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High-stability reference setup for photoacoustic spectroscopy

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Abstract. A simple and powerful reference technique for gas-coupled photoacoustic spectroscopy of strongly absorbing liquids and solids is presented. It consists in chopping the light beam simultaneously at two frequencies, while using the sample itself as the reference. This allows one to automatically compensate fluctuations in parameters like light source intensity, temperature or gas volume. This technique was tested with aqueous solutions of glucose and a CO_2 laser at 9.676 μm.

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Gas-coupled photoacoustic (PA) spectroscopy is an alternative to the more widely used spectroscopic techniques like transmission or reflectance spectroscopy, and is particularly well suited for the study of strongly absorbing liquids or solids [1, 2]. First discovered in 1881 by Bell [4], the gas-coupled PA effect has been widely studied in the last 20 years (see e.g. [3]). For high absorption coefficients, this effect is well described by the Rosencwaig and Gersho (RG) theory [5], which states that the pressure waves in the coupling gas are produced by the transfer of heat from the periodically irradiated sample into the contacting gas.

The PA technique presents several advantages in comparison with other spectroscopic techniques: it allows one to study opaque samples without the need of very thin cells, which can easily get obstructed, and it does not require special sample preparation [6, 7]. However, one disadvantage of this technique is that the PA effect depends on many parameters susceptible to fluctuations, like mean pressure, temperature, gas volume, gas composition, microphone sensitivity and, of course, light intensity. A very good reference setup is therefore necessary to ensure stable and reproducible measurements of the absorption coefficient.

The objective of our research project consisted of studying the feasibility of an industrial sensor based on the photoacoustic effect, adapted to online measurements of glucose and sucrose concentrations in water during beverage processing. Enhanced stability and a good signal precision were essential. However, liquid levels are susceptible to fluctuations in the PA cell during on-line measurements. Therefore the pressure inside the cell and the gas volume can not be kept perfectly constant. Outgasing of the liquid is also possible, thus modifying the gas composition. The temperature of the liquid can also vary. Moreover, cheap and industrial CO_2 laser sources are in general not power stabilized. A very good reference setup was therefore the key to our research project. We present in this paper a simple and powerful technique allowing one to automatically compensate fluctuations in the above mentioned parameters (patent pending). Initially developed especially for our industrial application, this technique can be easily extended to all kinds of PA spectroscopic measurements of strongly absorbing liquids and solids.

1 Theory

The basic principle of the gas-coupled PA effect, as described by Rosencwaig and Ghersho [5], is the following: the liquid or solid sample is enclosed in a cell with a transparent gas and is irradiated by modulated light, as shown in Fig. 1. Optical absorption by the sample gives rise to a temperature increase in the absorption zone. One part of the produced heat propagates to the surrounding gas leading to a pressure increase. A sound wave at the modulation frequency of the light is hence produced, and its amplitude is proportional to the amount of energy which is transferred from the absorbing zone to the contact gas.

The absorption length l_α and the thermal diffusion length μ_s are two important parameters in this process. They are given by the following expressions:

$$l_\alpha(\lambda) = \frac{1}{\alpha(\lambda)}, \tag{1}$$

$$\mu_s(f) = \sqrt{\frac{k_s}{\pi \varrho_s C_s f}}, \tag{2}$$

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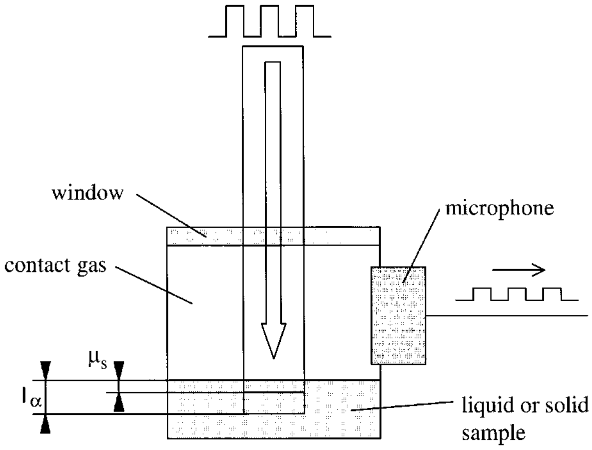

Fig. 1. The gas-coupled photoacoustic effect

where λ is the wavelength of the light, $\alpha(\lambda)$ the absorption coefficient of the sample at λ, k_s, the thermal conductivity of the sample, ϱ_s its density, C_s its specific heat and f the modulation frequency of the light. The absorption length, l_α corresponds to the depth beyond which most of the light is absorbed, and the thermal diffusion length, μ_s, corresponds to the depth beyond which temperature fluctuations cannot reach the surface.

