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Photoacoustic characterization of different food samples

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Photoakustische Charakterisierung von verschiedenen Lebensmitteln

Zusammenfassung. Die photoakustische Spektroskopie im Wellenlängenbereich von 350–700 nm hat sich als nützliches Instrumentarium zur Unterscheidung verschiedener undurchsichtiger, Licht streuender Proben erwiesen. Spektrale Eigenschaften pulverisierter Nahrungsmittelproben unterschiedlicher Korngrößen und Farbe wurden beobachtet. Die Ergebnisse zeigen, daß der Einsatz der Photoakustik in der Qualitätskontrolle für die Nahrungsmittelindustrie möglich ist.

Abstract. Photoacoustic spectroscopy in the 350–700 nm range proved a useful tool for discriminating between a variety of opaque, light-scattering samples. Spectral features originating from powdered food specimens of different colour and grain size were observed. These results suggest the feasibility of photoacoustics for quality control in the food-processing industry.

Introduction

In the past photoacoustic spectroscopy (PAS) was used in studies of inhomogeneous and light-scattering powdered samples [1–5]. Since de-excitation processes in these samples proceed along non-radiative channels, thermal excitation spectra of powders correlate well with their absorption spectra [6].

Biological specimens (such as food products) are complex mixtures of either chemically diverse compounds or chemically related molecules possessing significant differences in physical properties. As many food products are also powders, PAS might be useful for quality control in the food-processing industry [3, 7–9]. Establishing more objective selection and characterization criteria for flours is an example for potential PAS application in practice. Likewise, cosmetic qualities of foods have become increasingly important during recent years. As a result colour (just as quality, and nutritional factors) has achieved a more pre-eminent position for the consumer [10]. New techniques and instrumentation for colour measurements are therefore considered as useful additions to the laboratory.

It is well-known [1, 6, 11, 12] that magnitude of the PA signal is directly proportional to the fraction of energy absorbed by a sample. The absorbed energy in its turn is a function of light intensity distribution in the sample, which, when multiple scattering plays an important role, differs from that predicted by Beer's law. The physical effect of light scattering, which is also wavelength-dependent, is to reduce the optical penetration depth of the radiation into the sample [13]. In photoacoustic (PA), light scattering affects the PA signal in two different ways. In the first place there is a scattering on the cell walls that leads to correspondingly increased intensity of light in the cell, thereby giving rise to the acoustic signal. Moreover, light intensity distribution is influenced by internal scattering due to reflections and scattering on the surface of grains. When grain particles are loosely packed and relatively big, the light can reach deeper layers (under the sample surface) at distances that exceed the effective illumination depth (or effective optical penetration depth) of powdered samples (i.e. thickness across which the light intensity has decreased to a practically negligible value). It is the effective illumination depth that characterizes the intensity distribution in the cell. Although this quantity parameter is important whenever comparison of PA spectra of powdered samples of different grain size is anticipated, surprisingly no reliable method for its determination has been proposed so far. The main objective in undertaking the study described in this paper was to obtain PA spectra (350–700 nm range) of different flour and other powdered food specimens and to collect more data on parameters involved in the process of PA signal generation.

Materials and methods

The experimental set-up used to record the spectra of flours (all specimens were kindly provided by Gabona Tröszt, Budapest, Hungary) and samples of commercially available instant coffee and spices is shown in

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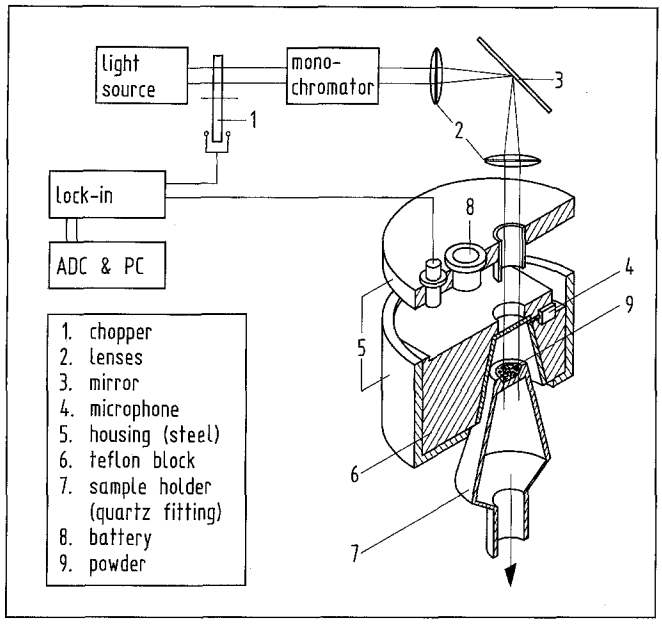

