1. INTRODUCTION

1.1. Why Detect Ammonia

In the human body, ammonia is mainly produced during catabolism of protein turnover or food digestion. The endogenous ammonia is accumulated in the bloodstream. The ammonia is highly toxic for the cells and organs and has to be eliminated. In a healthy individual, the blood ammonia concentration level is kept under 50 µM by the liver which transforms the ionic form of ammonia into urea. Urea is an uncharged neutral molecule with low reactivity and therefore far less toxic than ammonia which instead is a basic strong reactive molecule. Liver malfunction is the major cause of increasing concentration level of ammonia in the blood and may determine the encephalopaties. Free ammonia secretion is too low to account the decreasing of blood ammonia concentration, nevertheless ammonia is present at roughly the same blood concentration in most of body fluids including urine, saliva, breath and sweat. The urea is excreted into urine by kidneys. In case of kidney malfunction, nitrogenous waste starts loading in the patient bloodstream giving rise to toxic effects; well known pathologies due to elevated blood ammonia are dialysis dementia, dialysis disequilibrium syndrome, hepatic encephalopathy, uremic encephalopathy. Consequently, the blood of patients with renal failure must be frequently cleaned by mean of hemodialysis process. In some physiological and clinical studies, the determination of urinary ammonia can be of special interest because ammonia in the urine may serve as an index of the acid-base haemostasis of the body [1]. In addition, the urea can be converted by urease into ammonia and this may allow to quantify the body protein turnover.

Moreover, quantitative assays of ammonia can have further interest in environment pollution due to industrial processes regarding pig factories and industrial process plants for refrigeration, refining, manufacturing and cleaning processes [2, 3]. Humans cannot breath ammonia enriched air, having as consequence a strong airways inflammation during inhalation and a detrimental impact on the organ functions when, passing the alveolar barrier from the inhaled air into the blood stream, it reaches a toxic concentration in the circulating blood. The toxic limit in air has been assumed at 25 ppm.

For the above mentioned reasons, any study on the specific monitoring of ammonia trace concentration is very welcome, to be applied both in environment monitoring as well as in human health monitoring through analysis of breath or body fluids likewise urine or plasma [4]. The objective of the present work was to study the suitability of the photoacoustic spectroscopy technique to determine the ammonia concentration in urine.

1.2. What We Have Done

In the present paper we report the high resolution real time detection of ammonia traces in gaseous mixtures released by liquid samples; the work was carried out with a home made detector. The sensor was based on the Laser photoacoustic spectroscopy (LPAS) as depicted in the following section. LPAS is especially well suited to measure ammonia concentrations, due to...
its relative simplicity, ruggedness and overall sensitivity. The sensor is also useful both to environment monitoring as well as to breath test for monitoring overall ammonia concentration in the body. Detection of ammonia by laser photoacoustic spectroscopy methods is possible even in the presence of two abundantly absorbing species, i.e., CO$_2$ and H$_2$O, because of their distinct and characteristic fingerprint absorption very well distinguishable from NH$_3$ due to the high resolution character of the LPAS technique. In the next sections the LPAS technique and the experimental set-up will be introduced, the experimental steps will be described and the results will be reported.

2. DETECTION METHOD

The detection method used in the reported experiments is the laser induced photoacoustic spectroscopy (LPAS). The concept of photoacoustic spectroscopy is based on a quite old analogous technique, commonly named opto-acoustic spectroscopy, that has been employed for many years in the study of optical absorption phenomena in gases. To reduce the confusion with acusto-optic effect in which light interact with acoustic or elastic waves in a crystal, Rosencwaig [5] changed the name from opto-acoustic to photoacoustic for all photo-calorimetric studies, no matter how sample is: solid, liquid or gaseous. By mean of two types of photoacoustic cell (resonant and nonresonant), we analyzed liquid mixtures in which NH$_3$ was present. A resonant cell is definitely more sensitive that a nonresonant one, but the technical difficulties encountered in render it smaller, conducted us to design a nonresonant structure possessing a total volume of only 3 cm$^3$, in comparison with 2 l volume of the resonant one. This was twice convenient: first, the response time is reduced from minutes to seconds, and second it become possible to realize a more compact portable apparatus. We wanted to demonstrate that we can detect NH$_3$ at trace level, even reducing the sensitivity of our system by adopting the nonresonant cell instead of the resonant one. The results shown (see later in Section 3) that when using the nonresonant cell the signal intensity became approximately ten times lower, but the detection was still possible and the selectivity was not lost.

2.1. LPAS Apparatus

A common LPAS system is made by a light source (in our case a CW CO$_2$ laser), a light amplitude modulator (mechanical chopper), the measuring photoacoustic cell equipped with a signal transducer (sensitive microphone, tuning fork or piezoelectric transducer); refer to Fig. 1. The trace gas detection by photoacoustics is based on the selective absorption of the monochromatic IR radiation by the molecular species to be revealed. The collisional des-excitation processes, due to the resonant absorption of specific wavelength laser radiation, generate a pressure wave. The process of increasing/decreasing pressure in the closed volume of the photoacoustic cell produces acoustic waves, that are revealed by the sensitive microphones (20 mV/Pa) placed inside the cell.

2.2. LPAS Detection of Ammonia

Brewer and Bruce [6] used the same technique to determine the absorption coefficients of NH$_3$ at seventy seven laser lines in the 00$^1$–02$^0$ band at 9.4 µm and the 00$^1$–10$^0$ band at 10.4 µm. In that paper, the NH$_3$ was buffered with N$_2$ to 1 atm at 295 K; its concentration ranged from 30 to 200 ppm. For a clear view, we put on a bar graph the results of Brewer's study (see Fig. 2).

By using the HITRAN data base [7], we simulated the IR spectra of NH$_3$, H$_2$O, and CO$_2$ nearby 9 µm. As it can be seen from the simulated spectra (Fig. 3), the fortuitous perfect overlapping of both the 9R(30) laser emission line and the central line of the NH$_3$ absorption band in the same spectral region (9.22 µm), where ammonia shows a very strong absorption, represents a very advantageous situation; this represents an important criteria not only for increasing sensitivity but also for increasing the selectivity of ammonia detection. In addition, even considering the small contribution of the