

On the Use of Photoacoustic Spectroscopy for Investigating Adulterated or Altered Powdered Coffee Samples

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Modern photoacoustic techniques have been employed to assess the concentration of commonly encountered adulterants in powdered coffee samples. The feasibility of the method is demonstrated for samples containing a mixture of roast ground parchment, corn, and barley with pure coffee powder. Extension to multicomponent mixes is discussed.

The photoacoustic (PA) effect (Rosencwaig, 1980; Rosencwaig and Gersho, 1976; Aamodt et al., 1977; Cesar et al., 1979) has been recognized in the last few years as an important tool for studying optical absorption spectra of crystalline, powdered, and amorphous solids. The success of this new spectroscopic technique is essentially due to the fact that only the absorbed light is converted into pressure fluctuations in the gas cell (see Figure 1). The primary source of the acoustic signal in the cell arises from the periodic heat flow from the solid to the surrounding gas, as the solid is cyclically heated by the absorption of chopped light. Only a relatively thin layer of gas adjacent to the surface of the solid is assumed to respond thermally to the periodic heat flow from the solid to the surrounding gas. This boundary layer of gas is then regarded as a piston, generating the acoustic signal detected in the microphone. Since the magnitude of the periodic pressure fluctuations in the cell is proportional to the amount of heat emanating from the solid absorber, there is a close correspondence between the strength of the acoustic signal and the amount of light absorbed by the solid.

The field of photoacoustics has undergone extensive development in recent years and has made its way into the realm of the available techniques for assessing structural, compositional, etc. changes in solid samples (Rosencwaig, 1980). As part of our program aimed at exploring the potential of photoacoustics for evaluating some parameters of interest to the foodstuff industry, we report here a procedure developed to detect and quickly quantify presumed adulterants or alterants in roasted ground coffee. The adulteration is commonly accomplished by addition of roasted ground cereal grains, or their equivalent, and has become an important problem for those engaged in quality control in the packaged coffee industry. Needless to say, the amount and kind of adulterant are so chosen as to prevent direct visual or olfactive detection and may indeed go unnoticed even in the beverage brewed from such coffee mixes. It is no surprise, then, quantitative analysis of admixed adulterants frequently calls for elaborate chemical evaluation of coffee samples. A preliminary account of this work has been previously communicated (Lima et al., 1983).

METHODS AND MATERIALS

Our approach to the problem of evaluating adulterated coffee samples was based on the assumption that the modification of pure coffee by the admixture of some amount of one or more of the commonly used adulterants

(e.g., coffee parchment, corn, and barley) would make itself evident when the PA signals from similarly prepared, pure and adulterated coffee samples were compared. In fact, after a few attempts it became apparent that under our working conditions (equal mass samples tailored to have the same shape, compactness, and graininess) a definite trend was emerging regarding the PA signal dependence on the adulterant concentration (fractional weight) in the sample. We turned then on to a systematic investigation. For several mixes comprising binary combinations of coffee and parchment, barley, or corn, we have measured the PA signal as a function of the adulterant concentration. The results are shown in Figures 2-5. The data were acquired by exposing the samples to Ar/Kr ion lasers with beam power typically set at about 80 mW (a few different lines were used) with an otherwise standard gas microphone PA detection set up operating at a 300-Hz chopping frequency. Pill-shaped compressed (1-ton) coffee samples were made and mounted in the PA cell fitted with a Knowles microphone. The samples, all with the same 10-g total mass, were obtained by varying the relative amounts of coffee and adulterant in the mixture. In all cases, the adulterant was previously roasted and ground to attain the usual forms commonly found in adulterated products. Both coffee and adulterant were then passed through finely meshed sieves to secure approximately the same small-spread distribution of grain sizes in all samples. The linear behavior of the PA signal vs. concentration (weight/weight) is definitely evident in Figures 2-5. The solid lines represent a least-squares fit to the data. The incident wavelengths are also indicated in these plots.

