

Photoacoustic spectroscopy for fast and sensitive ammonia detection

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A photoacoustic (PA) spectrometer with H-type first longitudinal resonant cells for ammonia detection is developed. A new PA cell structure is designed to accelerate the drift velocity of the sample gas near the cell surface, so that the short response time at the flow rate of 100 sccm (standard cubic centimeter per minute) is achieved. The response time of 5 min and detection limit of 0.86 ppbv is reached for ammonia concentration measurement with a Teflon polytetrafluoroethylene (PTFE) cell. Further improvement could be expected when using a brass cell with a high quality Teflon fluorinated ethylene propylene (FEP) coating.

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Trace gas measurements with photoacoustic (PA) spectroscopy (PAS) provided highly sensitive and selective detection in continuous-flow mode^[1–3]. Attempts towards ammonia quantification based on PAS lately received attention due to its wide applications such as industrial process control, automotive exhaust analysis, environmental monitoring, and medical diagnostics^[4,5]. Unfortunately, ammonia is a notoriously adhesive molecule. The adsorption-desorption process caused by ammonia exchange between the cell surface and the gas phase in the PA cells always leads to errors in real time concentration measurements. Precautions are usually taken to eliminate the effect, primarily by carefully choosing materials of the cell surface, by heating the PA cells, and by applying the resonant PA cells operated in continuous-flow mode at high flow rates normally more than 500 sccm (standard cubic centimeter per minute)^[6–8]. However, experimentally it is not easy to guarantee the high flow rates especially in medical diagnostics for the pulmonary ventilation of an adult is 6000–8000 sccm and the available sample gas may be less than 1000 sccm^[9]. In this letter we introduce a photoacoustic spectroscopy with specially designed H-type PA cells for fast and sensitive ammonia detection at flow rate of 100 sccm.

An instrument layout of the PA measuring system is shown in Fig. 1. The laser source is based on a tunable

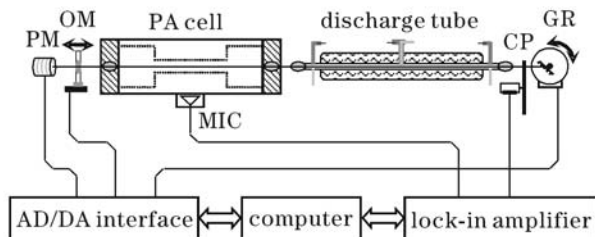


Fig. 1. Schematic diagram of the PAS for ammonia measurements. PM: power meter; OM: outcoupling mirror of CO₂ laser; MIC: microphone; CP: chopper; GR: grating for tuning the laser lines.

CO₂ waveguide laser that generates about 60 lines between 9.2 and 10.8 μm. The continuous wave (CW) laser beam is mechanically chopped and monitored by a thermopile power meter after partly passing through the out-coupling mirror. An H-type first longitudinal resonant PA cell is employed in the intra-cavity arrangement^[10]. Any absorbed radiation by the sample gas will, in general, be converted to thermal motion of the gas thus leading to a modulated pressure wave detected by the microphone mounted at the center of the PA cell. Then the PA signal is amplified and demodulated by a lock-in amplifier referenced by the chopper.

In ammonia monitoring, H-type first longitudinal resonant PA cells are used frequently^[4–8]. The sample gas firstly flows into a buffer located on the pressure node and then passes through the resonant cell as shown in Fig. 2(a). The flow buffers make it possible to minimize flow noise which increases proportionally to the flow rate. It is shown that H-type first longitudinal resonant PA cells achieve response time of several minutes at high flow rates (> 500 sccm).

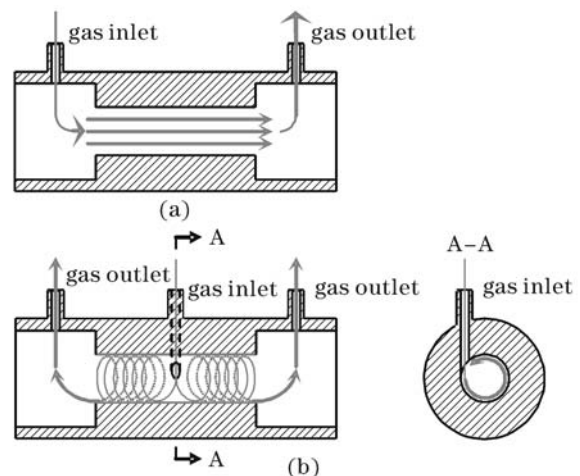


Fig. 2. Schematic description of the flow path in (a) the conventional H-type PA cell and (b) the specially designed one.

