Verification of the basic equation of gas phase photoacoustics

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The analytical performance of a photoacoustic gas detection system can be characterized by a sensitivity factor that can be defined in the following form:

$$S = \frac{PAS - A_0}{c} = \left(\frac{c_p}{c_V} - 1\right) \cdot P_{in} \cdot C_{cell}(f) \cdot \alpha_{spec} \qquad \text{Eqn. 1}$$

The sensitivity parameter of a gas phase photoacoustic system depends on two factors: on the frequency dependent acoustical properties of the measuring system and on the heat capacity ratio of the measured gas sample. As far as the earlier works on the measurement of the frequency dependence of the PA system sensitivity is concerned, they are recognized to be incomplete in a sense that the acoustic and the thermal properties are varied simultaneously [1] [2]. Based on the calibration of the PA system with an analyte buffered in various gas mixtures, a method is developed that unravels and quantifies both of these dependencies.

The measurement method starts by a two-phase calibration procedure that eliminates the effect of C_{cell} on the measured S factors. During its first phase a set of calibrations are executed by admixing a mixture of a heavy and a light noble gas (i.e., argon and helium, respectively) to methane in a way that the individual concentrations of the noble gases are varied while their total concentration is kept constant. In this way it is possible to vary the value of the sound speed while (c_p/c_V-1) remains constant, and so the frequency dependence of C_{cell} can be determined unaffectedly from the variation of (c_p/c_V-1). The second part of the proposed method is based on the calibration of the PA system with various gas mixtures that changes both the acoustic frequency of the measuring system and the heat capacity ratio of the gas sample as well. From the results of this second set of calibration the previously determined acoustic frequency dependence can be separated yielding the heat capacity dependence of the sensitivity parameter.

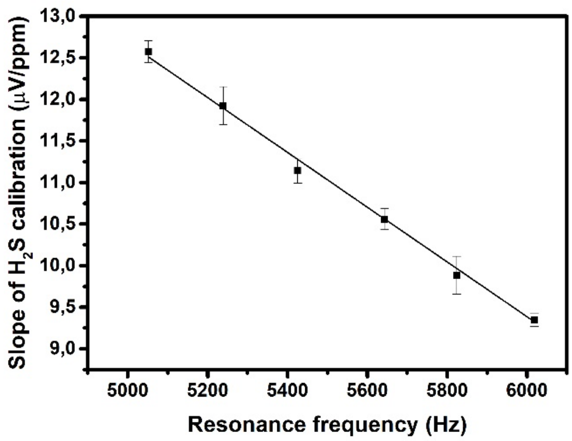

Fig. 1. Slope of the calibration lines as a function of resonance frequency determined during the first phase of the calibration

The reported measurements were executed by using one of the strongest absorption line (λ_1) of H_2S at 1574 nm and a second line (λ_2) that is accessible by the same light source and has an approximately four times smaller line-strength. Frequency dependence of the instrument was determined in the range from 5050 to 6000 Hz, using the λ_1 absorption line of H_2S. In this range a linear relationship was found between the slope of the H_2S calibration line and the resonance frequency for each gas composition. The (c_p/c_V-1) dependence was determined in the range from 0.32 to 0.5 by using both of the λ_1 and λ_2 absorption lines. After the frequency dependence was separated, a linear correlation was found.

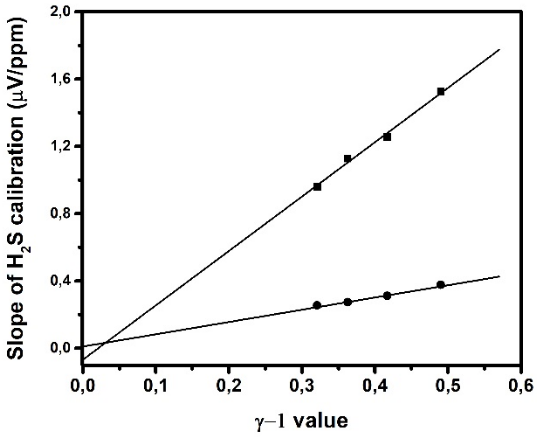

Fig. 2. Variation of calibration slope as a function of the γ-1 value. Squares represent points of the calibration using the λ_1, the circles indicate points using the λ_2 absorption line.

In conclusion, a novel method was developed for the determination of the effect of the two major sources of sensitivity parameter variation, i.e. the frequency dependence of the acoustical properties of the PA system and the variation of the heat capacity ratio of the measured gas with the gas composition, separately. Using this method, the sensitivity parameter of a H_2S measuring PA system containing a longitudinal differential PA cell and a near-infrared diode laser under wavelength modulation was determined and the results prove that - in accordance with the basic theory of photoacoustics - the sensitivity parameter separated from the frequency dependent acoustical properties is directly proportional to the (c_p/c_V-1) factor.

References

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