RESULTS AND DISCUSSION

The well-known theoretical description of the PA effect (Rosencwaig, 1980) yields a very clear ground on which to interpret the overall behavior of the PA signal from our samples. According to this theory, the PA signal S is described by

$$S = A \frac{\beta(\lambda)}{(k\rho C)^{1/2}} \quad (1)$$

where $\beta(\lambda)$ is the optical absorption coefficient at wavelength λ , k is the thermal conductivity of the material, ρ is the density, and C is the specific heat. All other factors, such as the gas thermal properties and the modulation frequency, have been lumped together in the constant A . For a mixture of materials 1 and 2, the PA signal can then be represented by

$$S = cS_1 + (1 - c)S_2 = S_2 + (S_1 - S_2)c \quad (2)$$

where c is the concentration of material 1 relative to the host material 2 and S_1 and S_2 are the bare signals from samples 1 and 2 and depend on the ratio of the optical absorption coefficient to the thermal properties, as given

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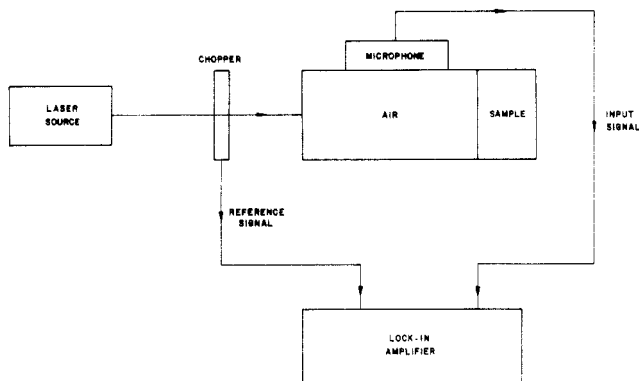


Figure 1. Typical PA experimental arrangement.

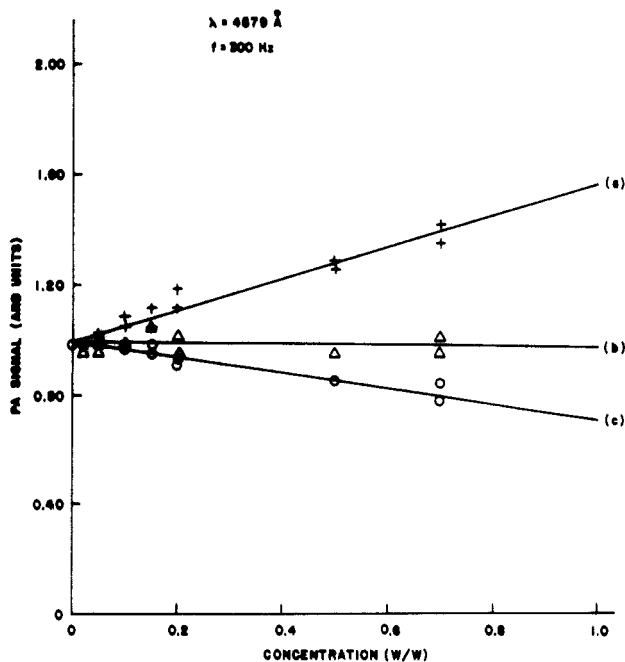


Figure 2. PA signal for the coffee-parchment (a), coffee-barley (b), and coffee-corn (c) mixtures, as a function of the adulterant concentration (weight/weight), at the indicated wavelength (λ) and modulation frequency (f).

by eq 1. Equation 2 accounts for the observed linear dependence of the PA signal on the adulterant concentration. Furthermore, it tells us that depending upon the relative sizes of the optical and thermal properties of the two components (i.e., $S_1 - S_2$), the slope, at a given wavelength, can be either positive or negative. For instance, take the case of the coffee-parchment mixture: at the wavelengths used in our experiment the difference $S_1 - S_2$ is rather pronounced and this is reflected in the large positive slope of the straight line fitted to the coffee parchment data shown in Figures 2-5. The case of the coffee-corn mixture affords an example of well discernible but negative slope. In contrast, the small difference between the ratios of optical to thermal properties for coffee and barley is quite apparent from the very small slopes displayed by the coffee-barley mixture curves in those figures. Overall, these slopes, at each wavelength, characterize the binary mixture system under consideration. To some extent then they work as the adulterants fingerprints.

The foregoing discussion suggests a general procedure for the determination of adulterants presumed to be present in a sample. First, the PA signal is measured from similarly prepared samples of pure substance (coffee in our case) and of pure adulterant (parchment, corn, and barley in our case). A previous scan of the sample using pho-

