Dual-Beam Thermal Lens Measurement of Condensed-Phase Sample at CO₂ Laser Wavelengths: Detection of Octadecanoic Acid in Carbon Tetrachloride

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Detection of monobasic, straight-chain saturated fatty acid (octadecanoic C18:0) in CCl₄, based on the thermal lens effect after excitation by CO₂ laser radiation at 934.9 cm⁻¹, is described for the first time. The achieved limit of detection (LOD = 0.3%) is comparable to that of the transmission infrared technique. Possibilities for further improvements in sensitivity and detection limit are also discussed.

Index Headings: Thermal lensing; CO₂ laser; Fatty acids; Octadecanoic acid; Trace detection.

INTRODUCTION

Fatty acids, forming the major constituents of edible oils, are either bound to glycerol (esterified) or dissolved in oil as free fatty acids (FFAs). The total content of FFAs in edible oil, considered as one of potential quality indicators, is usually expressed in percents. In oil of acceptable quality the tolerable FFA level should not exceed one percent. From this point of view a rapid, on-line method possessing adequate sensitivity is desired for quality control during technological processing of oil.

In order to determine the total FFA content, the acids can be analyzed indirectly by converting them into colored adducts which are subsequently measured colorimetrically.[1,2] More frequently, the determination of FFAs is carried out directly by titration[1] or by using spectroscopic methods.[1,3] The latter group of methods best suits the needs of quality control in oil-processing technology. In fact, absorption spectroscopy in the infrared region has been exploited for direct quantitative and qualitative studies of oils for some time,[1,3] despite the fact that vibrational absorption coefficients are almost one order of magnitude weaker than electronic absorption coefficients. For a conventional infrared absorption instrument, the minimum detectable concentration of FFAs is on the order of a few tenths of a percent. Since this detection limit does not meet the requirements for a practical oil-quality monitor, time-consuming and off-line titration techniques are still widely used.

In the past years, the application of lasers in the field of chemical analysis has increased substantially because of the specific characteristics of laser radiation. The class of photothermal and related spectroscopies has greatly benefited from increases in source intensity, leading to a variety of detection schemes that have improved the detection limits considerably. Photothermal detection in

combination with chromatography and electrophoresis separation techniques is a good choice whenever very high sensitivity and specificity are needed at a capital cost lower than that of mass spectrometry. Although photothermal detection schemes have been shown to provide both excellent sensitivity and low detection limits,[4] they are still not in widespread use. One of the possible reasons for this situation is the fact that nontunable lasers are generally used in photothermal experiments, restricting the range of wavelengths for absorption measurements. As novel, inexpensive, and compact lasers keep proliferating, the application of photothermal detection schemes is expected to expand in the immediate future.

Despite a considerable number of papers concerned with the use of thermal lens calorimetry for liquid-phase and low-absorbance measurement in the UV and visible regions, only one application of the same technique in the infrared (single-beam thermal lensing at 3.39 μm) has been reported so far.[5] This circumstance has probably occurred because of the high absorption coefficients of solvents in the infrared, and also because the so-called "enhancement factor" E, which characterizes the sensitivity of a thermal lens measurement, is inversely proportional to the wavelength of the laser source in a single-beam configuration. For the given solvent and the amount of incident power, the single-beam thermal lens absorption measurement in the infrared region will be less sensitive than at shorter wavelengths. Carter et al. have pointed out[5] that another difficulty, which arises when a single-beam thermal lens experiment is performed in the infrared, is the spot size dependence of the characteristic time constant (proportional to the wavelength-dependent radius of the pump source) and positional dependence of the thermal lens effect. These problems (except that of a high background absorption) are avoided when a dual-beam thermal lens technique is used.

