> peak at 3.318  $\mu\text{m}$  in the mid-IR spectrum was chosen to monitor the enhancement of the signal due to the SEIRA effect.

realisation of the SEIRA substrates, the model-driven fabrication of the microstructures and the investigation of different strategies to encapsulate the sensitive elements in porous environments to keep the CH<sub>4</sub> in close contact with the metal microstructures were the first fundamental steps of the research. Future steps will require the use of FTIR spectroscopy for characterising the substrate performances in laboratory-controlled conditions, through an *ad hoc* gas cell for the experimental tests of amplification of the CH<sub>4</sub> peaks on SEIRA substrates. Following this characterization, the calibration of the FTIR will be carried out by using CH<sub>4</sub> mixtures at different amount fractions and the calibrated setup will be used for the CH<sub>4</sub> quantification, allowing the subsequent test of the miniaturised sensors for CH<sub>4</sub> measurements in the field.

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Francesca Rolle<sup>a,\*</sup>, Eleonora Cara<sup>a</sup>, Cecilia Romeo<sup>a</sup>, Matteo Fretto<sup>a</sup>, Angelo Angelini<sup>a</sup>, Vittorio Bonino<sup>a</sup>, Giorgio Gatti<sup>b</sup>, Maurizio Cossi<sup>b</sup>, Leonardo Marchese<sup>b</sup>, Francesca Durbiano<sup>a</sup>, Stefano Pavarelli<sup>a</sup>, Marco Santiano<sup>a</sup>, Michela Segà<sup>a</sup>

<sup>a</sup> Istituto Nazionale di Ricerca Metrologica, Torino, Italy  
<sup>b</sup> Università del Piemonte Orientale "A. Avogadro" - UPO, Italy

\* Corresponding author.

E-mail addresses: [f.rolle@inrim.it](mailto:f.rolle@inrim.it) (F. Rolle), [e.cara@inrim.it](mailto:e.cara@inrim.it) (E. Cara), [cecilia.romeo@student.uva.nl](mailto:cecilia.romeo@student.uva.nl) (C. Romeo), [m.fretto@inrim.it](mailto:m.fretto@inrim.it) (M. Fretto), [a.angelini@inrim.it](mailto:a.angelini@inrim.it) (A. Angelini), [v.bonino@inrim.it](mailto:v.bonino@inrim.it) (V. Bonino), [giorgio.gatti@uniupo.it](mailto:giorgio.gatti@uniupo.it) (G. Gatti), [maurizio.cossi@uniupo.it](mailto:maurizio.cossi@uniupo.it) (M. Cossi), [leonardo.marchese@uniupo.it](mailto:leonardo.marchese@uniupo.it) (L. Marchese), [f.durbiano@inrim.it](mailto:f.durbiano@inrim.it) (F. Durbiano), [s.pavarelli@inrim.it](mailto:s.pavarelli@inrim.it) (S. Pavarelli), [m.santiano@inrim.it](mailto:m.santiano@inrim.it) (M. Santiano), [m.sega@inrim.it](mailto:m.sega@inrim.it) (M. Segà).