Development of a Double Beam, Dual Wavelength Thermal Lens Using a Helium - Neon Laser

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A single He - Ne laser was used to develop two types of novel pump and probe configuration thermal lens apparatus. In the first system, the He - Ne laser beam was split into a pump beam and a probe beam by a beam splitter. Two mirrors were used to direct the two counter-propagating beams and to cross at the sample. Alternatively, a pump and probe configuration was achieved from a single laser without the use of a beam splitter. This was accomplished with a special dual output laser, *i.e.*, a laser which provides output from both ends, front and back. The selectivity of these two systems is enhanced by measuring the thermal lens at two different wavelengths, 632.8 and 594 nm. These dual wavelengths were derived from the He - Ne laser by forcing it to oscillate at two transitions: $3s_2$–$2p_4$ (632.8 nm) and $3s_2$–$2p_8$ (594 nm). Preliminary results have indicated that these instruments are capable of detecting 0.03 μg of palladium(II) via the formation of an ion pair with crystal violet. A comparison is made of the two systems and their applications to general trace analysis.

Keywords: *Double beam laser; dual output laser; dual wavelength laser; thermal lens; helium - neon laser*

Photothermal phenomena, including the thermal lens, are based on the temperature rise that is produced in an illuminated sample by non-radiative relaxation of the energy absorbed from a laser. In the thermal lens effect, the radially symmetric, Gaussian intensity distribution (TEM_{00}) of the laser beam generates heat which is strongest at the centre of the beam because that is where the beam intensity is greatest. Consequently, a lens-like optical element is formed in the sample owing to the temperature gradient between the centre of the beam and the bulk material. The thermal lens effect is observable for laser beams in the power range of only milliwatts in samples normally thought to be transparent, and is thus suitable for the low absorption measurement of non-fluorescent molecular species. The first measurement of the thermal lens effect was performed by Gordon *et al.*[1] using a simple beam apparatus. Recent attempts have been made to improve the thermal lens measurement by using a double-beam configuration employing two lasers, a pump laser and a probe laser.[2–4] Compared to the single-beam arrangement, the double-beam technique allows lock-in detection, thus making it easy to use and also enhancing its sensitivity. Unfortunately, inherent disadvantages such as the requirement for a strict alignment of pump and probe beams, directional stability and chromatic aberrations still remain with this configuration.[5] Efforts have been made to ameliorate these restrictions by using a single laser double-beam configuration.[5–10] These techniques are highly promising as they preserve the benefits of both single-beam and pump and probe configurations while alleviating restrictions such as directional stability and chromatic aberrations. Unfortunately, the employment of such elements as a lock-in amplifer equipped with a notch filter and polariser impose restrictions[9] and generate background noise in these techniques.[6,7]

Pump and probe beams can be derived from a single laser by using either a beam splitter or a laser with dual output. The beam splitter splits the laser beam into a pump beam and probe beam and the two mirrors direct the two counter-propagating beams to cross at the sample. Such a system is simpler than the reported single laser double beam apparatus but still preserves all of the advantages. Further, the use of fewer optical elements reduces the reflection loss and background absorption.

It is inaccurate to assume that the laser can only provide output radiation from one end of its housing because, with correct choice of mirror set and removal of the housing, the laser can be forced to produce radiation from both ends. Such a dual output laser provides an excellent alternative for pump and probe beam experiments because one output can be used as a pump beam and the other as a probe beam.

The general custom of referring to the red 632.8-nm line as the visible He - Ne laser oscillation is inaccurate because laser oscillations can be produced in other visible He - Ne lines. Once the $3s_2$ level of the Ne is heavily populated, the laser transitions can be forced into a number of the 2p levels other than $2p_4$. In fact, a He - Ne laser operating at 594 nm ($3s_2$–$2p_8$ transition) and 543.5 nm ($3s_2$–$2p_{10}$ transition) has been reported.[11] The ability to provide multiple discrete lines, coupled with its low cost, stability and ease of operation, enables the He - Ne laser to serve as an excellent source. In spite of its potential, applications of the He - Ne laser to chemical analysis so far have been restricted to its red line, *i.e.*, 632.8 nm. A He - Ne laser could, however, be operated at various visible wavelengths simply by using a plasma tube with a high Q value and the correct output couplers.