With strongly absorbing samples, where the absorption length is much smaller than the sample thickness, two cases are considered by the RG theory:
(a) $\mu_s \ll l_\alpha$: In this case, only the part of the light which is absorbed inside the thermal diffusion length μ_s contributes to the signal, which is thus sensitive to variations in the absorption length l_α. The sound-wave amplitude is given by the following expression [5, 8]:

$$\delta P = \frac{\gamma_g P_0 P_l}{T_0 V_g} \frac{\mu_s^2 \mu_g}{k_s} \alpha, \tag{3}$$

where γ_g is the ratio of the specific heats of the gas, P_0 the mean pressure, P_l the light intensity, T_0 the mean temperature, V_g the gas volume, and μ_g the thermal diffusion length of the gas.
(b) $\mu_s \gg l_\alpha$: In this case, all the absorbed energy contributes to the signal, which is then independent of variations in the absorption length. The sound-wave amplitude is given by the following expression [5, 8]:

$$\delta P = \frac{\gamma_g P_0 P_l}{T_0 V_g} \frac{\mu_s \mu_g}{k_s}. \tag{4}$$

As the thermal diffusion length μ_s is inversely proportional to the square root of the modulation frequency f (2), it is possible to vary this length simply by changing the modulation frequency of the light. For spectroscopic measurements, the chopping frequency has to be set high enough so that the signal is dependent on the absorption coefficient of the sample, as in case (a). However, our idea was to take advantage of case (b) to use the sample itself as a reference, to cancel fluctuations in temperature, pressure, gas volume, laser intensity or gas composition.

The principle of our reference technique is the following: the beam is modulated simultaneously at two frequencies, f_1 and f_2. The frequency f_1 is chosen high enough so that the PA signal depends on the absorption coefficient of the sample, as in case (a), and the frequency f_2 is chosen low enough so that the PA signal does not depend on the absorption coefficient, as in case (b). The PA signal is then the sum of the components at each frequency:

$$\begin{aligned} S_{PA} &= S_{PA}(f_1) + S_{PA}(f_2) + \ldots \\ &= Q_{f_1} \delta P(f_1) + Q_{f_2} \delta P(f_2) + \ldots, \end{aligned}$$

$\delta P(f_1)$ being given by (3) and $\delta P(f_2)$ by (4). Q_{f_1} and Q_{f_2} are constants depending on how the light is chopped and on the response of the microphone. The ratio R_{PA} of the PA signal components at f_1 and f_2 is:

$$R_{PA} = \frac{S_{PA}(f_1)}{S_{PA}(f_2)} = \frac{Q_{f_1}}{Q_{f_2}} \frac{\delta P(f_1)}{\delta P(f_2)}. \tag{5}$$

By substituting (3) and (4) in (5), one obtains the following expression for the PA signals ratio:

$$\Rightarrow R_{PA} = \frac{Q_{f_1}}{Q_{f_2}} \sqrt{\frac{k_s}{\pi \varrho_s C_s}} \frac{f_2}{f_1^{3/2}} \alpha. \tag{6}$$

This ratio is independent of laser intensity, pressure, temperature, gas volume, and gas parameters. It depends only on the absorption coefficient and on the physical parameters of the sample. Note that in contrast to transmission spectroscopy, which depends only on the optical parameters of the sample, the ratio of the PA signals depends also on its density and thermal parameters. Hence it is not a technique suited to measure absolute absorption coefficients of substances.

Evaluation of relations (1) and (2) for aqueous solutions of glucose at 9.676 μm gives the following results.

