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Tunable ultraviolet visible photoacoustic detection Analysis of the sensitivity and selectivity provided by a xenon flash lamp

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Abstract

A fundamental understanding of the physical and chemical properties that dictate the absorption of pulsed light and subsequent release of heat to generate a transient pressure wave was used to test the concept of a multi-wavelength photoacoustic detector. Analysis of the wave equation predicts that with long-pulse excitation, i.e. microseconds FWHM, absorption by the solvent, and not electrostriction determines the limit of detection. Calculation of the mechanical to electrical conversion efficiencies of piezoelectric transducers shows that absorbed pulse energies of microjoules, typical of pulsed flash lamps, are sufficient to provide measurable photoacoustic signals. A pulsed xenon flash lamp (2 μs FWHM) which emits a broad spectrum over the UV and visible region is used as an excitation source to detect trace quantities of metals in aqueous solution using pulsed photoacoustic detection. In this work, dielectric mirrors were used to detect two analytes, CrO_4^{2-} (monitored at 355 nm) and Co^{2+} (monitored at 532 nm), simultaneously. This approach increases both the flexibility and selectivity of pulsed photoacoustic methods. We obtained a detection limit of 2.6×10^{-4} absorbance units per centimeter in aqueous samples. This work shows that pulsed lasers are not a necessity for ultra-sensitive photoacoustic spectroscopy. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photoacoustic; Xenon flashlamp; Chromium; Cobalt; Piezoelectric transducer; Spectroscopy

1. Introduction

The first report of the photoacoustic (PA) (also known as optoacoustic) effect goes back to 1880 when Bell [1] heard sound generated by a sample that was illuminated with modulated sunlight. Interest was revived in this phenomena in the 1970s with the introduction of the Rosencwaig–Gersho theory [2–5] describing this photoacoustic effect. At this point, photoacoustics utilized a gas-phase microphone which sensed the heating and cooling of a gas layer in thermal contact with the sample of condensed matter being irradiated by a modulated light source. This technique was limited due to the inefficient thermal diffusion into the gas. In the early 1980s, Patel and Tam [6] demonstrated an enhanced sensitivity over conventional and modulated techniques by using a pulsed laser and a piezoelectric transducer in direct contact with the liquid to measure small absorption coefficients. They showed that the high peak powers of pulsed light sources make them preferable to modulated light sources. While the piezoelectric

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transducer is not as sensitive as the gas phase microphone, piezoelectric transducers are more efficient due to improved acoustic impedence matching between the liquid and solid interfaces, avoiding the losses associated with liquid to gas impedence losses when using a gas phase microphone. The demonstration that photoacoustic spectroscopy is typically 2–3 orders of magnitude more sensitive than conventional absorbance techniques has led to PA spectroscopy being used to study a variety of chemical and physical processes in liquids [7–15]. Sensors based on photothermal methods have recently been designed to monitor Cr(VI) in water [16], pH and CO_2 [17], oil in water [18], and water in oil [19]. In previous work, we investigated the detection limits for Cr(VI) in aqueous solutions using pulsed laser spectroscopy [12,13]. Although a significant enhancement in detection limits was obtained compared with traditional spectroscopic methods, the technique was limited by availability of a pulsed tunable laser and a transient digitizing oscilloscope resulting in a sensitive but relatively expensive analytical technique. In subsequent work, we investigated the fundamental properties describing the conversion of the absorbed electromagnetic energy to the transient pressure change detected with a piezoelectric element [20,21]. Two important findings from our fundamental studies provide a direct bearing on the current work. First, only minute absorbed energy densities (ca. μJ/ml) are required to obtain a measurable piezoelectric signal given the sensitivity of commercially available piezoelectric transducers (ca. 6 mV/Pa).