One of the most important features of an analytical instrument is selectively, *i.e.*, the ability to differentiate one sample from another as real-time samples always contain more than one species. Unfortunately, most thermal lens apparatus operate with only pump laser wavelength which make them impractical for general analytical use. The selectivity of these techniques can be greatly enhanced by simply measuring thermal lens signals at two different pump

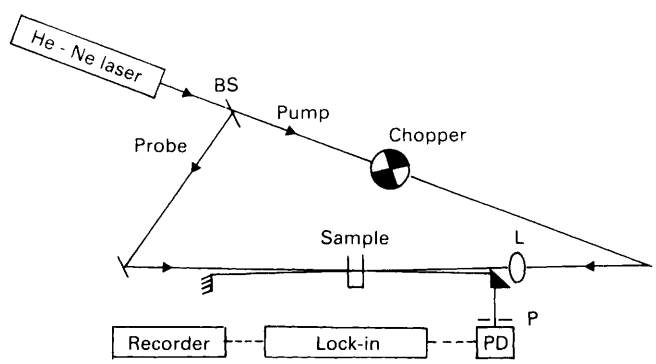

Fig. 1. Double-beam He - Ne laser thermal lens apparatus using a beam splitter. BS, beam splitter; PD, photodiode; L, lens and P, pin hole

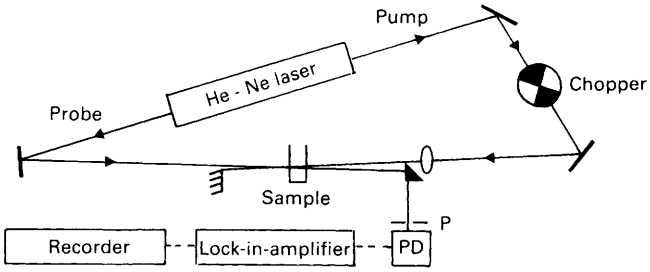

Fig. 2. Double-beam thermal lens apparatus using a dual output He - Ne laser

laser wavelengths, thereby improving their capability of fingerprinting and identifying a substance in solution.

Such considerations prompted the initiation of this study, which aimed to develop a pump and probe configuration thermal lens apparatus capable of operating at two different wavelengths; 632.8 and 594 nm, using a simple single He - Ne laser. In this paper, the two different schemes to achieve the pump configuration, *i.e.*, the beam-splitter method and the dual-output method, are discussed and their results are compared. Further, the selectivity of these systems was enhanced by performing the thermal lens measurement at two different wavelengths, 632.8 and 594 nm. The use of these systems to determine palladium(II) by solvent extraction and the applications of these techniques to general chemical analysis are discussed.

Experimental

Instrumentation

The He - Ne laser plasma tube used in this experiment was purchased from Particle Measurement Systems, Boulder, CO (Model SP-1M-SPL, small bore tube). With the correct selection of the mirror set, this plasma tube was able to provide single or dual output at single or dual wavelengths. The single output was achieved by using a concave mirror (R = 100 cm), dielectrically coated to reflect 100% of either 632.8 and 594 nm wavelengths, as the back mirror. Two different output couplers were used to achieve the output wavelength at 632.8 and 594 nm. They were concave mirrors (R = 100 cm), dielectrically coated for 1% transmission at 632.8 nm and 0.1% transmission at 594 nm. The output power was 6 mW for 632.8 nm and 1 mW for 594 nm.

Dual output was obtained from the same plasma tube by using a concave mirror (R = 100 cm) with 0.1% transmission at 632.8 nm as the back mirror. A 1% concave mirror (R = 100 cm) was used as the output coupler. This arrangement enabled the He - Ne laser to provide output from both ends: 5 mW from the output coupler and 0.5 mW from the back mirror. The schematic arrangements for the apparatus are shown in Figs. 1 and 2. In Fig. 1, a 60:40 transmission - reflection pellicle beam splitter was used to split the laser beam into a pump beam and a probe beam. The pump beam was modulated by a mechanical chopper (EG & G Princeton Applied Research, Model 196 variable-speed chopper) and focused by a 15 cm focal length lens. The probe beam crossed the pump beam at the sample. The crossing angle between the two beams was about 1°. The sample cell, which was a 1-cm quartz cuvette, was tilted slightly to avoid back-reflection. A right-angle prism was used to direct the probe beam through a 1 mm pin-hole into the photodiode (PD, Spectra-Physics Model 404 power meter). The distance between the sample and the PD was 1.8 m. The signal component from the PD, which was modulated at the chopper frequency, was synchronously detected in a lock-in amplifier (EG & G Princeton Applied Research, Model 5207). The lock-in amplifier time constant was maintained at 3 s.