$l_\alpha = 20\ \mu\text{m}$ for pure water,
$l_\alpha \cong 10\ \mu\text{m}$ for 200 g/l glucose,
$\mu_{water} = 4.7\ \mu\text{m}$ at $f_1 = 2000\,\text{Hz}$,
$\mu_{water} = 27\ \mu\text{m}$ at $f_2 = 60\,\text{Hz}$,

2 with $k_{water} = 0.585\,\text{W/m K}$, $P_{water} = 1000\,\text{kg/m}^3$, $C_{water} = 4180\,\text{J/kg K}$ and $\alpha(9.676\,\mu\text{m})$ varying between $\sim 500\,\text{cm}^{-1}$ for pure water to approximately $\sim 1000\,\text{cm}^{-1}$ for 200 g/l glucose. Therefore, $\mu_{water} < l_\alpha$ at 2000 Hz and $\mu_{water} > l_\alpha$ at 60 Hz. This is a rough approximation of case (a) and case (b) of the above described theory.

2 Experimental setup

The laboratory setup is shown in Fig. 2. The light source is a CO_2 laser of approximately 1 W power and a wavelength of 9.676 μm. The wavelength of 9.676 μm corresponds to a high absorption band of glucose. The light beam is modulated by two mechanical choppers which are electronically frequency stabilized. The low frequency one is obtained by a metallic wheel with two teeth, whereas the high frequency one is generated by a 27-tooth wheel. A gold-coated NiCu mirror sends the chopped laser beam through a ZnSe window into the cell.

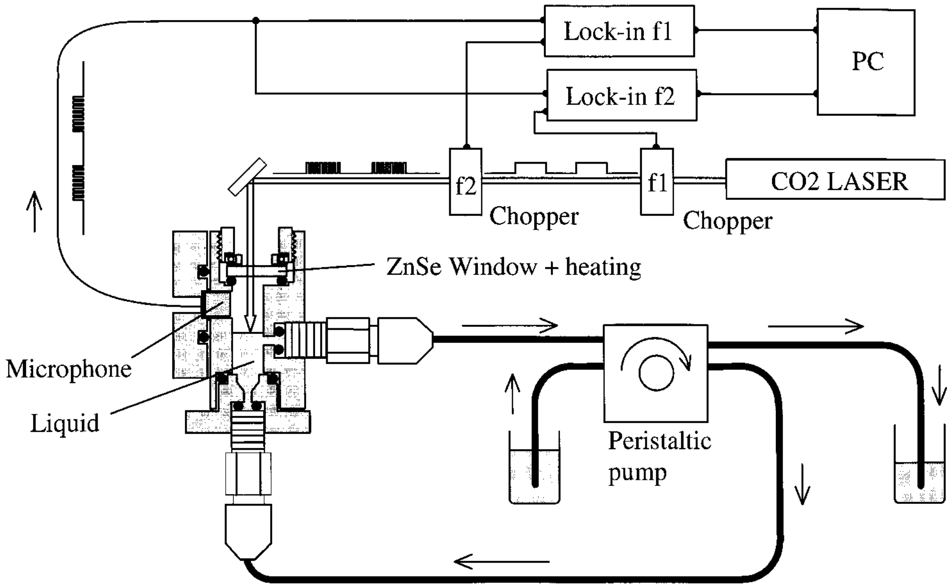

Fig. 2. Experimental setup

A simple home made window heating device consisting of a low powered resistor maintains the window temperature several degrees above the mean temperature in the cell. This avoids condensation on the window, which absorbs part of the incoming light and produces spurious PA signals.

The stainless steel cell contains a gas volume of approximately 0.28 ml, and a liquid volume of 0.3 ml. The PA signal is measured by a commercial miniature KE4 Sennheiser microphone of 5 mm diameter. A miniature microphone is necessary to minimize the gas volume. Indeed, relations (3) and (4) show that the PA signal is inversely proportional to the gas volume. Moreover, complicated geometries like narrow tubes connecting the sample and the microphone chambers have to be avoided with our reference technique, because they would create Helmholtz resonances [9, 10], whose frequencies vary with pressure, temperature and gas composition. The microphone output is then processed by two SR530 lock-in amplifiers, which are externally locked to the reference frequencies of the two choppers.