Analysis of Eq. (1) shows that the photo-induced pressure change is equal to the product of the thermoelastic properties of the solvent $[\beta/\alpha C_p \rho]$ and the density of the absorbed energy $[H_{th}/V_0]$ where β is the thermal coefficient of expansion ($^\circ C^{-1}$), α the isothermal compressibility (Pa^{-1}), C_p the molar heat capacity ($J\,^\circ C^{-1}\,g^{-1}$), ρ the density ($g\,ml^{-1}$) of the bulk solvent, H_{th} the quantity of absorbed energy (J), and V_0 the excitation volume (ml) [22,23]. For each μJ/ml absorbed energy, Eq. (1) predicts a pressure change of ca. 0.1 Pa for an analyte dissolved in water.

$$\Delta P = \frac{\beta}{\alpha C_p \rho} \frac{H_{th}}{V_0} \tag{1}$$

Second, an understanding of the mechanical to electrical efficiency of a piezoelectric element predicts it is advantageous to use low frequency transducers as shown in Eq. (2) where h is the thickness of transducer (inversely proportional to the frequency constant), K_{33} is a dimensionless coupling factor, d_{33} is the piezoelectric charge constant ($C\,N^{-1}$), ε_0 is the dielectric constant ($8.85 \times 10^{-12}\,A\,s\,V^{-1}\,m^{-1}$), and ε_r is the relative dielectric constant (dimensionless). To a first approximation, the thicker the piezoelectric element the greater the observable signal is.

$$\text{PA signal (voltage)} \sim \Delta P h \frac{K_{33} d_{33}}{\varepsilon_0 \varepsilon_r} \tag{2}$$

In addition to the predicted greater signal amplitude, a low frequency transducer can be adequately sampled with commercially available megasample/s data acquisition (DA) boards housed in a common laboratory personal computers (PC) eliminating the need for expensive fast transient digitizing oscilloscopes. Pulse energies of dozens of microjoules that are readily available with commercially available xenon flashlamps should provide a suitable (and less expensive) alternative to pulsed solid state or gas lasers. In addition, if we can devise a method to select wavelengths of interest, not only will we have tunability but the possibility of monitoring several wavelengths simultaneously to provide an enhancement in detector selectivity.

2. Experimental

2.1. Chemicals

Potassium chromate, cobalt sulfate, potassium phosphate, and nitric acid were used as received. The chromate stock solution was made in 5 mM phosphate (pH 8.0). The cobalt stock solution was made in 2% nitric acid. The method of standard addition was used to increase the chromate and cobalt concentrations in their respective sample cells which contained 5 mM phosphate (pH = 8) and water.

2.2. Instrumentation

A schematic of our photoacoustic detector is shown in Fig. 1. The excitation source was a Hamamatsu HP SQ xenon flash lamp (L4634) in a trigger socket (E2438-01) housed in a shield box (E2608) using a

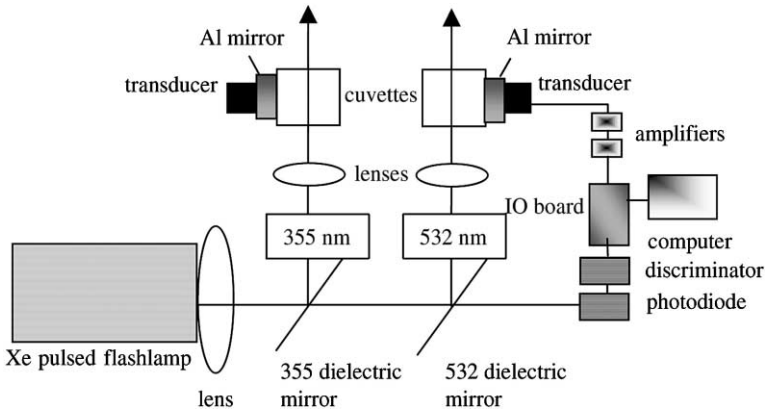

Fig. 1. Schematic of flash lamp pump photoacoustic spectrometer. A broad band 100 Hz xenon flash lamp is used as the excitation source. Selected wavelengths from the lamp are reflected off 45° narrow band dielectric mirrors: UV light at 355 nm is used to detect chromate and visible light at 532 nm is used to detect Co^{2+}. The samples are contained in 1 cm × 1 cm UV–VIS quartz cuvettes. A 150 KHz piezoelectric transducer is clamped against the side of the sample compartment and the reflected wavelength is focused through the sample parallel to the face of the acoustic transducer.