Recently, a model based on physically plausible assumptions was used to explain the contribution of high flow rates to fast response. The adsorption-desorption process in a tube can be described as^[7]

$$\frac{\partial c_g}{\partial t} = -\frac{v}{A(x)} \frac{\partial c_g}{\partial x} - \frac{dS}{dV} \frac{\partial c_s}{\partial t}, \quad (1)$$

where c_g is the ammonia concentration in the gas phase, c_s the surface coverage, v the flow rate of the gas along the tube, $A(x)$ the cross-sectional area, dV the infinitesimal volume, and dS the infinitesimal surface area of the tube. Equation (1) indicates that the change in volume density is determined by the flow of the gas and the exchange of molecules between the surface and the gas phase, while $\frac{\partial c_s}{\partial t}$ expresses the dynamic exchange given by adsorption and desorption rates^[11]

$$\frac{\partial c_s}{\partial t} = k_1 c_g (c_{s \max} - c_s) - k_2 c_s, \quad (2)$$

where $c_{s \max}$ is the maximum concentration of the surface coverage, and $k_{1,2}$ is the constant coefficient proportional to the drift velocity of the gas near the surface. Equation (2) indicates that one way to reduce the detrimental surface effects is to reduce the adsorption and desorption rates, the other is to make the exchange process reach equilibrium conditions in a short time. The latter is an indirect way working at higher adsorption and desorption rates: for a fast increase of the surface coverage, the desorption rate will also increase, whereas the effective exchange rate will decrease rapidly when the coverage reaches saturation conditions.

The high flow rates in H-type first longitudinal resonant PA cells result in high drift velocity of the gas near the cell surface which enhances the adsorption and desorption rates. Consequently the exchange process reaches equilibrium conditions rapidly. In this letter, the specially designed PA cell structure is used to accelerate the drift velocity and guarantees the response time of several minutes working at the flow rate of 100 sccm. Figure 2(b) gives the expected flow path in the PA cell. The sample gas is directed at a tangent into the gas inlet located at the center of the resonant cell and forced flowing in spiral along the surface. It can be estimated that the drift velocity of the gas near the cell surface is several times higher than that in the conventional PA cells for the same flow rate at the gas inlet while the flow path is much longer. Other improvements include the smaller S and effective V in result of direct injection of the sample gas without passing through the buffer volumes. Consequently, fast response may be achieved at lower flow rates.

In experiments, first longitudinal resonance of the PA cell occurred near 1631 Hz operating at normal temperature and pressure. The laser was amplitude modulated with a 50% duty cycle, yielding approximately 20 W of excitation power in the resonant cavity. Two lines were employed to interrogate ammonia. The large difference in absorption cross section at the neighboring 10R8 and the 10R10 CO₂ laser lines (20.5 atm⁻¹·cm⁻¹ at $\lambda = 10.334 \mu\text{m}$ and 0.542 atm⁻¹·cm⁻¹ at $\lambda = 10.318 \mu\text{m}$, respectively) allows one to correct background absorption in most cases^[12]. Through the 0.5-mm diameter

gas inlet, continuous flow was injected into the PA cell at 100 sccm and noise was not obvious under 170 sccm. By using mass flow controllers connected to a five-way switcher, the calibrated ammonia concentration of 10 ppmv was diluted with synthetic air down to the concentrations of ~ 100 ppbv, ~ 500 ppbv, ~ 1 ppmv, and ~ 5 ppmv, respectively. Teflon polytetrafluoroethylene (PTFE) tubing was chosen as gas supply line to minimize the effect of tubing wall adsorption.