The cell is connected to a peristaltic pump simulating on-line conditions. The two-way peristaltic pump allows one to introduce and to extract simultaneously the same amount of liquid. The cell is isolated from external air-borne acoustic noise by O-ring seals. The effect of these O-ring seals is spectacular: without them, the noise level of the microphones is much higher. It is indeed crucial to perfectly isolate the volume of gas enclosed in the cell from the air surrounding the cell. Possible noises propagating in the cell walls have almost no influence on the microphone noise level. Indeed, electrical microphones are almost insensitive to structure-borne noise. A lot of low frequency noise is generated by the pump, due to a piston effect on the gas volume enclosed in the cell. For this reason, we employed purging periods with the pump running alternate to measurement periods during which the pump is stopped. The whole process is controlled by the acquisition program, which records the signals coming from the two lock-in amplifiers as a function of time, and displays the PA amplitudes and phases at the two frequencies, and the ratio of the amplitudes.

Particular care must be taken in setting the parameters of both lock-in amplifiers. Every parameter, except the sensitivity has to be identical in both lock-in amplifiers, in particular the time constants. Differences in the time constant settings would result in different time responses for the two lock-ins and alter the reference process. Concerning the sensitivities, each one has to be set as high as possible for a given input signal, in order to lower the noise and to avoid non-linearities. Noise can also be reduced by choosing sufficiently high time constants, which would of course also slow down the time response of the whole system.

3 Results

All experiments were performed at the modulation frequencies of 60 Hz and 2000 Hz and with lock-in time constants of three seconds. Data were acquired every two seconds.

3.1 *Experimental tests of the reference method*

To test the long-term stability of our experimental setup, data were recorded over several hours, with pure water in the cell and no pumping. An example of the obtained results is shown in Fig. 3. The PA signal components at 60 Hz and at 2000 Hz (full thin line and dotted thin line) as well as the signal ratio (thick line) are displayed as a function of time. The PA signals at 60 Hz and 2000 Hz are proportional to the laser intensity of our CO_2 laser, which is not power stabilized. Except in the first twenty minutes during which laser fluctuations were exceedingly high, the signal-ratio precision is one percent.

The efficiency of this reference technique in compensating laser power fluctuations is clear in Fig. 4. During the first ten minutes, large laser intensity fluctuations were produced by deformations in its cavity during the warm up phase. Perturbations in the signal-ratio appear near the lowest intensity points, where the slope changes very rapidly, probably because of slight differences in the response time of the two lock-ins. During the next four minutes, a ZnSe window was