Infrared spectra of FFAs, the undesirable constituents of edible oils, are similar to those of triglycerides, also present in oil. In the frequency region covered by the emission of discretely tunable and powerful infrared CO and CO₂ lasers, triglycerides are characterized by absorption bands of the ester group (1745 and 1170 cm⁻¹) and of unsaturated glycerides (965 cm⁻¹). On the other hand, characteristic for FFAs is the existence of the strong carboxylic C=O band at 1710 cm⁻¹ and, in particular, the OH out-of-plane vibration centered around 935 cm⁻¹ within the 950–920 cm⁻¹ spectral region.[1,3] The minimum degree of spectral overlap between FFAs and the
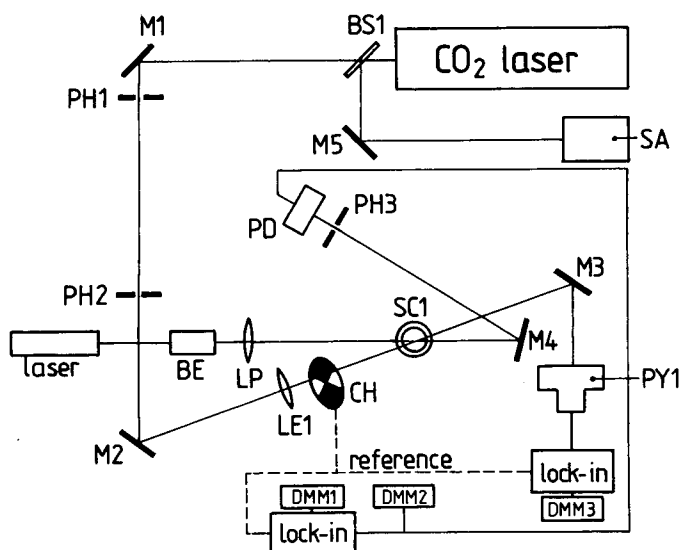
FIG. 1. Schematic diagram of the experimental setup used in this study.

bands of triglycerides is observed within the 950–920 cm^{-1} range (some degree of interference is expected only in the case of unsaturated triglycerides); hence this part of the spectrum appears as the candidate region for low concentration measurement of FFAs in oil.

In this work the infrared radiation (934.9 cm^{-1}) from a CO_2 laser was used to explore, for the first time, the potential of a dual-beam thermal lensing technique in measuring the concentration of octadecanoic acid dissolved in carbon tetrachloride that has a relatively low absorption coefficient (5 cm^{-1}) in the wavelength region of interest.[6] The results of this experiment are of potential interest in previously mentioned applications as well as for the development of new photothermal infrared detectors for chromatography.

EXPERIMENTAL

A schematic diagram of the experimental setup used in this study is shown in Fig. 1. The 150-mW radiation emerging from the home-made cw waveguide CO_2 laser was tuned to the $10P(30)$ transition at 934.9 cm^{-1} in order to excite the out-of-plane OH vibration of the FFA. At the ZnSe beamsplitter (BS1) a fraction of power is reflected into the Optical Engineering spectral analyzer (SA) for the identification of laser emission. The transmitted portion of the incident laser beam is by means of a plane mirror (M1), directed through two coaxial circular (adjustable) diaphragms (PH1 and PH2). The flat mirror (M2) reflects the modulated beam through a 20-mm-diameter and $f = 254$-mm ZnSe lens (LE1) (Janos Technology) that focuses the radiation into the sample cell (SC1). The focused beam reaches the cell after being periodically intercepted by a Scitec Instruments 300 mechanical chopper (CH) operating at 75 Hz. All measurements were performed in the static mode, i.e., with the nonflowing sample. After exiting the cell, the beam of the CO_2 laser is reflected on the plane mirror (M3) and sent to a home-made PVDF pyroelectric detector (PY1). The output of this detector (used to monitor the level of excitation power of the pump beam) is fed into a PAR 126A

lock-in amplifier, and the output of the latter is read from a Keithley 171 digital multimeter (DMM3).

Thermal lens effects were probed by an 8-mW He–Ne laser (Uniphase 1304 P), which provided a well-behaved source in terms of both long-term power and pointing stability. Its beam was first expanded (5:1) by a beam expander (BE) and then focused with a 150-mm lens (LP). The spot size diameter of the probe beam at the sample was about 4 mm; that of the pump beam was calculated to be 1.7 mm. Upon traversing the sample cell, the probe beam reaches a plane mirror (M4) where it is reflected and directed towards a PIN photodiode (PD) with a 2-mm × 2-mm photoactive surface, placed behind an adjustable diaphragm (PH3) serving as a pinhole. The signal from the photodiode is fed into the current-to-voltage converter (not shown in Fig. 1) before being processed by an EGG 905 single-phase lock-in amplifier. A digital multimeter (DMM2), Keithley Model 171, was connected in parallel with this lock-in amplifier. The relevant signals were calculated as ratios of the lock-in output to DMM1 (thermal lens effect values) and DMM2 (average probe beam intensity at the photodiode) readings. These ratios were further corrected in order to compensate for power fluctuations of the excitation beam (DMM3).

