



Regular article

Characterization of a photoacoustic system through neural networks to determine multicomponent samples



N.M. Zajarevich*, A.L. Peuriot, V.B. Slezak

UNIDEF-CONICET-CITEDEF, Juan B. de La Salle 4397, 1603 Buenos Aires, Argentina

HIGHLIGHTS

- New signal processing for measurement of concentrations of different gases in a mixture.
- Original application of artificial neural network.
- New contributions to photoacoustics signal processing.

ARTICLE INFO

Article history:

Received 7 April 2016

Revised 10 June 2016

Accepted 14 June 2016

Available online 27 June 2016

Keywords:

Photoacoustics

Neural network

Gas traces

ABSTRACT

Photoacoustic spectroscopy for trace gases detection, based on a CO₂ laser, can be used in a wide range of applications. The tunability of this laser in the mid-infrared (9.4–10.6 μm) allows the quantitative determination of different substances in multicomponent samples. In general, at traces level, the total photoacoustic amplitude at a certain wavelength may be approximated by a linear superposition of the amplitudes given by each of the species absorbing at that wavelength. However, in some cases, the sum of the individual signals is no longer valid. In particular, it is known the presence of CO₂ delays the acoustic signal in relation to the laser excitation due to the exchange of vibrational energy between CO₂ and N₂. This phenomenon generates a slow V-T energy relaxation from a metastable N₂ vibrational level and the sum of individual contributions may no longer be valid. Moreover, the resolution of a linear equation system has limitations, so the possibility to determine concentrations in photoacoustics based on neural network is proposed in this work. This procedure is tried in a particular case of a volatile organic compound, such as C₂H₄, and CO₂ in air. The results are compared with the ones obtained with a model based on rate equations.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The detection of gases traces is a very interesting subject because of its wide range of applications, like environment, biological processes and industry.

The photoacoustic (PA) spectroscopy used in this work to detect gas traces has advantages compared to other techniques because of its wide dynamic range, selectivity, sensitivity and low cost [1,2]. Particularly, selectivity due to the use of a tunable source allows the detection of multicomponent samples. Tunable mid-infrared sources like OPO, diodes, QCL, CO or CO₂ lasers allow exciting vibrational modes of different substances which spectra act as a real fingerprint, since each molecular species presents its own pattern. In most cases, where laser intensity and sample absorbance

are low, the absorption of light can be considered linearly dependent on concentration and power and, consequently, the PA signal also [3]. When several species are present in the sample and the relaxation of internal to kinetic energy is fast compared to intermolecular exchange times, each species contributes to the heating of the gas mixture separately and the PA signal can be written as the sum of individual contributions. Therefore, in photoacoustics the classical method to determine the concentrations of absorbing substances in a multicomponent sample is resolving a system of linear equations where each of them corresponds to the sum of contributions to heat of all the species at one given excitation wavelength. This method has limitations related on one hand, to the conditioning of the matrix characteristic of the equations system containing the absorption coefficients of the different substances in the sample, and on the other hand, to the background signal in the system. The conditioning is much better for values close to one, but we are limited by the different species absorption coefficients available at the laser wavelengths.

* Corresponding author.

E-mail address: nzajarevich@citedef.gob.ar (N.M. Zajarevich).

In some cases, the sample heating, therefore the PA signal, is not linearly related with the absorbed power because interactions between the excited species and between excited and buffer gas molecules produce a difference of phase between the PA signals coming from different species. Meyer and Sigrist [4] developed a model based on rate equations to describe the heat production in samples containing CO₂ in air upon excitation with a CO₂ laser and arrive to an expression which allows calculating the phase difference between the PA signal and the excitation. An early work by Wood et al. [5], related to atmospheric absorption of 10.6 μm radiation, describes the “kinetic cooling” of air due to the slow energy transfer from the excited CO₂ molecules to translation through N₂. The importance of the influence of collisional relaxation processes on the PA signal is also reported by Schilt et al. [6,7] and Barreiro et al. [8] in the case of CH₄ in N₂ and N₂-O₂.

Taking in account these phenomena, we can infer that a linear equations system as described above is not always representative of the generation of PA signals and the development of a model that describes the dependence the signal on concentrations may be complex, even impossible.

Nowadays, fast desk computer systems are accessible in any lab and the huge power of calculation of these devices suggests that computational methods, similar to those applied for pattern recognition, should be adequate to be applied to the signal processing in photoacoustics. Each pattern is composed by different concentrations of the molecular species that are contained in the sample. In this paper the feasibility of a method based on neural network processing, hence independent from the resolution of linear equations systems, will be studied to analyze multicomponent samples.

2. Theory

To test the signal processing for the determination of concentrations of various substances diluted in air at trace level an artificial neural network (ANN) was trained for application in samples containing CO₂ and C₂H₄ excited by radiation from a CW CO₂ laser. CO₂ is a substance that appears in any actual sample as its natural abundance is around 380 ppm. Furthermore, the importance of studying the detection of C₂H₄ traces lies in the fact that it consists of a natural hormone related to biological processes, particularly with the ripening of fruits and with emission from vegetables under stress conditions [9–11]. On the other hand, both species have an absorption spectrum with a very unique footprint within the region of the CO₂ laser emission.