power supply (C4479). The lamp provided 2 μs wide broadband (UV–VIS) pulses at 100 Hz. A 500 mm lens was used to help provide a collimated source. Select wavelengths from the flash lamp were reflected off 45° narrow band dielectric mirrors (−3 dB bandwidth 100 nm) mounted in series. In the current example, UV light at 355 nm (∼40 μJ/pulse) was used to detect CrO_4^{2-} and visible light at 532 nm (∼30 μJ/pulse) was used to detect Co^{2+}. Additional wavelengths could be monitored by adding subsequent dielectric mirrors. The aqueous samples were contained in conventional 1 cm × 1 cm quartz cuvettes. A low frequency piezoelectric transducer (Physical Acoustic Corporation (PAC) R15 sensor with a 150 KHz resonant frequency) was used to measure the acoustic signals. The transducer was clamped against the side of the cuvette with an aluminum mirror clamped between the transducer and the cuvette. The aluminum mirror served to prevent any pyroelectric effects due to scattered light hitting the detector that occurred with the discharge of the pulsed light source. Each reflected wavelength was focused using a 50 mm spherical lens through the sample parallel to the face of the acoustic transducer. The photoacoustic signals were amplified separately using two preamplifiers in series (Panametrics, model 5670, 40 dB and Stanford Research Systems, model SR240, five gain). A photodiode was used with a discriminator (Mech-Tronics, model 605) to provide a 5 V signal to trigger the data acquisition software. Pulse energy incident on the sample was measured with a Scientech P09 joulemeter.

2.3. Data acquisition and data analysis

Data acquisition software was developed to allow the user to set the timing gate, timing delay, and number of triggers to be averaged. The signal from the transducer was digitized on a National Instruments PCI 6110E Multifunction IO card capable of taking five megasamples on four channels simultaneously. Instead of taking data continuously, the period of interest was isolated by using the light source to trigger a delayed digital pulse which is used to gate the data acquisition. Data was taken for multiple shots (1000) and then averaged. A single amplitude value for each acoustic waveform was obtained by calculating the peak-to-peak amplitude (in the 7–13 μs region). Detection limits were calculated ($S/N = 3$) based on the standard deviation of the signal of the blank ($n = 20$).

3. Results and discussion

3.1. Photoacoustic signal detection

In a pulsed photoacoustic experiment, absorption of light generates an electronically or vibrationally

excited state intermediate. Nonradiative decay of the excited state intermediate generates an acoustic pressure wave due to the volume expansion created by the local increase in temperature as shown in the scheme below.

$$A + hv \rightarrow A^*$$

$$A^* \rightarrow A + \text{heat}$$

The pressure waves generated by heat released from nonradiative decay (i.e. internal conversion and/or vibrational relaxation) of the solute A^* and by electrostriction of the solvent can be detected with an ultrasonic transducer. The wave equation [24–26] governs the relationship between the photo-induced acoustic pressure wave (p) and the time profile of the excitation source pulse intensity (I) as shown in Eq. (3) where v_s is the velocity of sound, K_a is an absorption term and K_e is an electrostriction term.

$$\left(\frac{1}{v_s^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right) p = \left(K_a \frac{\partial}{\partial t} - K_e \frac{\partial^2}{\partial t^2}\right) I \tag{3}$$

It can be seen from Eq. (3) that two components contribute to the observed photoacoustic signal, absorption and electrostriction. The contribution due to absorption is proportional to a solvent-dependent term K_a as shown in Eq. (4) where A is the absorption coefficient. The contribution due to electrostriction of the solvent is proportional to K_e as shown in Eq. (5) where n is the refractive index of the solvent, c the speed of light, v_s the velocity of sound in the solvent, and γ is an electrostrictive coefficient.

$$K_a = \frac{A\beta}{C_p} \tag{4}$$

$$K_e = \frac{\gamma}{2ncv_s^2} \tag{5}$$

Electrostriction, which results from the constriction of the solvent into the region of high electric field when electromagnetic energy is passed through a dielectric medium, and competing absorption by the solvent are two major factors that set the limit of detection in pulsed photoacoustic experiments. An analytical solution to calculate a minimal detectable absorbance (α_{min}) by photoacoustic methods based on an electrostriction background has been determined by Lai and Young [26]. According to their approach, α_{min} is defined as the absorbance where the amplitude of the PA signal due to electrostriction is equal to the amplitude of the PA signal due to solute absorption. Eq. (6) provides the relationship between the minimal detectable absorbance, α_{min}, and β of the bulk solvent for a spatially gaussian excitation source and the thermal elastic properties of the solvent. Examination of Eq. (6) shows that the magnitude of the electrostriction signal is controlled by two important time scales: the pulse width of the excitation source (τ_p) and the acoustic transient time (τ_a), which is defined as the time it takes the acoustic wave to travel through the diameter of the excited volume in a cuvette cell.

