

# Determination of Ammonia Using Carbon Dioxide Laser Photoacoustic Spectroscopy Compared With Conventional Spectrophotometry\*

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The potential of carbon dioxide laser photoacoustic spectroscopy and the traditional Indophenol Blue colorimetric method for detecting gaseous ammonia have been compared. The results obtained with the two independent techniques are comparable in the range of concentrations studied.

**Keywords:** *Infrared spectroscopy of ammonia; colorimetric Indophenol Blue reaction; carbon dioxide laser photoacoustic spectroscopy; windowless resonant photoacoustic cell with automatic resonance tracking system; atmospheric pollution*

Nitrogen plays an active part in the acidification of soils, where it is mainly present as organic nitrogen. The main organic forms are the ammonium and very mobile nitrate ions. Under aerobic conditions, ammonia is readily converted into nitrate owing to the activity of *Nitrosomonas* and *Nitrobacter* bacteria.

Ammonia plays a significant role in the atmosphere, because it is the only highly soluble common base present. It can neutralize different acids; the ammonium ion,  $\text{NH}_4^+$ , is a frequently found constituent of atmospheric aerosols and fogs. Ammonia is produced by biological processes from organic nitrogen compounds and hence exists in both clean and polluted atmospheres. The Netherlands has a very intensive livestock farming industry and, therefore, the ammonia concentration in the air is the highest in Europe.

There are several methods of determining ammonia and  $\text{NH}_4^+$  in water, e.g., classical colorimetry, titration, ion-selective electrode methods and spectrofluorimetry. The most frequently encountered is the modified Indophenol Blue method, where ammonia is determined as an emerald green complex formed by the reaction of ammonia with salicylate and phenol-sodium hypochlorite solution, catalysed by sodium nitroprusside in a buffered alkaline medium of pH 12.8–13.<sup>1</sup>

The Indophenol Blue complex displays a broad absorption feature between 600 and 700 nm, with a maximum at 650 nm. A practical detection limit of  $<0.25 \text{ mmol m}^{-3}$  in the range 0–9.0  $\text{mg l}^{-1}$  of  $\text{NH}_4^+$  is obtained.<sup>2</sup>

Photoacoustic (PA) spectroscopy is a sensitive method for the measurement of low concentrations of gases and as such appears to be a very attractive technique for studying atmospheric pollution.<sup>3–8</sup> In recent years, numerous studies have demonstrated the feasibility of infrared laser PA spectroscopy for detecting ammonia in a variety of environmental and agricultural applications.<sup>9–15</sup>

Recently, a step-tunable carbon dioxide laser radiation source has been developed that, in conjunction with a windowless (open) resonant cell (with a high acoustic quality

factor), has been used for trace analysis of ambient ammonia.<sup>16</sup> The reason for undertaking this study, the results of which are described in this paper, was to investigate whether or not PA spectroscopy provides the same analytical results as the commonly recommended standard Indophenol Blue method.<sup>17</sup>

## Experimental

### Colorimetric Measurements

The actual measurements were carried out at 660 nm using the Technicon Auto-Analyser II continuous flow system.<sup>18</sup> The blank, reagents and samples were transported to the colorimeter by means of a peristaltic pump and the colour development took place at 37 °C. The cuvette of the colorimeter was 50 mm long and 1.5 mm in diameter.

The reagents for the colorimetric reaction were prepared following standard procedures.<sup>19</sup> Standard solutions of  $\text{NH}_4^+$  for calibration were prepared from  $(\text{NH}_4)_2\text{SO}_4$  (Merck, Darmstadt, Germany; *pro analysi*), sodium phosphate buffer (Merck, *pro analysi*) using a nitrogen-free NaOH solution (J. T. Baker, Phillipsburg, NJ, USA) and potassium sodium tartrate solution (Merck, *pro analysi*). The sodium salicylate-sodium nitroprusside solution (Merck, *pro analysi*) was kept in the dark and the sodium hypochlorite (Merck) solution was prepared fresh daily.

Before the colorimetric measurement, the ammonia was preconcentrated by bubbling the gaseous mixture through a dilute  $\text{H}_2\text{SO}_4$  solution in a midjet impinger in order to form ammonium sulphate. The absorbing solution was 0.0025  $\text{mol dm}^{-3}$   $\text{H}_2\text{SO}_4$  (Merck, *pro analysi*). Each midjet impinger held 50  $\text{cm}^3$  of the absorbing solution including the blank. The period of time for bubbling varied between 30 and 60 min depending on the ammonia concentration in the standard air sample. The volume of air sampled was recorded. After the collection of ammonia, the  $\text{NH}_4^+$  was determined by colorimetry using Indophenol Blue.