Fig. 1. The set-up used for measuring photoacoustic (PA) spectra of powdered flour samples: ADC, analogue to digital converter; PC, IBM compatible computer

Fig. 1. It comprises a 400-W xenon lamp (ILC Technology) the polychromatic beam of which was mechanically chopped (1) before entering Jobin-Yvon H-20 monochromator (spectral resolution of 8 nm). The beam was focused into a quartz cell (see detail in Fig. 1) by means of two glass lenses (2) and a plane mirror (3). The sample holder (7) is a cup

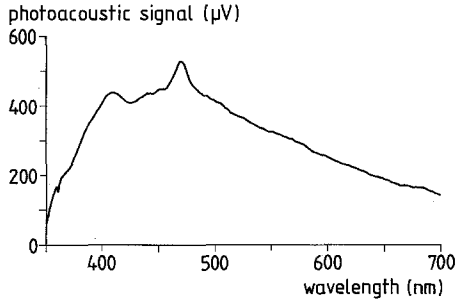

Fig. 2. Photoacoustic spectrum of carbon black

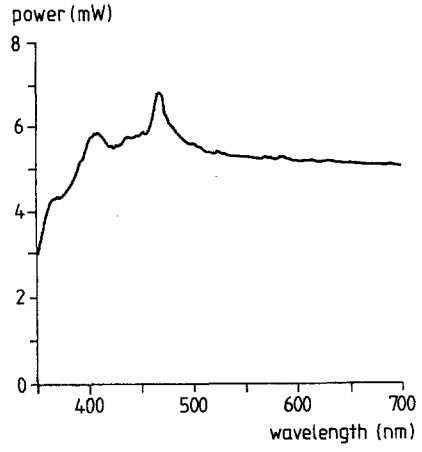

Fig. 3. Power spectrum of radiation incident onto the PA cell (used for normalization of the PA signal)

10 mm in diameter and 2 mm deep (distance measured from the bottom). The cell window and sample window are separated by a distance of 2 mm. The cell design allows easy loading (quantity of sample used in each measurement was kept as constant as possible) and enables removal of sample (9) without a need to change the position of the cell. This greatly faciliated performance of the measurements since no problems associated with alignment were experienced. Pressure fluctuations were measured with a Knowles EA-1954 microphone (4) powered by a battery (8). The signal was fed into Standford Research SRS preamplifier, the output of which was connected to a Standford Research SR510 lock-in amplifier. The output signal of the lock-in was interfaced to a IBM-compatible computer. The scan speed of the step motor was 1 nm/s; 40 data points were taken each second. The arithmetic averages of these 40 points were used to construct the spectra displayed in Figs. 4–8. The chopping frequency used in all the measurements was 70 Hz because the signal to noise ratio was found optimal at that value. The thermal diffusion lengths (μ) of carbon black, air and flours at this frequency are 640, 313 and 20 μm, respectively. For carbon black, the thermal diffusion length is much larger than the dimension of the grains whereas for flours it is of the same order of magnitude.

In photoacoustics it is customary to normalize the PA spectra in order to eliminate wavelength dependence of the source. In previous studies [2–5, 7–9, 11, 12], the PA spectra of powders were normalized to the PA spectrum of carbon black taken as a reference sample. The basic idea behind such as approach is the assumption that carbon black absorbs equally strongly throughout the entire spectral range. However our own measurements indicate (Figs. 2 and 3) that the PA signal of carbon black and the power spectrum of the lamp show the same trend for wavelengths shorter than 500 nm. Above this wavelength the PA signal of carbon black decreases (Fig. 2), whereas the power of the xenon lamp (showing several peaks between 400 and 500 nm) remains nearly constant (Fig. 3). Below 350 nm the measurements are no longer accurate because of a substantially reduced signal to noise ratio due to lens absorption. The PA spectra (Figs. 5, 7, and 8) were normalized by ratioing their magnitudes (recorded at 5-nm incremens) directly to the power spectrum of the xenon lamp. The reproducibility of the set-up before each measurement was tested consistently by measuring the PA signal from carbon black at two preselected (maxima at 400 and 467 nm) wavelengths.