$$\alpha_{min} = \frac{K_e \times (C_p/\beta)}{(\tau_p^2 + \tau_a^2)^{1/2}} \tag{6}$$

In our previous work with the layered prism cell geometry [20], we showed that the detection limit was controlled by the electrostriction component and not by solvent absorption. However, by using an experimental geometry that provides either a variable acoustic transient time or an increase in pulse width of the excitation source, the magnitude of the electrostriction component can be minimized. For the geometry used in this work, a cuvette with the excitation source propagating perpendicular to the detector [27] ($\tau_a = 2$ and $\tau_p = 2\,\mu s$) yields theoretical α_{min} ca. $5 \times 10^{-5}\,cm^{-1}$ in water, significantly lower than the reported absorption coefficient of water at 350 nm ($4.6 \times 10^{-4}\,cm^{-1}$), 530 nm ($5.1 \times 10^{-4}\,cm^{-1}$) [28]. Thus, theory predicts in this long-pulse geometry, absorption by the solvent, not electrostriction, sets the limit of detection.

3.2. Experimental verification of predicted selectivity and sensitivity

To test the theoretical predictions of detection limits with microjoule of long-pulse excitation we used dielectric mirrors to reflect selected wavelengths from a xenon flash lamp. For the pulse energies used in our experiments, using Eq. (1) we calculate ΔP of ca. 34 mPa and ΔP of ca. 28 mPa at 355 and 532 nm, respectively, due to the absorption of the solvent, water. [1] Our previous work has shown pressure changes on the order of mPa to be sufficient to generate a measurable pho-

[1] Calculated for irradiated volume $V_0 = 0.125$ ml, absorbance water $= 4.6 \times 10^{-4}\,cm^{-1}$.

toacoustic signal [20]. Furthermore, we can measure an absorbance of about one-half the background signal (solvent only, no solute) with reasonably reproducible excitation pulses. Each reflected wavelength was focused and passed through a standard quartz cuvette parallel to a 150 KHz transducer which was in acoustical contact with the cuvette. In the geometry used in the present experiment, the cobalt and chromate were analyzed simultaneously in two separate cells. Alternatively, two or more wavelengths could be reflected through the same sample compartment in parallel. The signal from the different excitation wavelengths could either be interleaved using a single transducer, storing the data on separate channels, or they could be temporally resolved by having the transducers stacked one on top of the other with the corresponding excitation beams running parallel to the stacked transducers. Analysis of the initial rise and fall of the transducers would assure that interference from the other wavelengths will be avoided.

To demonstrate multiple wavelength analysis with the current experimental apparatus, standard additions of chromate and cobalt solutions were added to their respective cells so that each addition increased the absorbance of the solution by ca. 0.0013 absorbance units. For each standard addition, five waveforms of 1000 averaged shots each were collected (20 waveforms for the initial blank solutions). Photoacoustic waveforms for increasing cobalt concentrations are shown in Fig. 2. The photoacoustic signal at dilute solute concentration is due to the sum of the absorbance of the solvent and the solute. No electrostriction signals were observed with the long-pulse excitation source as we previously observed with short-pulse excitation [20]. A calibration plot is shown in Fig. 3 and shows the peak-to-peak amplitude (in the 7–13 μs region) as a function of absorbance units. Because the photothermal methods are an absorbance measurement we prefer the convention of listing detection limits in absorbance units instead of concentrations. This provides a means of predicting detection limits for any species if the extinction coefficient is known. In general, the sensitivity defined in this approach is applicable to any species that absorbs at the wavelengths investigated in this work so long as the species is photo-stable and does not have a significant fluorescence quantum yield. The detection limits that we calculated from the experimental data are currently set by competing solvent absorbance. A stable reproducible pulsed light source and signal averaging enhances the ability to measure small absorptions by a solute in the presence of competing solvent absorption. Statistical analysis of the background signal (solvent only, no solute) suggests that we can statistically measure one part solute absorption on top of two parts solvent absorption with the pulsed flash lamp. The standards used in this work are in essence detection limits at the given wavelength. The