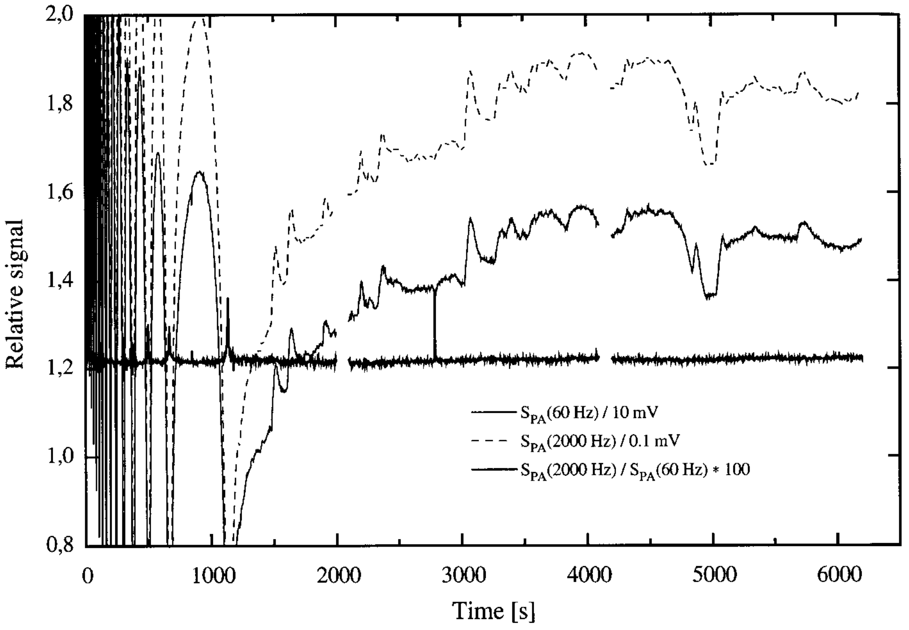

Fig. 3. Long-time stability with pure water

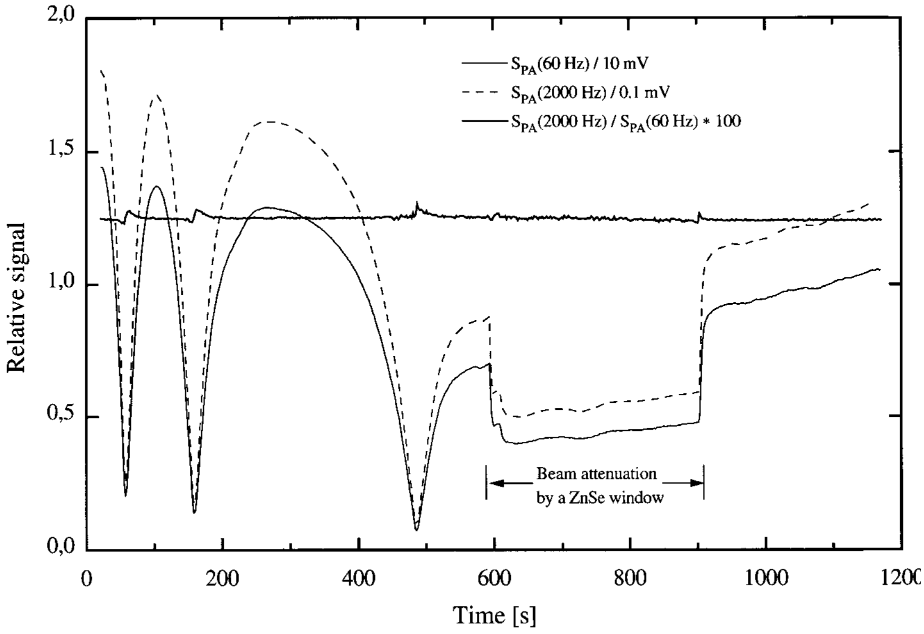

Fig. 4. Compensation of laser intensity fluctuations

placed in front of the laser head in order to reflect back part of the beam. A 30% attenuation of the laser intensity was thus produced, but the signal-ratio remained stable within one percent.

Further experiments were performed to test the effect of liquid temperature and of liquid level fluctuations. An example of measurements during which different amounts of water were injected in the cell is displayed in Fig. 5. Acquisitions were stopped when the pump was running, to avoid low frequency noise. The signal ratios are the same for liquid volumes of 0.2, 0.3 and 0.4 ml. Unfortunately, the effect of the liquid level on the PA signal directly at 60 Hz and at 2000 Hz is not visible here because of the instability of the laser intensity. (This confirms once again the usefulness of our reference technique when working with unstable laser sources.) The signal-ratio was not perturbed either when the liquid temperature was varied between 5 °C and 65 °C, as shown in Fig. 6.

The efficiency of our reference technique to compensate fluctuations in laser intensity, liquid level and liquid temperature was confirmed by these experiments. No tests were done concerning the effect of pressure fluctuations. However, there are some limitations. In particular, the signal-ratio depends strongly on the position of the incident beam in the cell. A two millimeter displacement of the beam from the central position in the cell produces a 15% increase in the signal-ratio. These fluctuations are perhaps produced by a spurious PA signal coming from the cell walls. Another detail is not completely understood: though the signal-ratio is most of the time stable within one percent for several hours, unexplained fluctuations sometimes appear after pump runnings and even after