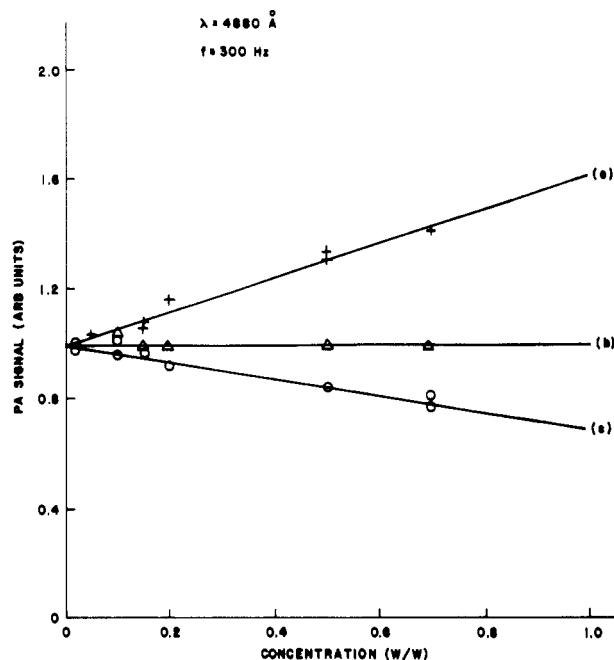


Figure 3. PA signal for the coffee-parchment (a), coffee-barley (b), and coffee-corn (c) mixtures, as a function of the adulterant concentration (weight/weight), at the indicated wavelength (λ) and modulation frequency (f).

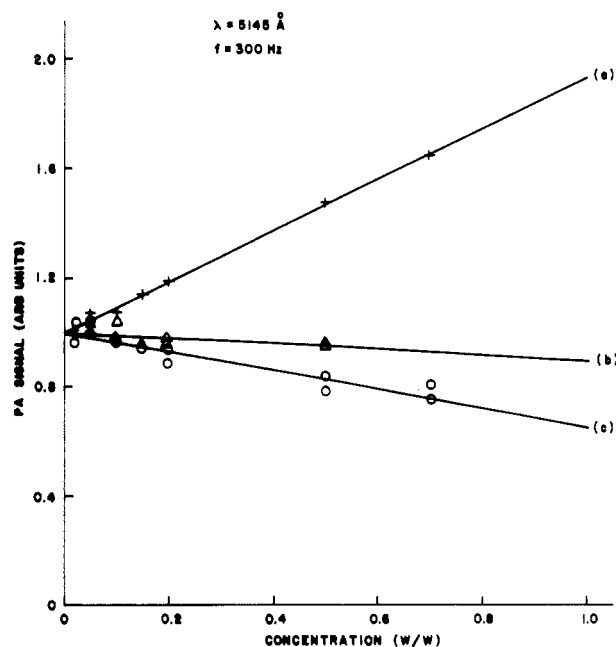


Figure 4. PA signal for the coffee-parchment (a), coffee-barley (b), and coffee-corn (c) mixtures, as a function of the adulterant concentration (weight/weight), at the indicated wavelength (λ) and modulation frequency (f).

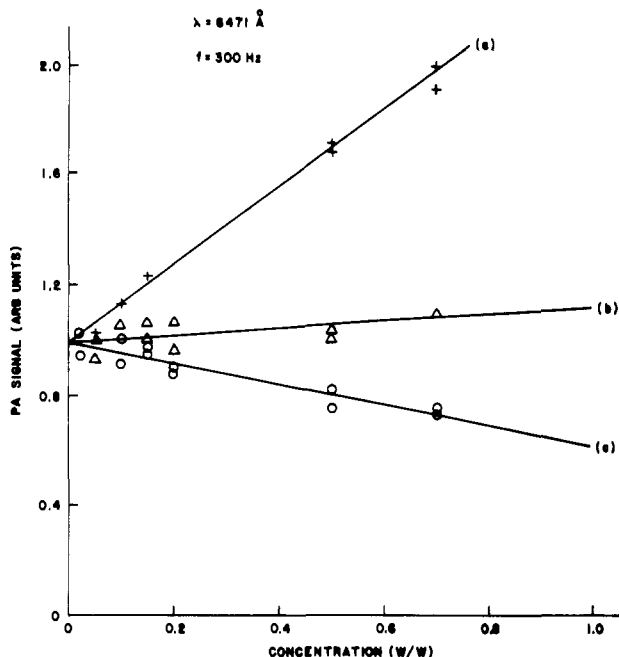
toacoustic spectroscopy may help to ascertain the adulterants present. Second, following the procedures given in this work, the linear behavior is checked for each of the samples comprising the substance-adulterant binary mixtures of interest and the corresponding slopes are obtained. The measured PA signal $S(\lambda)$ of the adulterated substance sample under analysis can be expressed as

$$S(\lambda) = S_p(\lambda) + \sum_{i=1}^N m_i(\lambda) f_i \quad (3)$$

where $S_p(\lambda)$ is the pure substance PA signal at wavelength λ , $m_i(\lambda)$ is the slope corresponding to the i th adulterant-substance binary mixture determined as above at wave-