Fig. 2 shows the systematic arrangement for the apparatus using the dual output He - Ne laser. As mentioned previously, the dual output laser provided output power from both ends: 5 mW from the front and 0.5 mW from the back. The 5 mW beam was used as the pump beam and the 0.5 mW as the probe beam. The pump beam was folded by two mirrors, modulated by a mechanical chopper and focused by a lens with a focal length of 15 cm before illuminating the sample. The probe beam was directed to cross the pump beam at the sample. The crossing angle between the two beams was about 1°. The detection system is similar to that in the beam-splitter apparatus.

Crystal violet [tris-*p*-(dimethylamino)phenylcarbonium chloride, Aldrich Chemicals], palladium(II) chloride (Aldrich Chemicals), potassium thiocyanate (Mallinckrodt) and dimethylglyoxime (Matheson Coleman & Bell) were used as received. The concentration of crystal violet in methanol was checked spectrophotometrically (ε_{590} = 6.6 × 10^4 l mol^{-1} cm^{-1}.[12] Standard palladium solution was prepared from palladium(II) chloride in dilute hydrochloric acid and standardised gravimetrically with dimethylglyoxime.[13] The absorption spectra were measured on a Perkin-Elmer 320 spectrophotometer.

Procedures

The method for palladium determination is based on the ion-pair formation between the palladium anion and a basic dye.[14,15] The complexes formed will then be extracted into the organic solvents as they are generally soluble in non-polar solvents.[14,15] The procedure used in this work is similar to the extraction method using rhodamine B.[13] Crystal violet was, however, used in this work as it has low fluorescence quantum yield and hence, high thermo-optical yield. Typically, 5 ml of 4.5 M sulphuric acid, 1 ml of 2.5 × 10^{-2} M potassium thiocyanate solution and 2.5 ml of 10^{-3} M crystal violet solution were added to a separating funnel containing 0.1 to 10 mg of palladium(II). The mixture was diluted to 25 ml with water and extracted with 5 ml of butyl acetate. The aqueous phase was discarded and the organic phase was washed with 10 ml of 0.9 M sulphuric acid. Measurements were made on the organic phase after centrifugation. The calibration graph was determined using different volumes of standard palladium(II) solution.

Results and Discussion

Fig. 1 shows the double-beam thermal lens apparatus using the beam-splitter method. In this apparatus, the spot size of the beam waist at the sample cell is estimated, according to the method described in reference 16, to be 0.15 mm. This was done by measuring the spot size at two different positions. Knowledge of the spot size (w) and crossing angle (Ψ = 1.0) of the pump and probe beams permits the calculation of the interaction length (l) between the two beams: $l = 2w/\sin \Psi$ = 1.7 cm.[17] Therefore, the induced thermal lens within the sample was completely monitored by the probe beam because the path length of the sample cell used in this work was only 1 cm.

Generally, the output power (P_o) of a laser is given by[18]

$$P_o = \frac{8\pi n^2 h\nu\Delta\nu A}{\lambda^2 (t_2/t_{spont})} T \left[\frac{(g_0)}{(Li + T)} - 1\right] \quad \ldots \quad (1)$$

where n is the refractive index, h is Planck's constant, ν is the frequency, A is the cross-sectional area of the mode which equals to v/l where v is the volume and l is the length of the lasing medium; g_0 is the unsaturated gain per pass; T is the mirror transmission and Li is the sum of the residual loss, λ is the wavelength and t_2 and t_{spont} are the stimulated and spontaneous emission lifetimes of the upper lasing level,

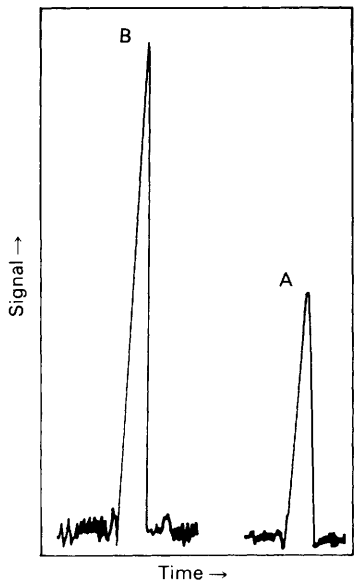

Fig. 3. Thermal lens signals of 1.0×10^{-5} M crystal violet in methanol taken (A) on the beam splitter apparatus and (B) on the dual output apparatus. These signals and those in Fig. 4 were obtained by putting the sample into the apparatus, recording the signal and then removing it