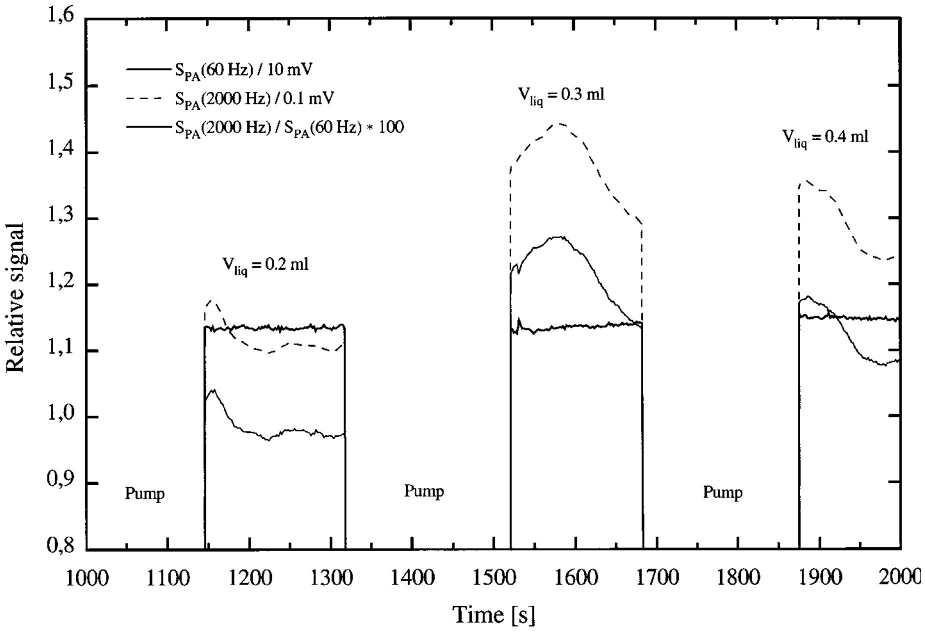

Fig. 5. Compensation of liquid level fluctuations

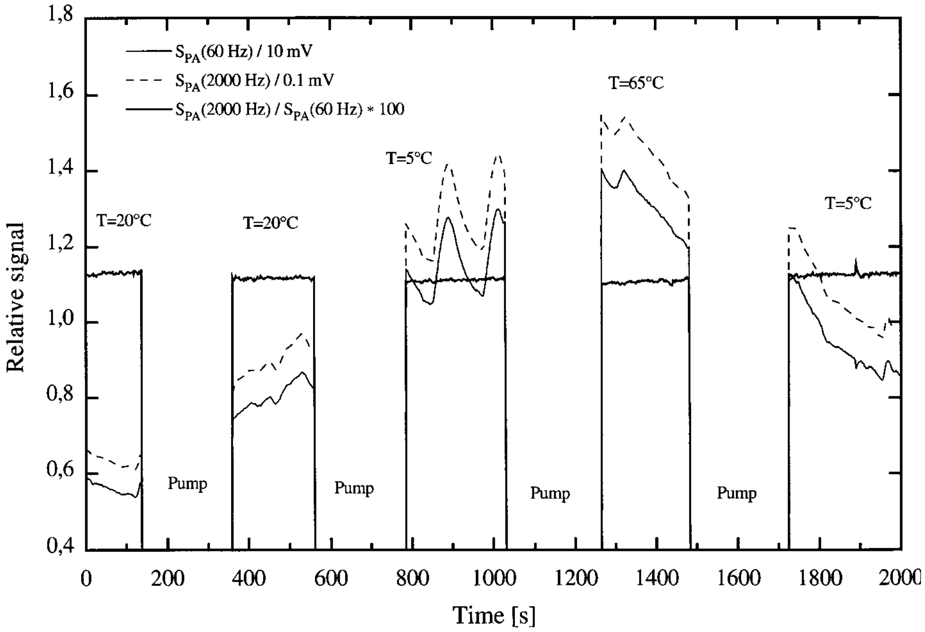

Fig. 6. Compensation of liquid temperature fluctuations

cell openings. These fluctuations, occasionally reaching up to 14% of the signal-ratio, appear in two particular situations: when the setup is not used for a few days, or during a series of pump runnings. When the experimental setup is not used for a few days, and then tested again, the signal ratio sometimes differs from before. Most of the time, the signal ratio is stable within one percent during a series of pump runnings, but sometimes, it varies after each pump purging. We suspect in the first place that these problems arise when the amount of liquid inside the cell drops drastically. Indeed, when the setup is not used for a few days, part of the liquid evaporates and gas bubbles are formed in the tubes connecting the cell to the pump, as well as in the cell itself. Moreover, during some series of pump runnings, the amount of liquid exiting the cell is slightly different than the amount of liquid entering the cell and, therefore, only a very small amount of water is left in the cell after a while. In all these cases, spurious signals could be produced on the cell walls and even on the walls of the plastic tubes connected to the cell. Hence, we strongly suspect that these sporadic fluctuations are caused by failures of the liquid delivery into the cell.

3.2 *Application to glucose concentration measurements*

Glucose concentrations ranging from 0 to 200 g/l were measured with this experimental setup. One example of the obtained results is presented in Figs. 7 and 8. The time dependence of the PA signals at 60 Hz and at 2000 Hz as well as the signal ratio are shown in Fig. 7. The corresponding