The response time of the PA cell was investigated by suddenly changing the ammonia concentration with the five-way switch. Figure 3 shows the measured concentration variation with time for two different PA cells, a Teflon PTFE cell and a Teflon fluorinated ethylene propylene (FEP) coated brass cell. The PA signal rises rapidly at first and then reaches a steady level slowly after switching gas flow from the synthetic air to a selected mixture. The instantaneous rise of the PA signal is caused by the fast gas exchange for the small cell volume (diameter = 1 cm, length = 10 cm) at 100 sccm flow rate. The rather slow increase is attributed to the adsorption loss of ammonia to the cell walls, while the equilibrium time is minimized mainly by the special cell structure described above and also by choosing low surface energy materials (Teflon PTFE and Teflon FEP) for small $c_{s \max}$. In contrast to the Teflon PTFE cell's rise time $\tau_{90\%} \approx 5$ min, the Teflon FEP coated brass cell shows a lagged rising and falling. This might be caused by the defective Teflon FEP coating since the spray coating treatment usually contains a certain degree of porosity which results in the slow exchange of ammonia resident in crevices and pores.

After reaching a constant level, the signal measured with the Teflon PTFE cell was averaged for the time period as indicated in Fig. 4. The plot confirms the linearity of the sensor response to ammonia concentration. From it we can also estimate that the detection limit defined by the unit signal-to-noise ratio (SNR = 1) is 0.86 ppbv when measuring synthetic air for 30 min at the beginning of the experiments.

Comparing with the brass cell, a small decrease in the acoustic signal amplitude is observed for the Teflon PTFE cell (see Fig. 5). This could be explained as that the polymers deform easily under acoustic pressure and thus slightly reduce the cavity Q . Although the Teflon

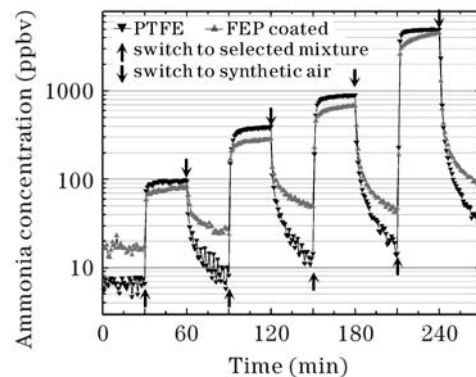


Fig. 3. Response of two PA cells made of Teflon PTFE and brass coated with Teflon FEP to different ammonia concentrations.

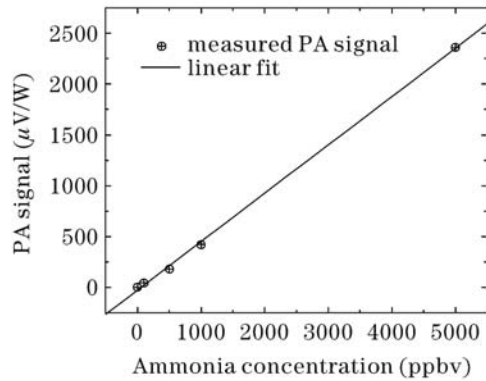


Fig. 4. Calibration curve of the Teflon PTFE cell demonstrates the linear dependence of the PA signal on the ammonia concentration.

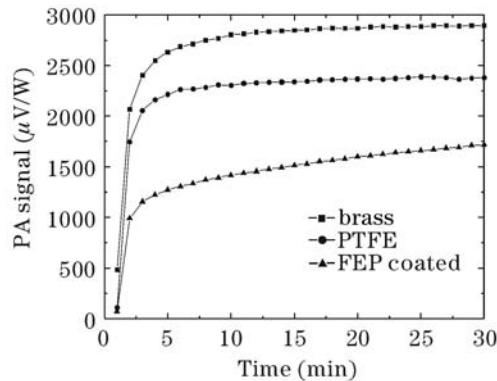


Fig. 5. Comparison of PA signals of 5-ppm ammonia for brass cell, Teflon PTFE cell, and Teflon FEP coated brass cell.

FEP coated brass cell is considered to be an improved one for its rigid substrate and smooth slick surface, the surface blemish generated in spray coating process makes the cavity Q to be the lowest.

In summary, a photoacoustic spectroscopy with specially designed H-type first longitudinal resonant PA cell is demonstrated. The ammonia exchange process reaches equilibrium conditions in a short time by accelerating the

gas drift velocity near the cell surface. The ammonia concentration measured with the Teflon PTFE cell indicates that the rise time $\tau_{90\%} \approx 5$ min at 100 sccm flow rate is achieved. Also a fast response PA cell with higher cavity Q is supposed by elaborately coating the brass cell with Teflon FEP in the future.

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