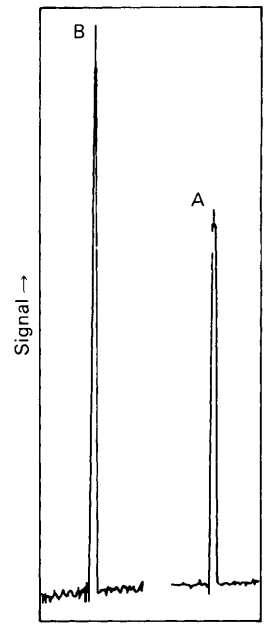

Fig. 4. Thermal lens signals of 1.0×10^{-5} M crystal violet in methanol. (A) 632.8 nm, 2 mW pump beam and (B) 594 nm, 0.5 mW pump beam

respectively. It is clear that the output power from both ends of a laser equipped with two transmission mirrors having transmission T_1 and T_2 should be proportional to T_1 and T_2, respectively, because the other terms of equation (1) are constant. In fact, the dual output power from the He - Ne laser equipped with 1 and 0.1% transmission mirrors was found to be 5 and 0.5 mW, respectively. The spot size of the pump beam (5 mW beam) at the sample cell was estimated to be 0.13 mm, which corresponds to a 1.5 cm interaction length. This value is similar to that of the beam-splitter method (1.7 cm) and is much longer than the path length of the sample cell (1.0 cm). Therefore, the measured thermal lens signals on the two systems are comparable.

Fig. 3 shows the signals of 1.0×10^{-5} M crystal violet in methanol, excited with the 632.8 nm beam, measured on the beam-splitter apparatus (A) and dual output apparatus (B). The signal obtained from the dual output apparatus is almost twice as sensitive as that measured on the beam-splitter apparatus. The difference in the intensity of the pump beam in the two systems is probably responsible for this observation. The intensity of the pump beam at the sample cell in the dual output apparatus was 4.0 mW whereas it was only 2.0 mW from the beam-splitter apparatus. The total output of the He - Ne laser in the latter apparatus was 6 mW. Its intensity is decreased to 2.0 mW at the sample cell because it was split by the (60 : 40) beam splitter prior to the sample. Further loss due to the two surfaces of the beam splitter also adds to the decrease of the pump beam. The response of the two systems seems to be identical when the difference in the pump beam is taken into account. This is expected because the two systems have similar pump beam spot sizes at the sample and interaction lengths.

The selectivity of the systems is enhanced by measuring the thermal lens at two different wavelengths, 632.8 and 594 nm. The dual wavelengths were derived from the He - Ne laser by forcing it to oscillate at two transitions $3s_2$–$2p_4$ (632.8 nm) and $3s_2$–$2p_8$ (594 nm) with a proper set of mirrors. The output power for the 632.8-nm line was 6 mW but only 1 mW was obtained for the 594-nm line. This is probably due to the fact that the gain for the $2s_2$–$2p_8$ which is responsible for the 594-nm oscillation is much less than in the $2s_2$–$2p_4$ transition (632.8 nm).[10] Signals of 1.0×10^{-5} M crystal violet in methanol excited with the 632.8-nm beam of the 2 mW beam-splitter apparatus (A) and 594-nm beam of the 0.5 mW dual output apparatus (B) are shown in Fig. 4. The noise is better with the 632.8-nm excitation than with the 594-nm beam. This improvement is probably due to the higher intensity of the probe beam for the red (2 mW) compared to 0.3 mW for the orange. Normalising the two signals, assuming the signal is proportional to the pump laser power, gave (594-nm signal/693-nm signal) = 5.85. As the thermal lens technique is the measurement of heat produced by the absorption of light by the sample, this ratio corresponds to the ratio of absorption at 594 and 632.8 nm. The ratio is in good agreement with the value of 5.83 which was obtained from the absorption measurement on a conventional spectrophotometer ($\varepsilon_{594} = 6.0 \times 10^4$ l mol^{-1} cm^{-1} and $\varepsilon_{632.8} = 1.03 \times 10^4$ l mol^{-1} cm^{-1}).