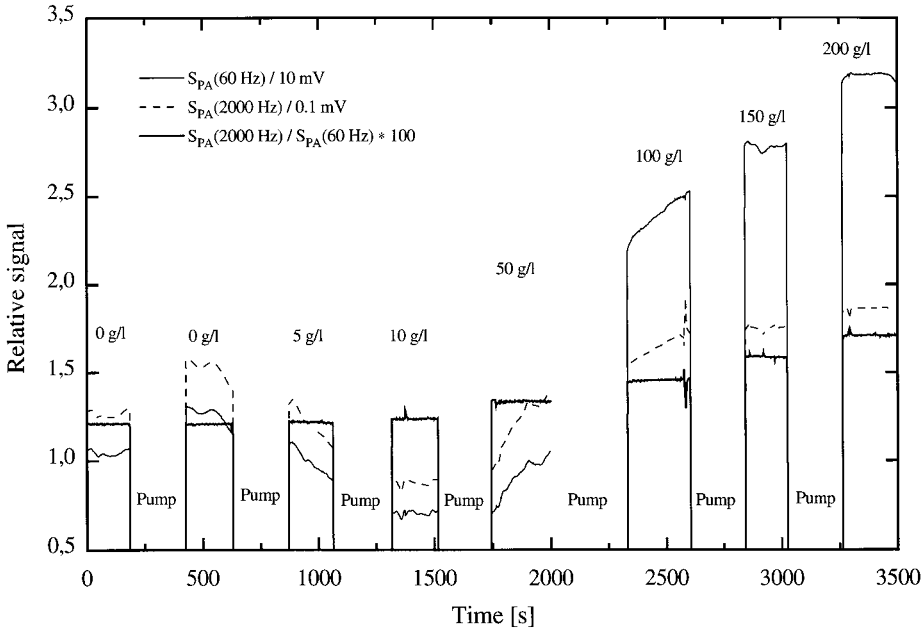

Fig. 7. Time acquisitions with various glucose concentrations

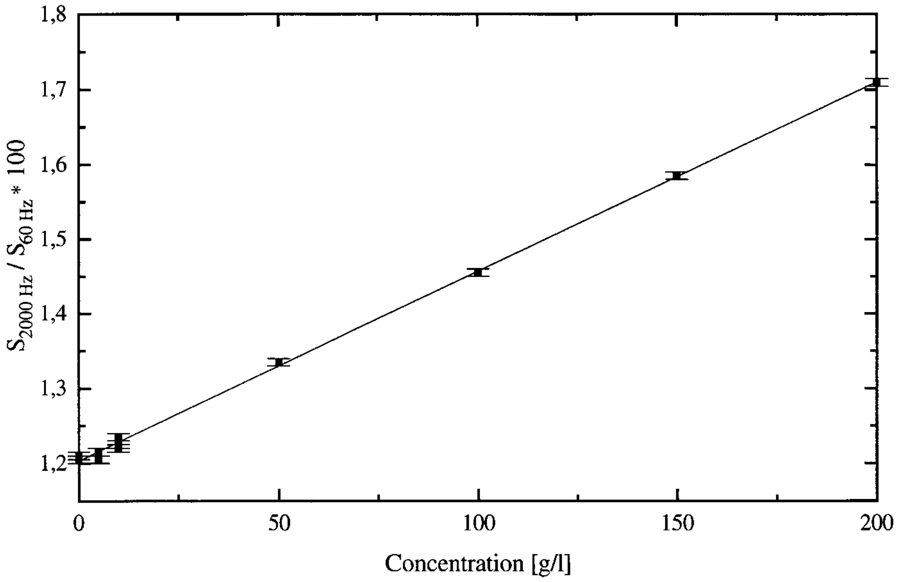

Fig. 8. Signal ratio in function of glucose concentration

graph of the signal-ratio as a function of glucose concentration is shown in Fig. 8. The signal-ratio is clearly linear for glucose concentrations ranging from 0 to 200 g/l. A glucose concentration of 100 g/l produces a 21% increase of the signal ratio in comparison with pure water. As the signal precision is approximately one percent, this corresponds to a detectability limit of 5 g/l and to a concentration measurement precision of 6 g/l near the concentration of 100 g/l.[1] A factor 5 improvement of these results would be necessary in order to have a competitive industrial sensor adapted to glucose measurements in beverages. These results are summarized in Table 1.

Another point has to be taken into account when considering glucose concentration measurements. A glucose concentration of 100 g/l produces an increase of 70% of the PA signal at 2000 Hz, in comparison with pure water. (This is not apparent in Fig. 7 because of laser intensity fluctuations.) The effects on the signal-ratio are three times lower, because the PA signal at 60 Hz varies also because of changes in the thermal parameters k_S, ϱ_S and C_S with glucose concentration. In comparison with other reference setups where a pure water sample is taken as a reference, the sensitivity of our technique is three times lower. However, our reference setup ensures much more stable and precise results, because the measured liquid itself is taken as the reference, and the measurement and reference signals come from the same cell, contact gas and microphone.

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[1] That corresponds to the standard glucose concentration of the beverages we are interested to measure.

4 Conclusion

