High-sensitivity monitoring of VOCs in air via FTIR spectroscopy using a multipass gas cell setup

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Summary. — The exposure to volatile organic compounds (VOCs) constitutes a serious environmental health concern. Currently, different typologies of sensors are able to track the VOCs presence in workplaces, but they are limited in terms of chemical selectivity and sensitivity. Here, we apply Infrared (IR) spectroscopy combined to a multipass cell in order to extend the sensitivity of this technique down to the part per million (ppm) level. We calibrate the system for four compounds of interest and finally test the recognition performances on mixture of VOCs.

1. – Introduction

VOCs are toxic organic chemicals having low boiling temperature, therefore they can evaporate at room temperature being easily inhaled [1,2]. Their presence is widespread in human activities, *e.g.*, in industrial processes, building materials, plastics production, waste burning; they are also present in detergents, propellants, varnishes and solvents [3,4]. It is now well accepted that long exposure to these compounds may cause serious health risks and, in the worst cases, cancer [4,5]. Therefore, the possibility of

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monitoring the VOCs presence in atmosphere with high sensitivity is of primary importance in environmental studies. Currently used detection tools for VOCs, *e.g.*, gas sensors based on semiconductors [6-8], micromechanical resonant sensors [9] and Photo-Ionization Detectors (PIDs), have limited working range (from 10 to $100\,\mathrm{ppm}_v$) and insufficient specificity to chemical species. Gas chromatography and mass spectroscopy, on the other hand, are highly sensitive, but have the disadvantage to be laboratory-based technique. Terahertz (THz) and Infrared (IR) vibrational spectroscopies are efficient detection techniques, particularly in discriminating between different substances, thanks to their unique molecular absorption lines, with a very high spectral accuracy [10-12]. In order to identify a series of VOCs and estimate their concentrations, we used a FTIR spectrometer coupled to a multipass cell. It allows a significant improvement of measurement sensitivity thanks to the increase of optical pathlength. VOCs mixtures are also characterized to address the discriminating capability of the method when different VOCs are present simultaneously in the atmosphere.

2. – Materials and method

We studied four compounds: styrene (C_8H_8–Purity $\geq$ 99.0% Carlo Erba Reagents), acetone (C_3H_6O–Purity $\geq$ 99.5% Sigma Aldrich), ethanol (C_2H_6O–Purity $\geq$ 99.8% Sigma Aldrich) and isopropanol (C_3H_8O–Purity $\geq$ 99.9% Sigma Aldrich). A Bruker Vertex $70\,\mathrm{V}$ IR interferometer equipped with GEMINI Mars Multi-Pass Gas Cells $2\,\mathrm{L}/10\,\mathrm{M}$ (pathlength = $10\,\mathrm{m}$, volume = $2\,\mathrm{L}$) has been used. The cell is connected to an evaporation chamber ($0.6\,\mathrm{L}$ in volume), where a commercial Photo-Ionization Detector (PID) (TA-2100 Styrene Detector Mil-Ram Technology) is installed, for real-time monitoring of the evaporated VOC. Here, different amounts of liquid VOCs are introduced; when the equilibrium condition is reached, the valve connecting the chamber to the multipass gas cell is opened. This has been pre-evacuated with a turbomolecular and a diaphragm vacuum pump (Edwards T-Station 85) so that the gas to be analysed easily flows and distributes into the cell. Ten spectra are collected for each VOC concentration, at 64 scans, with spectral resolution of $2\,\mathrm{cm}^{-1}$ in the 400–$5000\,\mathrm{cm}^{-1}$ frequency range. Spectra analysis is performed using OPUS$^{\mathrm{TM}}$ 8.2 software.

3. – Results and discussions

Middle infrared (MIR) absorption spectra of the investigated VOCs are reported in fig. 1(a). Characteristic spectral features are recognized for each VOC and those showing the minimal spectral overlap are selected as a fingerprint. We chose: the peak at $910\,\mathrm{cm}^{-1}$ for styrene (CH out-of-plane bending in the aromatic ring [13,14]); for acetone the broad band at $1229\,\mathrm{cm}^{-1}$ (CC_2 antisymmetric stretching [14]); for ethanol the region between 1010–$1100\,\mathrm{cm}^{-1}$ (combination of CH_3 wagging, CCO antisymmetric stretching and CH_3 rocking [15]) while for isopropanol the peak at $953\,\mathrm{cm}^{-1}$ (CH_3 rocking [16]). Quantitative analysis is based on the Beer–Lambert equation $A(\nu) = lC\epsilon(\nu)$ [12] where $A(\nu)$ is the absorbance (adimensional) of the characteristic bands for each VOC, l is the optical path of the cell (cm), C the VOC concentration (ppm) and ϵ ($\mathrm{ppm}^{-1}\mathrm{cm}^{-1}$) the absorption coefficient; finally, ν is the frequency (cm^{-1}). We obtained the calibration curves for our VOCs by correlating the integrated absorbance over pathlength $A_i(\nu)$ of the characteristic VOC peak with the estimated ppm_v from the simultaneous PID readings. Data are linearly fitted with OriginPro$^{\mathrm{TM}}$ and the goodness of each fit is estimated through the root-mean-square error parameter (RMSE) (see fig. 1(b)). The slope
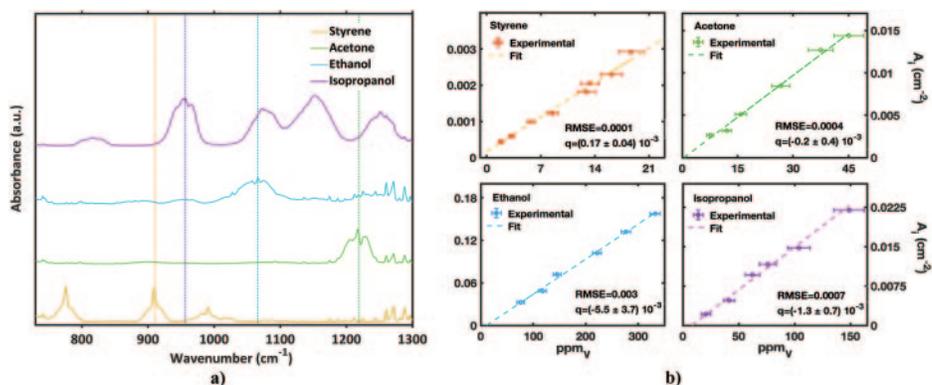
Fig. 1. – Comparison of IR absorbance spectra (a) and calibration curves (b) of styrene, acetone, ethanol and isopropanol in the spectral region between 750 and $1300\,\mathrm{cm}^{-1}$. Spectra in panel (a) have been shifted to provide a better comparison.