Results

Barium sulphate (a white powder) was investigated first. For such a sample the effective gas volume is very close to that used in actual measurements. The spectrum (normalized to a power spectrum of the xenon source) is wavelength-independent in the spectral range 350–700 nm (Fig. 4A), in contrast to that normalized to the PA spectrum (Fig. 4B) of carbon black (conventional normalization). Since wavelength dependence in Fig. 4 resembles that expected for the white sample, the normalization procedure suggested here seems justified.

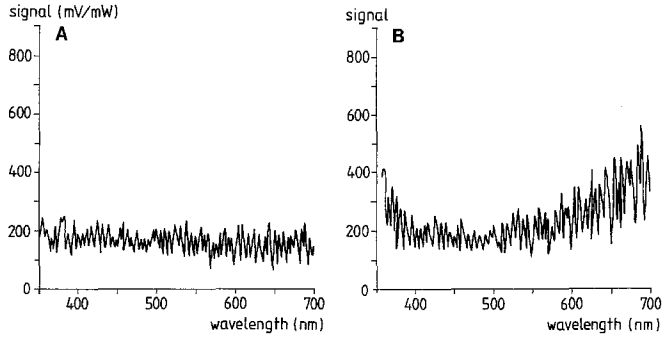

Fig. 4A,B. Photoacoustic spectra of $BaSO_4$ powder normalized according to the method proposed here (**A**) and ratioed to carbon black (**B**)

Powder spectra of flours

The flour specimens investigated all differed in colour and grain size. There were a few white flours such as fine and normal bread, pastry and rice flours. The soya flour, corn grits and corn flour are yellow, whereas whole wheat flour, wheat flour and rye flour contained some brown-coloured grains. Finally, dried pea flour has a greenish colour.

Figure 5A shows PA spectra of white bread flours; all had absorption bands around 370, 385 and 410 nm. Above 410 nm the PA signal decreases rapidly and drops to a nearly zero at 700 nm. The grain size affects the magnitude of the signal; as an example normal bread flour can be discriminated from fine bread flour (Fig. 5A). The signal from fine bread flour is lower than that obtained with normal bread flour because the grain diameter (d) is smaller than the thermal diffusion length ($d<\mu$); therefore less heat is deposited into grains. Figure 5B shows the PA spectra of yellow-coloured specimens. Again, absorption bands common to all specimens were observed near 370, 385 and 410 nm. In general, the overall spectral features of yellow flours appeared broader than for white flours. The effect of different grain size on amplitude of the PA signal can also be seen

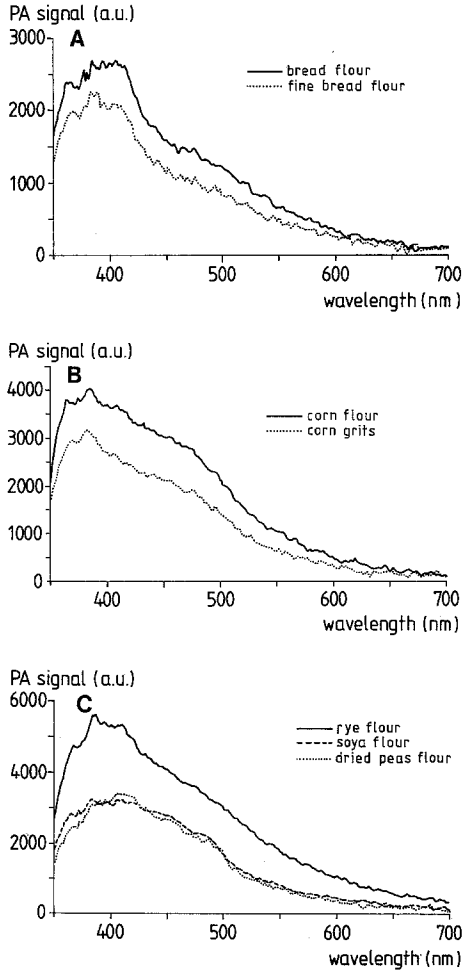

Fig. 5A–C. Photoacoustic spectra of flours. **A** Bread flour and fine bread flour. **B** Corn flour and corn grits. **C** Rye flour, soya flour and dried pea flour: a.u., PA signal divided by the power of the xenon lamp (Fig. 3)