Table I. Slopes of the Binary Mixture Plots Deduced from Figures 2-5 and the Photoacoustic Signals (in mV) at the Indicated Wavelengths and a Chopping Frequency of 300 Hz

wavelength, Å	coffee-parchment mixture, slope $\times 10^3$	coffee-corn mixture, slope $\times 10^3$	coffee-barley mixture, slope $\times 10^3$	pure coffee sample signal, mV	quaternary mixture sample signal, mV
4579	5.70	-2.90	-0.30	2.250	2.280
4880	6.20	-3.10	-0.55	2.040	2.070
5145	9.40	-3.50	-1.00	1.870	1.930
6471	14.50	-3.70	1.40	0.307	0.477

**Figure 5.** PA signal for the coffee-parchment (a), coffee-barley (b), and coffee-corn (c) mixtures, as a function of the adulterant concentration (weight/weight), at the indicated wavelength (λ) and modulation frequency (f).

length λ , and f_i is the concentration of the i th adulterant in the sample (to be determined). Thus, with the data collected as indicated above for N different wavelengths (N = number of presumed adulterants in the mixture), one can set up a system of N linear equations like eq 3. By solving this system, one finally gets the values of the unknowns f_i .

As it can be readily appreciated from Figures 2-5, our procedure can discern adulterant concentration in a coffee-adulterant mixture down to the 1% region, which compares quite favorably with other current practices. We shall come back to this point below.

To give a fully worked demonstration of the above procedure, we have performed an experiment with a quaternary mixture using a coffee sample containing 10% parchment, 10% corn, and 10% barley. For this triply adulterated coffee sample, we have measured the PA signal at four wavelengths (4579, 4880, 5145, and 6471 Å). The values of the slopes for the various binary mixes at each of these wavelengths, as obtained from Figures 2-5, are given in Table I. Also given in Table I are the values of the PA signal, at each wavelength, for both the pure coffee sample and the triply adulterated coffee sample. Notice that since we have only three unknowns f_1 , f_2 , and f_3 (the concentrations of parchment, corn, and barley, respectively, in the sample) but have four linear equations like eq 3, one for each wavelength, we can use this redundancy to check our procedure for consistency in the determination of the f_i 's from any of the selections among the four possible combinations comprising any three of the four distinct wavelengths. The values of the f_i 's as determined

Table II. Consistency Check (Independence on the Wavelength Set Chosen) for the Data Reduction Procedure for Determining Adulterant Concentrations in a Quaternary Mixture of Coffee + f_1 % of Parchment + f_2 % of corn + f_3 % of Barley

set of wavelengths, Å	f_1 , %	f_2 , %	f_3 , %
4579/4880/5145	13.3	14.2	15.2
4579/4880/6471	14.3	16.2	15.7
4579/5145/6471	13.9	15.1	17.6
4880/5145/6471	13.7	14.6	17.9
av values	13.8	15.1	16.6
spread (r.m.s.)	0.4	0.9	1.3

from each of these combinations are collected in Table II. We shall quote as the experimentally determined values of f_1 , f_2 , and f_3 the corresponding averages given in Table II. We have thus for the experimentally determined concentrations of parchment, corn, and barley the values 13.3 ± 0.4 , 15.0 ± 0.9 , and 16.6 ± 1.3 , respectively. The agreement between the nominal values (sample preparation) of the concentrations and the above evaluation, deduced from photoacoustic measurements, is quite good for the cases of corn and parchment. However, for the case of barley the agreement is not so good. The reason for this is that this particular adulterant happens to have thermal and optical responses, at the wavelengths considered, that resemble very closely those for pure coffee, which results in the small slopes seen in Figures 2-5, as we have already pointed out. It is possible that by using infrared radiation one may attain better resolution for barley in ternary, quaternary, or more complex coffee mixtures. The consistency of our procedure (independence of the f_i 's on the particular choice of wavelengths) is fully supported by the relatively small spread of the values of the f_i 's, as deduced from the measurements performed at each set of wavelengths.