The PA signal from these samples, when the excitation source is a CO₂ laser, is phase shifted with respect to the excitation. This time mismatch is due to the quasi-resonant energy exchange between the 2349 cm⁻¹ vibrational level of the CO₂ molecule, excited by the laser, and the N₂ vibrational level at 2330 cm⁻¹, which is metastable. Following this exchange, a delay between the PA signal and the laser excitation occurs as a slow V-T energy relaxation occurs from the N₂ excited level.

Based on a model of rate equations which describes the populations of the involved vibrational levels [4], a system of linear equations is obtained for the signal amplitude in phase with the laser excitation (Eq. (1)) for samples containing CO₂:

$$S_i \cos(\theta_i) = K_d P_{0i} \left[\sum_{j=1}^{n-1} C_j \sigma_{ij} - \left(\frac{\nu_{N_2}}{\nu_{las}} - 1 \right) \cdot C_{CO_2} \sigma_{CO_2} \right] \quad (1)$$

where K_d is the PA setup constant, P_{0i} the laser power at the i -line, C_j the concentration of the j -substance, σ_{ij} the absorption coefficient of the j -substance at the i -wavelength, S_i the signal amplitude and θ_i the phase with respect to the excitation. The term corresponding to the CO₂ contribution, which includes the ratio between the N₂ wavenumber (ν_{N_2}) and the laser wavenumber, reflects the energy

exchange already explained. In previous works [12–14] we measured the phase of the PA signal from CO₂ which resulted around 165°. In real cases a term including amplitude and phase is added to Eq. (1), which represents the background coming from windows heating, external noise or scattering.

The aim of applying ANN, and not using the model of population rates, is avoiding the errors introduced by the approximations thereof and the need of knowledge of the absorption coefficients values at the CO₂ laser lines.

3. Experiment

The resonant PA system uses a home-made tunable CO₂ laser with maximum power 5 W at the 10P(20) line. The gaseous sample is contained in an aluminum cell with a 70 mm long and 12 mm wide resonator and quarter wavelength buffers at both ends. The beam that propagates through the cell axis is modulated by a chopper (Thor Labs MC1000) at the resonance frequency around 2200 Hz. The phase reference comes from a fast Pyroelectric detector (Infra Tec, LME-501-63) which receives part of the laser radiation. At the same time, the signal from this detector is useful for normalizing the PA signal with respect the incident power. The microphone signal acquisitions together with the pyroelectric signals are both digitized with a PC sound card. In order to get good precision, the microphone signal must be previously amplified to obtain values near the sound card saturation level. With this scope a digital amplifier (Stanford Research Systems SR560) is programmed so as to choose the most adequate amplification factor. The computer performs the calculations characteristic of synchronous detection [15]. In Fig. 1 the experimental setup is shown.

Different samples were prepared in a vacuum line, starting from tubes provided by L’Air Liquide of CO₂ (O₂ ≤ 30 ppmV, H₂O < 50 ppmV, CH₄ ≤ 20 ppmV), C₂H₄-N₂ (600 ppmV ± 25 ppmV) and chromatographic air (H₂O ≤ 5 ppmV, CO + CO₂ ≤ 0.5 ppmV, C_nH_m ≤ 1, purity ≥ 99.95%) and measuring the partial pressures with a MKS Baratron capacitance manometer. An average error of 10% is estimated for the partial concentrations due to the manufacture of three components mixtures with highly rarefied proportions. We chose the concentration ranges of the targeted compounds (CO₂ between 1.25% and 2.68%; C₂H₄ between 0.79 and 36.4 ppmV) according to the limitation imposed by the precision of the PA system and by its background signal. This range is adequate for some industrial applications, like analysis of gases from car exhausts [16] and of air samples from a fruit storage chamber [4].

Ten PA signal amplitude and phase measurements are performed for each mixture at two laser lines properly chosen. Particularly, the C₂H₄ spectrum presents the greatest contrast at the 10P(14) y P(16) laser lines (7:1), as the CO₂ instead shows a slowly varying profile.

The ANN is composed by four entries, amplitude and phase at the 10P(14) y 10P(16) lines and two outputs, the concentrations of the two minor components. In Table 1 the measurements used for training are shown, taking also in account the previously measured PA background signal from a chromatographic air sample (amplitude 0.46 mV/W and phase 24°), which includes windows heating by light absorption, scattering and environmental noise. The values of phase and normalized amplitude ($A_i = S_i/P_{0i}$, $i = 1$ for 10P(14), $i = 2$ for 10P(16)) in Table 1 are the average of 10 measurements for each mixture in the closed cell using an integration time constant of 1 s.

After several trials the chosen structure was feedforward with three layers of 10 neurons each. The training algorithm is Levenberg Marquardt backpropagation. Backpropagation [17] is a learning method which consists in applying an input pattern as stimulus

Download English Version:

<https://daneshyari.com/en/article/1784005>

Download Persian Version:

<https://daneshyari.com/article/1784005>

[Daneshyari.com](https://daneshyari.com)