Table 1. Results of the measurements on powdered flour samples. The magnitude of the signals (S′) and their relative magnitudes at three different wavelengths (385, 410, 475 nm) are given

No.	Flour brand (colour)	S'_{385} (–)	S'_{410} (–)	S'_{475} (–)	S'_{385}/S'_{475}	S'_{410}/S'_{475}	S'_{385}/S'_{410}
1	Bread flour (w)	1.00	1.00	1.00	1.00	1.00	1.00
2	Fine bread flour (w)	0.85	0.77	0.71	1.20	1.08	1.10
3	Pastry flour (w)	0.59	0.61	0.53	1.11	1.15	0.97
4	Wheat flour (b)	0.61	0.58	0.59	1.03	0.98	1.05
5	Rye flour (b)	2.13	2.02	2.46	0.87	0.82	1.05
6	Whole wheat flour (b)	1.59	1.40	1.59	1.00	0.88	1.14
7	Corn flour (y)	1.54	1.39	1.90	0.81	0.73	1.11
8	Corn grits (y)	1.19	0.99	1.30	0.92	0.76	1.20
9	Soya flour (y)	1.22	1.22	1.58	0.77	0.77	1.00
10	Dried peas flour (g)	1.18	1.29	1.50	0.79	0.86	0.91
11	Rice flour (w)	0.52	0.43	0.44	1.18	0.98	1.21

w, white; b, brown; y, yellow; g, greenish

when inspecting spectra of corn grits and corn flour. If the grain size is (much) larger than the thermal diffusion length, i.e. $d \gg \mu$ (such as for corn grits), the signal decreases because fewer grains are irradiated. In addition, the surface/volume ratio decreased with increasing grain size. Figure 5C shows the PA spectra of three differently coloured (yellow, green and brown) flours. The dried pea flour is the only sort that has a maximum signal at 410 nm. Soya flour exhibits a broader spectrum whereas rye flour resembles that of the bread flour and also produced the highest signal of all the samples.

In order to quantitatively compare different flours, the magnitude S of the PA signals at 385, 410 and 475 nm were normalized to the signals obtained with normal bread flour at the same wavelengths, yielding the dimensionless ratios (S′) shown in the first three columns of Table 1. Careful inspection of all the spectra suggests that most differences are observed near 475 nm.

From Table 1 there is a direct relationship between the magnitude of the PA signal and the colour of the flour: compare, for example, corn powders (7 and 8) to wheat (4) and rice (11) flours. Compared to coloured flours, white flours yielded only a small signal. The spectrum shape also provides some informaiton about the colour of samples. For example, yellow-coloured flours (corn and soya) can be discriminated from other coloured specimens (columns 4 and 5). The ratio S'_{385}/S'_{475} (column 4 in Table 1) decreases in the order of sample colour. The reproducibility of the measurements was satisfactory (error was typically within 5%).

The light distribution in powders

Both internal reflections within the grains as well as the wavelength-dependent reflectance (R) at the surface of flour grains considerably affected [14] the magnitude of the PA signal (as shown in Table 2).

Next, the role that effective illumination depth (defined above) of the radiation plays in the generation of PA signal in various flour specimens was explored in more detail. This was done by comparing the PA signals measured with the

Table 2. The wavelength-dependent reflectance (R) for a typical flour specimen [14]

Wavelength (nm)	R (–)
400	0.75
500	0.87
600	0.94
700	0.97

cell loaded with a specific flour to those obtained from a thin layer (≈0.5 mm) of the very same flour specimen placed on top of a relatively thick backing layer of carbon black. Pure carbon black produced typically a miximum PA signal of 500 μV at 467 nm (Fig. 2) whereas the signal originating from pure flours at the same wavelength varied in the 10–20 μV range (Fig. 6).

In a two-layer sample (flour on top of carbon black) an increase in the PA signal is expected for larger effective illumination depths. Even a minor fraction of transmitted light is sufficient to produce a PA signal with a magnitude that might be comparable to that of the flour. The contribution of carbon black to the signal may be estimated by comparing the non-normalized signals from pure flour to signals obtained from the very same flour on top of the carbon black. Two spectra showing the largest overall difference are depicted in Fig. 6. For soya flour (Fig. 6A), the differences were not very obvious at shorter wavelengths and the contribution of carbon black (trace a) became significant above 500 nm. For larger grains, carbon black prevailed (trace a in Fig. 6B) over that of wheat-meal (trace b in Fig. 6B). The largest PA signal due to the contribution of carbon black (approx. 50 μV at 467 nm) was about 10% smaller than that obtained when the cell was loaded with pure carbon black For small grains (Fig. 6A) the amplitude decrease was substantially lower (about 2%). Scattering also reduces the optical penetration depth and at shorter wavelengths scattering is larger than at longer wavelengths, as seen in Fig. 6.