It has been reported that cationic dyes such as rhodamine B and crystal violet form complexes with palladium(II) ions via ion-pair interactions.[14,15] This complex formation is particularly useful in chemical analysis because it permits the extraction of the metal ion from the aqueous phase into the organic phase as the ion-pair complexes are more soluble in organic solvent. Further, the ion-pair extraction is especially suited for the thermal lens measurement. This is because the sensitivity of this technique is proportional to the temperature coefficient of the index of refraction dn/dT of the solvent and inversely proportional to the thermal conductivity, and organic solvents usually have higher dn/dT and lower k values compared with those of water.[16]

The palladium(II) ions were extracted from the aqueous phase into the butyl acetate phase by forming a complex between the ion and the crystal violet. The absorption spectrum of this Pd - crystal violet complex, taken on a Perkin-Elmer 320 spectrophotometer, is shown in Fig. 5. This complex has a relative low absorptivity at 632.8 nm. The thermal lens signal of this complex was measured using the dual output apparatus with 5 mW pump beam power at 632.8 nm and the calibration graph is shown in Fig. 6. The calibration graphs exhibited a linear response (correlation

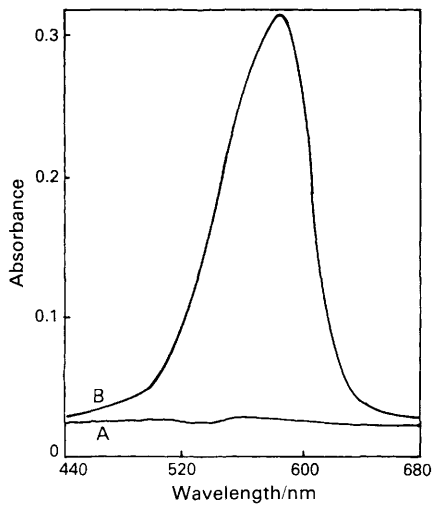

Fig. 5. Absorption spectra of (A) blank and (B) of 3.9 μg of palladium(II) - crystal violet complex extracted into 5 ml of butyl acetate

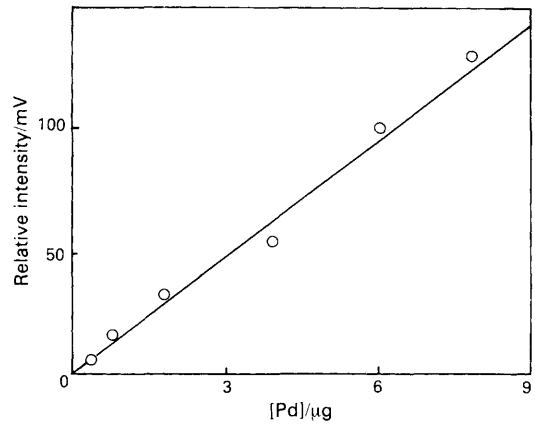

Fig. 6. Calibration graph for palladium(II) in butyl acetate layer measured with 5 mW excitation laser power at 632.8 nm, chopped at 5 Hz

coefficient, $r = 0.998$) over the Pd^{2+} concentration range 0.38–7.8 μg. The limit of detection, LOD, defined as the total amount of palladium(II) ion in 5 ml of butyl acetate which yielded a signal twice the standard deviation of the blank, is estimated to be 0.03 μg for 5 mW pump power chopped at 5 Hz. It corresponds to 4.0×10^{-4} absorptivity. This value is obtained with a He - Ne laser beam at 632.8 nm as an excitation source. As Fig. 5 indicates, the absorptivity of the palladium - crystal violet complexes at this wavelength is relatively low; it is about 15% of that at the maximum absorption at 585 nm. In spite of this low absorptivity, the LOD value found in this work is comparable to the 0.04-μg value obtained for Pd^{2+} by fluorimetry via rhodamine B ion-pair complexing.[13] It is more informative to compare this LOD value with other values obtained using different thermal lens techniques. However, because the LOD values reported for other techniques were measured with different pump laser power, it is perhaps more suitable to base the discussion in terms of *PA* value where *P* is the pump beam power and *A* is the absorptivity. The use of the *PA* value is justified as it was found that thermal lens signal is proportional to pump laser power.[2,3] The 2.0×10^{-3} mW *PA* value found in this work is comparable to the 3.0×10^{-3} or 5.6×10^{-3} mW value obtained on a cross-beam technique using a beam splitter[6] or a polariser.[8] It is also comparable to the value found on a double beam - two laser system with a high power argon ion laser as a pump laser.[19]

It has been demonstrated that a highly sensitive thermal lens apparatus can be constructed by using a simple He - Ne laser with very simple optical elements. Advantages of the apparatus include the inherent benefits of both single-beam and pump probe configuration while alleviating restrictions such as directional stability and chromatic aberrations. Compared with other single laser - double-beam techniques,[5–10] this dual output laser technique provides better beam quality, employs fewer and simpler optical elements and thus reduces the complexity due to unwanted back-reflection or background absorption.

Experiments are now in progress to optimise this apparatus and to enhance its selectivity by using a tunable laser as an excitation source.

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