### Photoacoustic Measurements

A schematic diagram of the experimental set-up is shown in Fig. 1. The source used was a laboratory-made, tuned grating infrared carbon dioxide waveguide laser (L) operating on a

\* Presented at the XXVII Colloquium Spectroscopicum Internationale (CSI), Bergen, Norway, June 9–14, 1991.

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flowing mixture of helium, nitrogen and carbon dioxide (18 + 3 + 1) at a pressure of 75 mbar in the plasma tube. The power output was typically of the order of several watts on more than 80 discrete laser transitions. The laser was equipped with a dither frequency stabilization system (DFS), which was based on the piezo-bimorph plates mounted on the rear side of the grating. The laser power was monitored by a laboratory-made poly(vinylidene difluoride) Kynar foil pyroelectric detector (D) and a lock-in amplifier (LI 1) (Type 128A, Princeton Applied Research, Princeton, NJ, USA). A fraction of the radiation power was sampled by a beam-splitter (BS) in order to monitor the emitting laser transition on the carbon dioxide laser spectrum analyser (SA) (Optical Engineering, Santa Rosa, CA, USA).

The amplitude modulation (2 kHz consistently used throughout the experiment) was accomplished by means of a mechanical chopper (Ch) placed in front of the laser output mirror. The chopper frequency was maintained at a constant value at the given frequency by the phase-lock-loop-like feedback circuitry. The acoustic signals were detected by a condenser microphone (Mic) (Type 4176, Brüel and Kjær, Nærum, Denmark) placed at the pressure maximum of the first azimuthal mode of the cell. The sensitivity of the microphone was  $50 \text{ mV Pa}^{-1}$  under normal operating conditions. Following the pre-amplification (Type 2645, Brüel and Kjær) the signal was fed into a two-phase lock-in amplifier (LI 2) (Type 3961, Ithaco, Ithaca, NY, USA) equipped with a bandpass pre-amplifier with a quality factor of 5; the integration time was 10 s. The noise level achieved was 200 nV in all measurements. The filtered and amplified microphone signal was monitored on the oscilloscope. Amplitudes of all PA signals were registered on the chart recorder and normalized to the transmitted power of the laser.

#### Photoacoustic cell

The windowless cell (C) possesses some intrinsic advantages over the conventional cell design as neither the window material nor the gases adsorbed on the window surface could contribute to the generation of the unwanted signals.

The cell, manufactured from brass, is essentially a cylinder provided with two additional identical smaller (8 mm in diameter) tubes (one at each side of the cylinder).<sup>20</sup> Such tubes function as quarter wavelength acoustic impedance converters, minimizing the acoustic losses of the resonant chamber through the coupling hole. This approach leads to an almost complete acoustic blocking of the cell, enabling cell operation at a high quality factor ( $Q = \text{approximately } 400$ ).<sup>21</sup>

The acoustic amplification of the resonant chamber is a sensitive function of temperature and gas composition, as these influence the speed of sound and hence the resonance

frequency. In order to eliminate the signal changes due to the uncontrolled drifting of the resonance frequency of the cell, an electronic resonance frequency tracking system (RFT) capable of instantaneously matching the chopper modulation frequency to that of the cell has been developed and used.<sup>16</sup> This system consists of an acoustic oscillator [chamber, microphone, amplifier, piezo-sound generator (PSG)] and a coupling circuit to generate the appropriate external reference signal for the chopper controller. The frequency determining feedback element of the oscillator is the cell itself and the coupling circuit divides the oscillator frequency to the measuring acoustic frequency, *i.e.*, the chopper frequency.

#### Gas handling system

Gas mixtures were prepared from analytical-reagent grade gases and used without further purification. Very clean, 5.0 nitrogen (99.999%) (Hoekloos, Amsterdam, The Netherlands) was utilized as a diluting gas. A certified gaseous mixture of ammonia in nitrogen (100 vppm) (parts per million by volume) was provided by UCAR Speciality Gases (Union Carbide, Nieuw Vennep, The Netherlands). This mixture was further diluted dynamically in the separate buffer reservoir before being admitted into the PA cell. The total flow rate of the mixtures was kept below  $1 \text{ l min}^{-1}$  in order to reduce the acoustic noise generated by the streaming gas.<sup>22</sup> The flow of each gas was controlled by means of a calibrated flow meter (Model 1355, Sho-Rate, Brooks Instrument B.V., Veenendaal, The Netherlands). All measurements were carried out with the cell at atmospheric pressure.

