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LASER THERMAL LENS EFFECT AND ITS APPLICATION TO TRACE SOLUTES DETERMINATION

Y. Deng, R. Sheng and M. Wang

Department of Chemistry, University of Wuhan, Wuhan, China

Résumé - L'effet de lentille thermique pour du Cu(AA)₂ dans plusieurs solvants organiques est observé. La concentration minimale détectable est 12 ppb de Co, ce qui correspond à 0,06 ng de Co dans le volume du faisceau, en utilisant un laser He-Ne de 1,2 mW et une cellule de 5 cm.

Abstract - The laser thermal lens effect of Cu(AA)₂ in several organic solvents is observed. A minimal detectable concentration of 12 ppb Co corresponding to 0.06 ng Co in in-beam volume, is achieved using a 1.2 mW He-Ne laser and a 5 cm cell.

In 1965, GORDON et al.(1) first reported the laser thermal lens effect. Since then, a number of workers has studied and reviewed the physical properties of this effect and its application (2-10). More recently, thermal lens spectrophotometry has been used for calorimetric determination of inorganic ions. DOVICH and HARRIS(11) have first used a 4 mW He-Ne laser for the determination of trace levels of Cu(II) ion with EDTA. The determination of Fe(II) ion has been reported with bathophenanthroline disulfonate using an Ar⁺ laser (12). The signal in the conventional spectrophotometer is measured indirectly as the difference between the incident and transmitted radiation. It is therefore difficult to improve the detection sensitivity of apparatus. However, thermal lens spectrophotometry could measure directly the absorbed radiation energy and thus achieve very high sensitivity. This is demonstrated in our study.

The laser thermal lens effect of Cu(AA)₂ in five organic solvents is observed using a He-Ne laser (λ=632.8 nm). The time required by reaching steady state, the dependence of detection sensitivity on the position of sample in the light path and some factors influencing the effect are studied.

The experimental apparatus is shown in Fig.1. When the laser beam pass through the sample solution, a defocussing negative lens is formed and a dispersed T : 1.5 mW He-Ne laser with TEM₀ mode.
L : focussing double convex lens.
S : light barrier S₁, S₂ : pinhole
C : light splitter.
SC : sample cell.
D₁, D₂ : photosensitive triode detector.
SC-16 : UV record oscilloscope.

Fig.1 - Schematic diagram of experimental apparatus.
light spot can be observed at the optical distance of several meter from the sample cell. The laser thermal(lens) effect can be detected by measuring the light intensity (in the centre of the beam) at Z>>z. It can be expressed as \((I_0-I_\infty)/I_\infty\) or \(\Delta I/I_\infty\), where \(I_0\) is the photoelectric current at \(t=0\) and \(I_\infty\) is the photoelectric current at the steady state of thermal lens.

\(\text{Cu(AA)}_2\) is prepared and purified by the method of reference (13). \(\text{PAN-Co(III)} - \text{CHCl}_3\) solution is prepared by the method of reference (14). All other solvents are analytically pure.

The following results are obtained.

1. The time required by reaching steady state is determined by the photothermal property of solvent and distance of sample from beam waist. The calculated and observed thermal lens formation curves are shown in Fig.2. Steady state is maintained at \(t > 5 t_C\).

2. The dependence of thermal lens effect of \(\text{Cu(AA)}_2 - \text{CHCl}_3\) on the position of sample cell in the light path is shown in Fig.3. It can be seen that \(\Delta I/I_\infty\) is maximum at \(Z=8\) cm. This result is consistent with the calculated value 8.2 cm.

3. The absorption enhancement (E) is strongly affected by the solvent used, laser power and wavelength. Their effects are shown in Table I, Fig. 4 and 5, respectively.

It can be seen from Table I and Fig. 4 that there is a linear relationship between \(\Delta I/I_\infty(PA)^{-1}\) and \(dn/dt\ \kappa^{-1}\). The E is greater the more large product of \(dn/dt\ \kappa^{-1}\). The E/P of water is only 0.21 and its use is limited.

Fig. 5 shows that for a given solvent, the E depends linearly on laser power in the range of lower power.
The relationship between $\Delta I/I_\infty$ and sample absorbance ($A$) is approximately linear in certain ranges of $\Delta I/I_\infty$. A approximately linear relationship is found for Cu(AA)$_2$-CHCl$_3$ when $\Delta I/I_\infty$ is 0.4 - 2.0.

Table I - Effect of some solvents on absorption enhancement.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$dn/dT$ (1) $(X \times 10^{-4}/^\circ C)$</th>
<th>$k$ (1) $(mW/cm ^\circ C)$</th>
<th>$dn/dT \cdot k^{-1}$ $(X \times 10^{-4} \text{cm/mW})$</th>
<th>$E/P$ (2) $(\Delta I/I_\infty) \cdot I/P$ (3) $(mW^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl$_4$</td>
<td>5.8</td>
<td>1.025</td>
<td>5.66</td>
<td>8.94</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>5.8</td>
<td>1.146</td>
<td>5.06</td>
<td>8.00</td>
</tr>
<tr>
<td>Benzene</td>
<td>6.4</td>
<td>1.440</td>
<td>4.44</td>
<td>7.02</td>
</tr>
<tr>
<td>Methylbenzene</td>
<td>5.6</td>
<td>1.330</td>
<td>4.21</td>
<td>6.65</td>
</tr>
<tr>
<td>Methanol</td>
<td>3.9</td>
<td>2.010</td>
<td>1.95</td>
<td>3.08</td>
</tr>
</tbody>
</table>

(1) Data taken from reference (5); (2) calculated by $dn/dT \cdot (\lambda k)^{-1}$; (3) measured experimentally, $p=1.25$ mW, $[\text{Cu(AA)}_2]=1.48 \times 10^{-3}$ M.

Fig. 4 - Effect of solvent on $E$

Fig. 5 - $\Delta I/I_\infty \sim P$ relationship.

Fig. 6 - $\Delta I/I_\infty \sim A$ relationship

Cu(AA) - CHCl$_3$ solution

$p = 1.15$ mW.
Fig. 6 indicates that laser thermal effect can be used to detect trace solutes. The experimental determination of trace PAN-Co(II) is made using a 1.2 mW He-Ne laser and a 5 cm cell. The working curve is shown in Fig. 7. It shows that in the range of 12-50 ppb, the curve has a good linearity. A minimum detectable concentration of 12 ppb Co is achieved, corresponding to 0.06 ng in in-beam volume. Later, the above apparatus is improved by using a lock-in amplifier and a 4 mW He-Ne laser. In this case a minimum detectable concentration of 1.8 ppb Co is achieved. The sensitivity is about 6 times higher than the earlier. Compared with the conventional spectrophotometric analysis of Co(II) with PAN, the sensitivity is considerably more high.

Our calculations have indicate that if the detection sensitivity of ΔI/I∞ is 0.005, it is possible to measure the absorbance as low as 3 x 10⁻⁶ cm⁻¹, using a 20 mW He-Ne laser and a 10 cm cell. If the absorbance (A) of substance to be determined in CHCl₃ is 2.5 x 10²₆M the minimum detectable concentration would be 10⁻¹⁰M.

The study shows that laser thermal lens spectrophotometry is a new useful technique for ultratrace analysis.

REFERENCE