The above measurements suggest that due to a short effective illumination depth the PA signal is generated in the uppermost layer (0.5 mm) of powdered sample (the effective ilumination depth increases for larger grains as concluded by careful inspection of traces a and b (Fig. 6)). This implies that with the present cell design radiation does not reach the cell walls, which has two important consequences. First, the contribution of the cell walls is minimized and secondly only small quantities of flour are needed to produce satisfactory spectra.

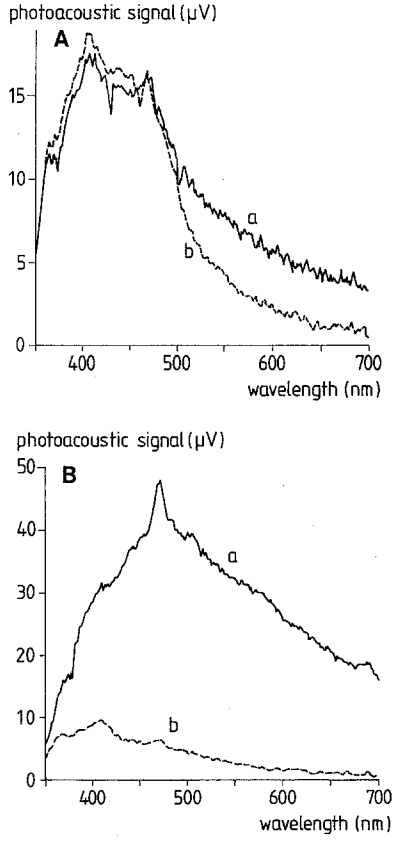

Fig. 6A,B. Photoacoustic spectra of carbon black covered by a thin layer of flour (*a*) and of the flour alone (*b*). **A** Soya flour. **B** Wheat meal

Photoacoustic spectra of spices and coffee

In order to demonstrate the feasibility of the PA method, spectra of a few more food products were measured. Figure 7 features spectra of hot pepper, black pepper and pizza spices, whereas Fig. 8 shows PA spectra of two instant coffee brands: Paloma, Compack Budapest and Nescafe (CAP) Collombie (100% arabica beans). At first sight, the samples appear very much alike, but their PA spectra are quite differ-

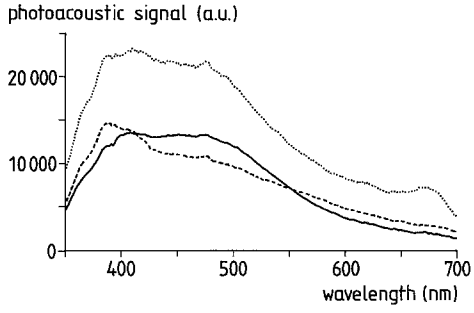

Fig. 7. Photoacoustic spectra of three different spices. (–) Hot pepper; (– – –) pizza spices; (. . . .) black pepper

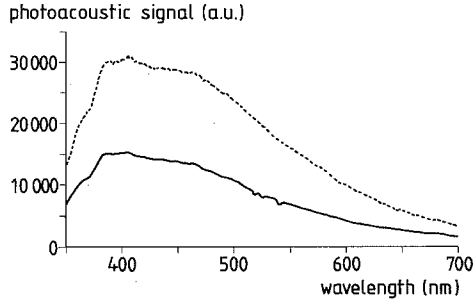

Fig. 8. Photoacoustic spectra of instant coffee. (–) Coffee Paloma; (– – – –) Nescafe (CAP)

ent. We conclude that the PA technique apears capable of producing reproducible spectra of powdered food samples (discrimination of different flours based on origin, colour and grain size is possible), suggesting its usefulness for quality control purposes.

It was shown that light intensity distribution near the surface increases due to the scattering and that a large fraction of incident light is reflected out of the sample. For this reason no energy can reach the bottom of the sample; in addition, only small quantities of sample are required. The use of quartz optics will further improve the sensitivity of the PA method. This might eventually also allow the use of the PA method for determination of basic amino acids, present in almost all biological samples.

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