provides the absorption coefficient of the specific normal mode excited through IR radiation, whereas the intercept (q), likewise the integrated zero-concentration absorbance, is expected to approach zero. Comparing the calibration curves with the spectra of unknown VOCs concentrations, we were able to estimate their concentrations. Exploiting IR spectroscopy, we tested the detectability of gas compositions both on binary and ternary mixtures (acetone/ethanol, styrene/acetone, styrene/ethanol and one ternary mix of styrene/acetone/ethanol). These compounds have negligible chemical interaction, therefore the total absorbance of the gas mixture can be considered as the sum of the linear absorbances of individual compounds [17, 18]. When characteristic peaks of different VOCs appear clearly distinguishable and separate, we just integrated the subjacent area (colored region in fig. 2(a)) and from this, using the calibration curves, we obtained the concentration value in ppm_v. In the $840\text{--}920\,\mathrm{cm}^{-1}$ and $980\text{--}1010\,\mathrm{cm}^{-1}$ frequencies ranges, styrene and ethanol showed significant peak overlap, therefore, a fitting approach is necessary for mixtures containing both VOCs. The mixture spectrum X_{mix} can be
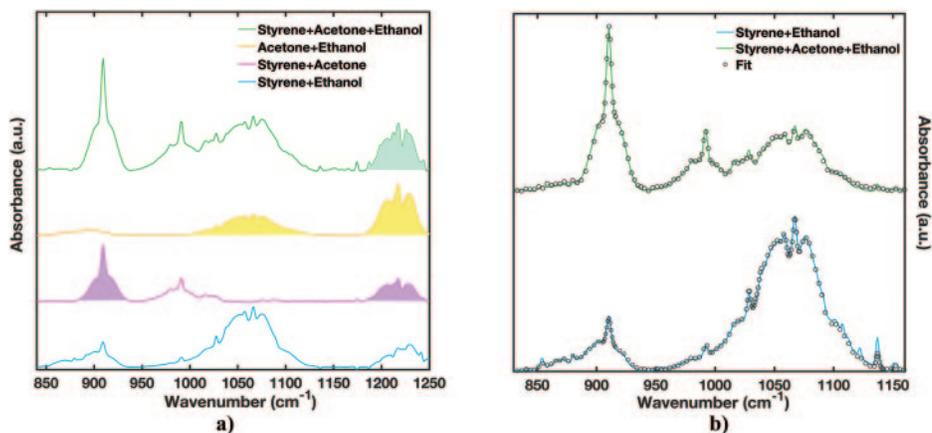
Fig. 2. – (a) Comparison of IR absorbance spectra of VOCs mixture. (b) Fit of styrene/ethanol and styrene/acetone/ethanol spectra in the region $850\text{--}1150\,\mathrm{cm}^{-1}$.

represented as the sum of singular spectra multiplied by a factor representing the VOC concentration: $X_{mix} = \alpha X_{ethanol} + \beta X_{styrene}$. By minimizing the difference between the experimental mixture spectrum and the linear combination of experimental single components, we obtained the fitted single components spectra and, referring to the calibration curves, we extrapolated the concentrations of each component. Fitting results are reported in fig. 2(b). The reliability of these estimated values is verified comparing the sum of the extrapolated concentrations of single VOCs with the initial PID reading of the whole mixture concentrations, confirming a good agreement in the detection of VOCs concentrations below current sensor system sensitivity. For example, the analysis on the styrene/ethanol/acetone mixture provides the extrapolation of the single concentration being respectively $C_{styr} = (6.6 \pm 0.5)\,\mathrm{ppm}_v$, $C_{eth} = (14.3 \pm 7.4)\,\mathrm{ppm}_v$ and $C_{acet} = (5.6 \pm 1.3)\,\mathrm{ppm}_v$.

4. – Conclusions

In this work, we applied IR spectroscopy for detecting a series of VOCs of environmental and occupational interest. We studied the feasibility of IR spectroscopy as an alternative, powerful tool for quantifying VOCs in air, taking the advantage of its sensitivity by using a multipass gas cell. We calibrated the technique for a set of compounds (styrene, acetone, ethanol and isopropanol) and extended the sensitivity to the part per million (ppm). In order to mimic real conditions present in indoor environments, binary and ternary VOCs mixtures were analyzed. The results point out the capability of our setup to discriminate the different chemical species which may be present simultaneously in the atmosphere, thanks to their specific spectral features. This study paves the way for the design of conceptually new highly-sensitive devices for environmental monitoring.

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