A simple and powerful reference technique for gas coupled PA spectroscopy of strongly absorbing liquids and solids has been presented. It consists of chopping the light at two frequencies, a high frequency at which the PA signal depends on the absorption coefficient, and a low one at which it does not, and in taking the ratio of the signal amplitudes at these two frequencies. In the theoretical part based on the well-known Rosencwaig and Gersho theory, we demonstrated that the PA signal-ratio is independent of parameters like temperature, gas volume, pressure or laser intensity. It was shown to depend only on the absorption coefficient of the sample; and on its density and thermal parameters.

Experiments were performed to test this principle, confirming the efficiency of this reference method to compensate fluctuations in laser intensity, liquid level and temperature. During measurements lasting for several hours, the signal-ratio was stable within one percent, even with laser intensity fluctuations of several tens of percents. This reference setup was then used to measure glucose concentration in water, ranging from 0 to 200 g/l. As predicted by theory, the response of the system was linear within this concentration range. With one percent precision in the signal-ratio, we achieved a glucose detection limit of 5 g/l, and a measurement precision of 6 g/l near 100 g/l concentration. With further improvements in the precision of the signal-ratio, a factor 5 improvement of these results is expected.

This reference technique allows the use of the measured liquid itself as the reference. Moreover, both measurement and reference signal, come from the same cell, laser beam, contact gas and microphone. Fluctuations in laser intensity, temperature, pressure, gas composition, liquid level or even microphone sensitivity produce the same effects in the two signals. Initially developed for the specific industrial application of on-line measurement of glucose in beverages, this technique can be easily extended to all kinds of PA spectroscopic measurements, for strongly absorbing liquids and solids.

Table 1. Glucose concentration measurements: summary of the results

	Experimentally realized	Industrial requirements
Precision of signal ratio	±1%	±0.2%
Limit detectability	5 g/l	1 g/l
Measurement precision near 100 g/l	6 g/l	±1 g/l

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