Optical-Feedback Cavity-Enhanced Absorption spectroscopy detects ppt traces of Formaldehyde for the validation of air plasma treatment system

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Non thermal plasma and especially Dielectric Barrier Discharge represent a very promising solution for air pollutant abatement at low concentration what is a key issue for indoor air treatment. Plasma/catalyst coupling is studied since many years but very few studies consider the treatment of molecule at a ppb level which is a realistic level for odours. The reason for that is the difficulty of detection of volatile organic compounds below ppm level. In this work we have developed a new detection system for formaldehyde which is a very good tracer of pollution level.
A Mid-Infrared Optical Feedback-Cavity Enhanced Absorption Spectroscopy (OF-CEAS) system has been implemented for highly sensitive trace gas detection and has been applied to the validation of the efficiency of a plasma/catalyst coupling device for formaldehyde destruction.

The growing interest for non thermal plasma (NTP) in environmental applications is due to their high chemical reactivity at a low energetic cost. The most advanced application of NTP for environment is the abatement of diluted pollutant, especially for indoor air treatment.

Dielectric Barrier Discharge (DBD) and Corona discharges in air are the most frequently used discharges for volatile organic compounds removal [1].

Plasma alone cannot insure to treat Volatile Organic Compounds (VOC) without any undesired by-products. Therefore plasma is very often coupled with adsorbent and/or catalytic materials. Several systems are already on the market in spite of the lack of validation of such systems at low concentration of pollutant. Indeed, odours usually correspond to VOC concentration below ppm level. The sensitivity of the diagnostics the most commonly used for studying the efficiency of plasma/catalyst coupling such as FTIR or gas chromatograph does not provide sensitivity high enough to validate the destruction of a pollutant with an initial concentration of less than 1 ppm. Therefore, we have developed a new system capable to detect formaldehyde in ppt range.

Formaldehyde is indeed a good indicator of indoor pollution level since it is among the major by-products of decomposition of many different pollutant categories. In addition, formaldehyde is carcinogen itself and released by many solvents.

The aim of this work was then to develop a sensor based on cavity enhance absorption spectroscopy with optical feedback in order to validate the efficiency of our plasma/catalyst coupled reactor for the destruction of VOCs at realistic concentration of pollutant.

The detection system is based on a continuous wave Distributed Feed Back Quantum Cascade Laser (DFB-QCL), realized at Thales-III-V lab [1]. This single mode laser emits at a wavelength of 5.65 μm at room temperature. It has been employed to match molecular fundamental vibration transitions of formaldehyde (H_2CO) , which possess in this spectral region significantly stronger absorption features compared to the near infrared.
OF-CEAS is a very sensitive technique, which combines absolute calibration performed by Cavity Ring Down Spectroscopy together with the fast response time of Cavity Enhanced Absorption Spectroscopy. It has been largely used until now, above all, in the near infrared region, in medical diagnosis [2], as well as in atmospheric gas analysis, and is being commercialized by a French company (AP2E).

After only one year of the first demonstration of QCL based OF-CEAS [3], we have built a compact and robust instrument capable to perform fast measurements of H_2CO, which will be applied both in plasma diagnostic and environmental (especially indoor) concentration monitoring of this specie.
The laser radiation, which can be tuned over about 7 cm^{-1} by temperature, is directly coupled to a high finesse (HF) V-shaped cavity, by means of an aspheric lens of 1.87 mm focal length. The particular shape of the HF cavity allows just the intra-cavity radiation to feed back to the laser and as a result to optically lock the laser frequency in rapid succession to each cavity mode in the range covered by a laser current scan. Spectral data points correspond to cavity modes, which are uniformly spaced and offer a spectral resolution of 150 MHz (0.005 cm^{-1}) for a 1m long V-shape cavity with a spectral definition in the 10 kHz range. In addition the high reflectivity of the mirrors provides an optical interaction path of about 10 km.

Working at a cell pressure of about 50 mbar, with a sample gas flow in the range of tens standard cubic centimeter (sccm), a minimum detectable absorption coefficient of 1×10^{-9} cm^{-1} was demonstrated in 100 ms of integration time (single laser scan) which for CH_2O corresponds to a detection limit of 120 ppt. A preliminary study of the Allan Variance of the measured data shows that averaging over 10 seconds yields an improvement of 10 times, leading to a detection limit down to the 10 ppt range.

Thanks to this very sensitive tool a packed bed like DBD reactor was evaluated in terms of formaldehyde destruction with different adsorbant/catalytic materials such as TiO2, Al2O3 as well as MnO2. The adsorbents are located inside the plasma reactor or downstream the discharge. The initial concentration of formaldehyde is varied from 100 ppb to 10 ppm and the destruction efficiency is studied with varying input energy into the plasma.

Conclusions

For the first time a detection system with sensitivity compatible with concentration level of odours has been developed and then used for the validation online of plasma/catalytic reactor. The good results obtained on formaldehyde destruction in ppb range represent an important step forward the development of really efficient indoor air treatment devices.

References

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