An exploded view of the sample cell is shown in Fig. 2. Two ZnSe flats (2) (each 25.4 mm in diameter and 3 mm thick) provided with an O-shaped Teflon® rim (3) of the appropriate size and thickness are mutually separated by means of a 200-μm Teflon® spacer (4). The latter is formed by two identical half-round washers that, when put together, define a small channel (used to accommodate the liquid sample) and form the central hole to allow undisturbed passage of the laser radiation through the cell along the horizontal axis. The assembled cell was held together in the aluminum housing (5) equipped with 100-μm-diameter tubing for admission of the sample. The two end caps (1), each provided with a central hole, are bolted to the housing.

Straight-chain saturated octadecanoic acid ($C_{18}H_{36}O_2$; specified purity grade >99%) was kindly provided by Unilever Research Laboratories, Vlaardingen, The Netherlands and used in this study without further purification. Standard solutions of octadecanoic acid (the concentrations varied from 0.9 to 4%) have been prepared by dissolving appropriate amounts of this FFA in carbon tetrachloride CCl_4.

RESULTS AND DISCUSSION

Initial efforts to detect the presence of octadecanoic FFA in CCl_4 were hampered by relatively poor pointing stability of the pump laser. The beam of the pump laser "wanders" in time, and hence the intensity profile at the location of the sample changes in an unpredictable manner. Fortunately, it was possible to substantially reduce the effect of beam walk on the measurement by inserting the beam expander (BE) in front of the focusing lens (LP), as shown in Fig. 1. The radius ω of the probe beam (initially 125 μm) increased, therefore, by a factor of about 15 to reach $\omega \approx 2$ mm at the sample. As a result, a relatively smaller area of the probe beam was affected by the pump beam walk. The performance of the setup improved significantly, but the residual effect of beam walk
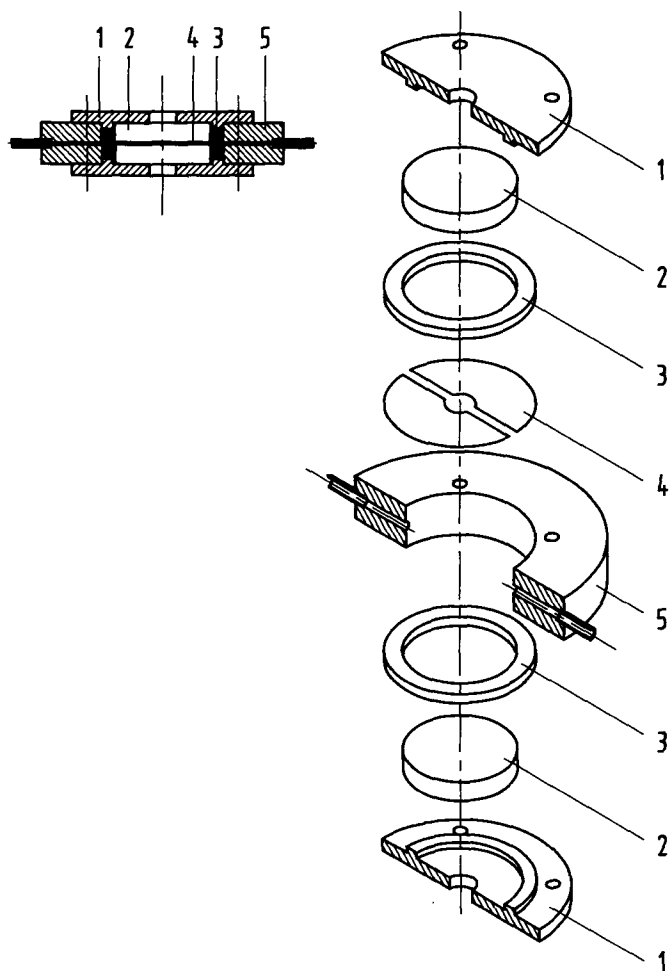
FIG. 2. Sample cell used for thermal lens detection of FFAs: end caps (1); ZnSe windows (2); Teflon® rim (3); spacer (4); and aluminum housing (5).
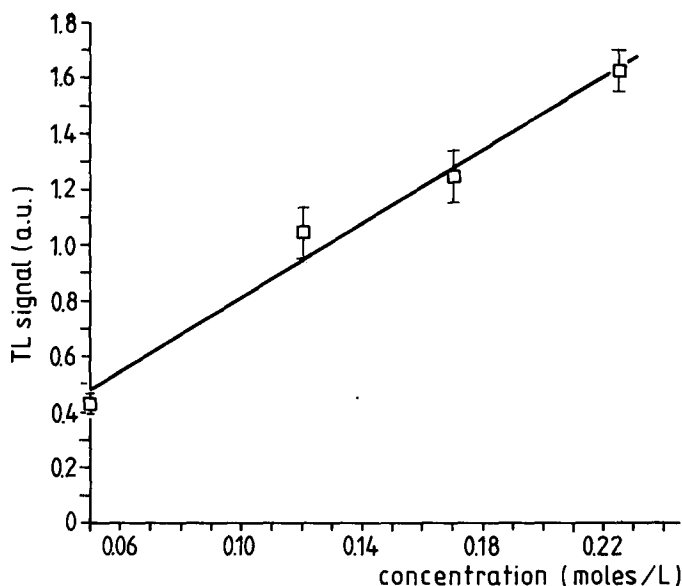