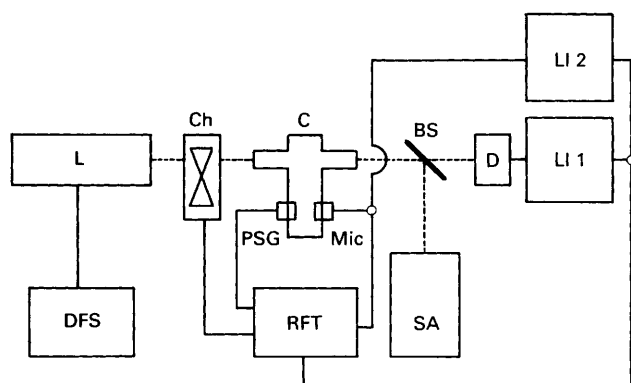
### Results and Discussion

The ammonia was measured using seven different samples within the concentration range 4.9–17.8 vppm. The samples were produced by dynamic dilution of the certified standard gas (100 vppm ammonia in nitrogen). The samples were measured using both the PA and colorimetric methods, and the analytical results were compared.

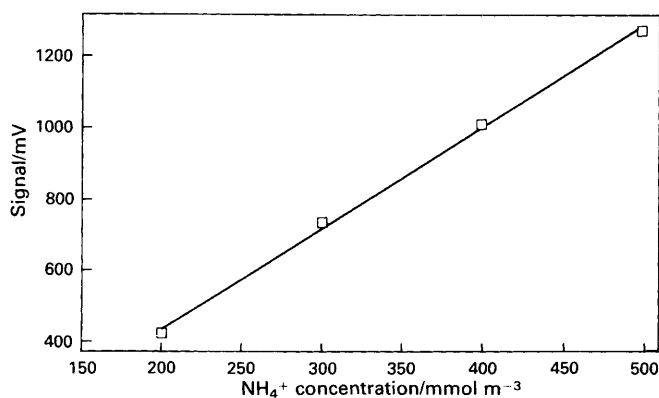
#### Colorimetric Measurements

The calibration graph of the  $\text{NH}_4^+$  complex was obtained using a series of standard samples, the concentrations of which varied from 200 to 500  $\text{mmol m}^{-3}$  of  $\text{NH}_4^+$ . The signal was corrected for noise and baseline drift. The calibration graph (Fig. 2) was found to be linear with a correlation coefficient of 0.999.

Occasionally, the degree of reaction between ammonia and  $\text{H}_2\text{SO}_4$  acid was controlled by adding another impinger in series with the first. The absorption times were varied between 45 and 75 min in order to obtain similar colorimetric responses. Both solutions were analysed using the Indophenol Blue method and the results are shown in Table 1.



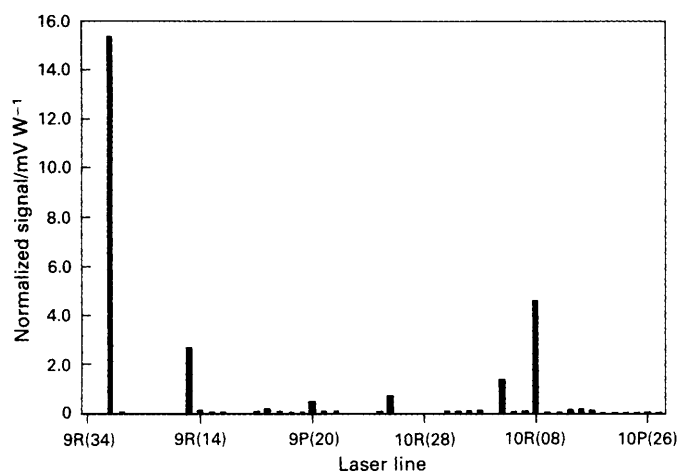
**Fig. 1** Experimental arrangement for  $\text{CO}_2$  laser PA spectroscopy in conjunction with a windowless cell: L,  $\text{CO}_2$  laser; DFS, dither frequency stabilization; Ch, chopper; C, windowless cell; PSG, piezo-sound generator; Mic, microphone; RFT, resonance frequency tracking system; BS, beam splitter; SA, spectrum analyser; D, PVDF light detector; and LI 1, LI 2, lock-in detectors