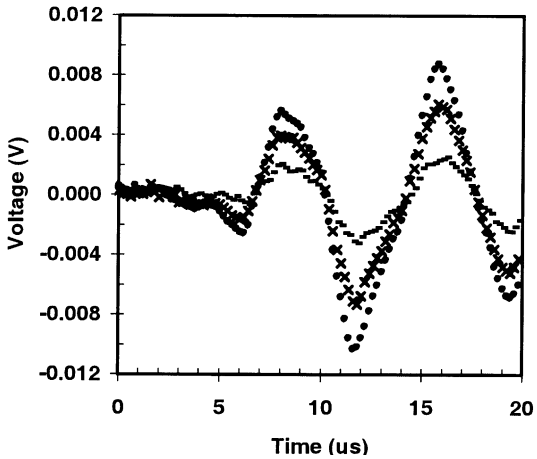

Fig. 2. Photoacoustic waveforms obtained for increasing concentrations of Co^{2+}: $A = 0.0013$/cm (-), $A = 0.0039$/cm (×), $A = 0.0065$/cm (●).

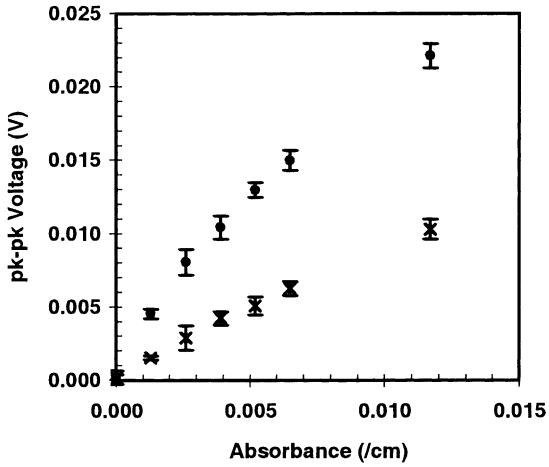

Fig. 3. Photoacoustic response vs. absorbance for two different analytes at two different wavelengths: Co^{2+} at 532 nm (●), CrO_4^{2-} at 355 nm (×). The error bars are ±2 standard deviations.

detection limits at 532 nm (determined with cobalt) and at 355 nm (determined with chromate) are 2.6×10^{-4} and $4.4 \times 10^{-4}\,cm^{-1}$ absorbance units, respectively. This corresponds to a detection limit of ca. 6 ppb chromate. Note, that this value is for *direct* detection chromate, no added complexing agent to enhance chromate absorbance was used in this study. When chromate is mixed with 1,5-diphenylcarbazide (DPC), a strongly absorbing complex results (absorbance max. ~540 nm, $\varepsilon = 0.739\,ppm^{-1}$). Using our detection limit determined at 532 nm, this corresponds to a LOD of ca. 0.35 ppb for the DPC-chromate complex with a xenon flash lamp, very comparable to photothermal methods that require laser excitation. [2]

4. Conclusions

Analysis of the fundamental parameters that describe the conversion of absorbed pulsed electromagnetic energy to a transient pressure gradient shows that the intensity provided by pulsed xenon flash lamps provide acoustic pressure pulses that can be readily detected with low frequency ultrasonic transducers.

Combining a pulsed xenon flash lamp with PC data acquisition of the photo-induced response from sub-MHz transducers provides the capability of simultaneous multiply wavelength detection. This approach should yield enhanced selectivity with comparable sensitivity at a fraction of the cost and space of conventional pulsed photoacoustic methods that use pulsed lasers and transient recorders. These new results show that sensitive absorption spectroscopy using photoacoustic techniques can be obtained circumventing the requirement of using of a pulsed tunable laser and a fast transient digitizer.

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[2] See [16], detection limit = 0.1 ppb.

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