Finally, we would like to comment on the possible relevance of the above-described PA-based method for the assessment of adulterants or alterants in foodstuffs, the control of which is of interest to the food industry. In fact, such control is an important demand, for instance, for those who need to maintain legally enforced quality standards or, in some other cases, for those who deal with products in the form of few-component solid mixtures and who need to specify composition in their product labels. Both situations are the case, for instance, in the powdered coffee industry. On one side, the sale of packaged powdered coffee in the major coffee-consuming countries is generally subject to specific regulations dealing either with the forbidden addition of adulterants or with the allowed, but controlled, admixture of flavor or aroma alterants (e.g., the admixture of declared amounts of chicory to coffee seems to be a common practice in some coffee-consuming European countries). As to adulteration, random sampling of the product sold by retailers has often uncovered fraudulent admixtures (usually roasted corn and/or coffee parchment) frequently within the 5-10% range, though reports of 20%, or more, adulterations are not at all uncommon (Cortez, 1983). It is thus clear that to the pack-

aged coffee industry, to give one example, our new procedure, as reported above, may prove of significant practical interest. To contrast it with a current situation, it should be mentioned that, most commonly, the available methods for assessing coffee adulteration fall, essentially, in two categories. To one of them belong those based on rather expensive and complex identification, and quantification, of some chemical constituents unequivocally associated with the adulterant only, and/or based on the search for noticeable changes in the relative content of some specific coffee related chemical constituents as compared to known values for pure coffee standards. To the other category belong the more popular, but rather coarse (low resolution), practice of directly confronting microscope-aided observations of equivalent samples of pure and adulterated powdered coffee samples (in the case of parchment this process might eventually allow for some kind of mechanical separation of the adulterant). Once some difference in texture is observed, the process is often followed by the evaluation of water-soluble solids obtained by strong extraction from coffee brewed by using the mixture under analysis. The residual content after a given amount of the beverage is evaporated is measured and compared against a similarly prepared sample from the beverage made with pure coffee. Aside from the inability of the method to tell apart different adulterants, all such methods suffer from rather poor resolution, not to mention the fact that marked alterations in the residue can be brought about by other sources intervening in the process

(Cortez, 1983). Therefore, it does seem that the present method of photoacoustic evaluation of solid mixtures provides an adequate alternative for use in the powdered coffee industry, as well as in other similar food industries, one which compares quite favorably with other available methods. Needless to say, the same procedure applies to the determination of relative concentrations of any kind of solid (powdered) multicomponent mixture provided the aforementioned conditions are obtained.

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High-Performance Liquid Chromatographic Analysis of Fenridazon-potassium in Wheat Grain and Straw

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A high-performance liquid chromatographic residue analytical method is described for the analysis in wheat grain and straw of the chemical hybridizing agent fenridazon-potassium, potassium 1-(4-chlorophenyl)-1,4-dihydro-6-methyl-4-oxopyridazine-3-carboxylate. The method employs mild alkaline extraction, copper-activated Chelex 100 column chromatography, and liquid-liquid partition. Quantitation is by ion-pair, reverse-phase liquid chromatography with UV detection at 285 nm. Recoveries averaged $87.4 \pm 11.3\%$ for wheat grain and $86.2 \pm 16.8\%$ for wheat straw. Method sensitivity is 0.05 and 0.10 ppm for grain and straw, respectively.

Fenridazon-potassium, potassium 1-(4-chlorophenyl)-1,4-dihydro-6-methyl-4-oxopyridazine-3-carboxylate, is a wheat hybridizing agent. The hybridizing agent inhibits wheat pollen formation while maintaining the normal fertility of the female portion of the wheat flower.

Metabolism studies in wheat utilizing radioisotopically labeled fenridazon-potassium have demonstrated that residue resulting from use is the parent compound (Fisher and Peirson, 1978). Residue levels of field samples are greater than 0.10 ppm for wheat grain and straw. Therefore, we developed a highly sensitive residue analytical method that determines the presence of the hybridization agent in wheat.

Samples are homogenized and extracted with petroleum ether to remove lipophilic constituents. Fenridazon-potassium is removed from the wheat grain or straw matrix by sodium bicarbonate extraction and separated from coextractives by column chromatography through copper-activated Chelex 100 chelating resin and liquid-liquid solvent partition. Quantitation is by ion-pair, reverse-phase high-performance liquid chromatography (HPLC) at 50 °C with UV detection at 285 nm. Calibration is performed by peak height using external standards. The limit of quantitation for wheat grain and straw is 0.05 and 0.10 ppm, respectively.

EXPERIMENTAL SECTION

Chemicals and Reagents. All organic solvents were HPLC grade from Burdick and Jackson. Ammonium hydroxide and hydrochloric acid were Mallinckrodt reagent

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