FIG. 3. Net normalized thermal lens signal plotted against the concentration of octadecanoic acid dissolved in carbon tetrachloride. The measurement is made at the $10P(30)$ transition of the CO_2 laser.

still impeded performance of reliable FFA concentration measurements at a level below 1%.

Despite a relatively short sample length, the effect of absorption of $10P(30)$ laser radiation by the samples (the molar absorptivity ϵ of octadecanoic acid is 79 L mole^{-1} cm^{-1})^3 must be taken into account. Therefore, measured signals S (from DMM1) in Table I were corrected by introducing a dimensionless factor F, defined as $F = (1 - T)/A \cdot \ln 10$, which accounts for power loss due to absorption in the sample. The parameters A and T (where $T = 10^{-A}$) are the absorbance and transmittance of the sample, respectively. Measured amplitude P_{pyro} (proportional to the amount of the pump laser power after passing through the cell) of the lock-in signal read from DMM3 must also be corrected with the use of $P_{in} = P_{pyro}/T$ to

obtain the amplitude P_{in}, corresponding to the actual incident power. In order to find the average relative power P_{av} inside the sample, one uses the relationship $P_{av} = P_{in} F$. The magnitude of the signal S (proportional to the thermal lens) measured by the lock-in amplifier and read from DMM1 is then divided by I_0 (average probe beam intensity displayed on DMM2) to get the values corresponding to thermal lens signal $TL = S/I_0$, i.e., relative changes in the probe beam intensity. Finally, values for normalized thermal lens signals TL_{nor} (listed in the last column of Table I) are calculated with the use of $TL_{nor} = TLP_0(1/P_{in}F)$ where P_0 is the initial value of P_{in} [in our case $P_0 = 65$ mV (at 75 Hz), corresponding to a pump laser power of 150 mW]. To obtain net thermal lens signals (plotted in Fig. 3), we consistently subtracted the background signal (0.2 a.u.) measured from the blank from the TL_{nor} values in Table I. The linear relationship ($R = 0.994$) between the net normalized thermal lens signal and concentration of the octadecanoic acid (Fig. 3) was found. On the basis of the slope of the calibration curve detection limit, 0.018 M or approximately 0.3% [at the signal-to-noise ratio (S/N) = 3] of octadecanoic acid was calculated for the given experimental system.

Despite the expected high sensitivity of the thermal lens method, this limit of detection (LOD) is comparable to values obtainable by conventional transmission infrared spectrometry. As a matter of fact, for the given experimental conditions (CCl_4 as solvent, 632.8-nm probe

TABLE I. Parameters and factors used for correction of measured signals and calculation of normalized thermal lens signals.[a]

C (%)	C (M)	A	T	$1/F$	P_{pyro} (mV)	P_{in} (mV)	S (mV)	I_0 (mV)	TL (a.u.)	TL_{nor} (a.u.)
0	0	0	1	1	65	65	25	125	0.2	0.2
0.89	0.05	0.079	0.834	1.096	51	61.1	70	130	0.538	0.627
2.1	0.12	0.1896	0.646	1.233	32	49.6	85	110	0.773	1.249
2.97	0.17	0.2686	0.539	1.342	26	48.2	80	100	0.8	1.448
3.86	0.225	0.3555	0.441	1.464	22	49.9	115	120	0.958	1.827