**Fig. 2** Calibration graph of the  $\text{NH}_4^+$  ion complex

**Table 1** Amount of ammonia absorbed in the first and second impingers

Sample	NH <sub>3</sub> in gas (vppm)	NH <sub>4</sub> <sup>+</sup> in solution/ mmol m <sup>-3</sup>		Absorption time/ min
		First impinger	Second impinger	
1	17.8	506.1	0.55	45
2	12.7	491.3	—	45
3	10.1	396.6	—	45
4	6.9	444.9	0.68	60
5	6.3	413.7	—	60
6	5.7	408.2	0.57	60
7	4.9	425.9	—	75

**Fig. 3** Photoacoustic spectrum of ammonia

### Photoacoustic Measurements

The PA absorption spectrum (9400–10600 nm) of 100 vppm ammonia in nitrogen was determined at 48 separate lines (Fig. 3) of the carbon dioxide laser. The most suitable laser transition for ammonia measurement is that coinciding with the 9R(30) line.

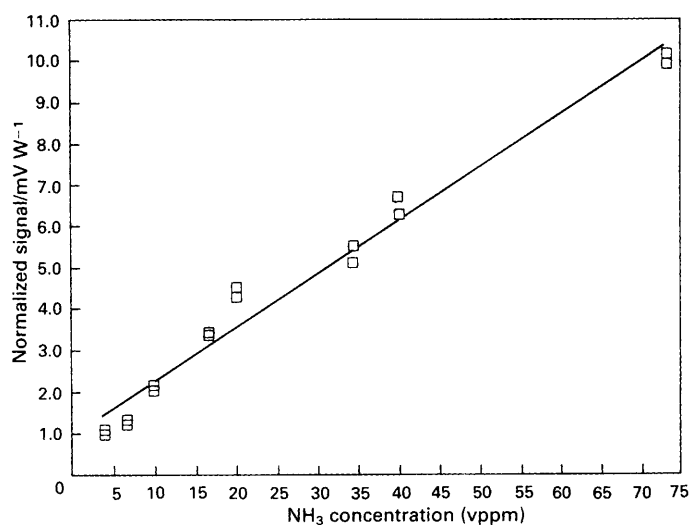
The calibration graph of ammonia at the 9R(30) laser line (9220 nm) was obtained using a series of standards (concentrations ranging from 3.8 to 73.4 vppm of ammonia). The background signal level was about 2200 nV with a laser power of 0.6 W under typical operating conditions. The calibration graph shown in Fig. 4 can be fitted to a straight line with a correlation coefficient of 0.998. The calculated detection limit, defined as the concentration corresponding to twice the background signal, was 4.3 ppb.

The results obtained from PA spectroscopy and Indophenol Blue measurements are compared in Table 2. The data indicate that the two independent techniques give the same results in the concentration range studied.

### Conclusion

This work confirms the suitability of laser PA spectroscopy for the accurate determination of ammonia. The major advantages are its relative simplicity and the ability for real time measurement, without the need for sample preparation.

The sensitivity of the catalysed Indophenol Blue method is approximately 1.3 ppb at 100 kPa and 25 °C.<sup>17</sup> At present, the sensitivity of the PA approach, used in this work, is limited by the background (about 2 μV) signal (sum of blank absorption, wall scattering losses, flow noise, acoustic pick-up, etc.). However, the background level is one order of magnitude above that of the intrinsic microphone noise. The background

**Fig. 4** Normalized acoustic signal versus concentration of ammonia at the 9R(30) laser line**Table 2** Comparison of colorimetric and PA methods for detection of ammonia

Sample concentration (vppm)	Measured concentration (vppm)	
	Indophenol Blue	PA
4.9	5.1	4.8
5.7	5.8	5.6
6.3	6.4	6.2
6.9	7.6	6.8
10.1	9.9	9.8
12.7	10.5	12.3
17.8	18.2	17.3

signal is susceptible to further suppression and consequently additional improvement of the sensitivity might be anticipated by means of the use of extra acoustic filters and better microphones and through the utilization of a differential detection scheme for automatic background correction. As in PA spectroscopy the signal is directly proportional to the incident power, the detection limit might be improved even further by using either a higher power or an intra-cavity arrangement.

The authors acknowledge the help of Dr. Henk Jalink, Dr. Hans Sauren and ing. Cees van Asselt of the Department of Agricultural Engineering and Physics of Wageningen Agricultural University. The authors are grateful to Neeltje Nakken of the Department of Soil Science and Geology and Hillion Wegh of the Department of Air Pollution of Wageningen Agricultural University for their practical help and Anton Janssen for technical assistance. Participation of A. M. S. at the XXVII CSI was supported by the PHARE 152 project.

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Paper 1/04314E

Received August 19, 1991

Accepted October 21, 1991