[a] Note: $P_{in} = P_{pyro}(1/T)$; $(1/F) = A \ln 10/(1 - T) = A \ln 10/(1 - 10^{-A})$; S is the signal from the lock-in proportional to TL; I_0 is the average probe beam intensity read off from DMM2; $TL = S/I_0$; $TL_{nor} = TLP_0(1/F)/P_{in}$; $P_0 = 65$ mV.

beam wavelength, 150-mW excitation power), the enhancement E of the thermal lens signal[4] [defined as $E = 0.52P(\mathrm{d}n/\mathrm{d}T)/(\lambda k)$, where P is the laser power, $\mathrm{d}n/\mathrm{d}T$ is the temperature coefficient of sample's refractive index, λ is the probe beam wavelength, and k is the thermal conductivity of the sample], compared to Beer's law response, was calculated to be 738. However, detection limits of thermal lens spectrometry are background-noise limited. In this experiment, the background (solvent) signal (0.2 a.u.) ranged from 11 to 32% of measured values with a standard deviation exceeding 20%. As a consequence of such high background signal and its relative noise, absorbances lower than 0.028 could not be measured. As already stated, the background noise in measurements described here is affected by the pointing instability of the pump laser.

Improvement of the laser pointing stability is therefore an absolute necessity if the analytical potentials of thermal lens spectrometry are to be fully exploited. The construction of an automatic system (based on the combined use of the infrared quadrant pyrodetector and two scanning mirrors) to stabilize the position of the CO_2 laser has recently been completed; its performance is currently being investigated.

Another important fact that should be kept in mind is the recognition that, in every dual-beam thermal lens measurement there is the potential danger of the occurrence of simultaneous photothermal deflection and thermal lens effects. This phenomenon takes place whenever the propagation directions of the pump and probe beams are offset by some value. Because of the "beam walk" discussed above, the offset between the two beams also varies in an uncontrollable fashion. Such an effect produces an additional contribution to the signal detected by a diode PD and cannot be disregarded at higher absorbances.

As far as the performance of the experimental setup is concerned, some additional improvements might still result from optimizing the modulation frequency, establishing an optimal position of the photodiode (relative to that of a sample), using a photodiode with a larger active area, and, finally, optimizing the PH3 diaphragm's diameter. This approach assists in further reducing the effect of the pump laser's pointing instability (when sampling larger portions of the probe beam around its axis, the changes in the beam mode could be averaged out).

Besides reducing the relative background noise, the LOD can also be improved by virtue of lowering the background signal level itself. In thermal lens spectrometry, the background signal is efficiently supressed by using a differential thermal lens arrangement.[7] Such a configuration was demonstrated to be capable[7] of reducing the background noise level by a factor as high as 50. However, if the absorption is significant, the use of a conventional differential thermal lens arrangement[7] does not provide a remedy because of the unknown amount of power that enters the second cell. However, this problem can be circumvented by adopting the concept of so-called

obliquely crossed differential thermal lens spectrometry.[8] The striking feature of this method (already tested for determination of FFAs in combination with chromatography[9]) is that the presence of the FFA is detected as a change in a thermal lens signal resulting from the absorbance differences between the bulk solvent (containing a strongly absorbing additive) and a weakly absorbing FFA. We anticipate that, in the infrared spectral range, this approach will represent an additional contribution to the selectivity of the technique without the need for an absorbing additive.

CONCLUSION

In conclusion, dual-beam CO_2 laser thermal lens spectrometry has proved capable of detecting FFA concentration of octadecanoic acid dissolved in CCl_4 at a level of 0.3% (measurement with static solution). This value is comparable to the LOD attainable with transmission infrared spectrometry; however, as discussed above, the potential of the infrared thermal lens technique is yet to be exploited. By the reduction of both the background signal by a factor of 20 (differential arrangement) and the relative background noise from the present 20% (or higher) to a few percent (which is typical for thermal lens experiments), a minimum measurable concentration of 0.001% or better is expected.

The possibility of building a low-cost dedicated instrument (a fixed-frequency CO_2 laser and a lock-in amplifier with a limited range of modulation frequencies are at present available at affordable prices), with a LOD superior to that of a conventional infrared transmission spectrometer, undoubtedly justifies the pursuit of further investigations of infrared thermal lens measurements in condensed-phase samples.

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