Optothermal spectroscopy is a technique used for studying optical absorption in a wide range of materials. The measurement is done by detecting the heat generated by the absorption of radiation. This is done by means of a sapphire window in thermal contact with the sample under study. A common configuration for optothermal spectroscopy is shown in figure 1.

![Optothermal Detector Diagram]

Figure 1. Cross sectional view of the optothermal detector.

The detection unit consists basically of a thin sapphire plate ("window") and a ring shaped piezoelectric crystal glued together. The sample to be studied is placed on top of the sapphire. A light beam of suitable wave-length is directed from below. The beam passes through the hole in the piezoelectric crystal and through the sapphire. Absorption of the light in the sample is followed by heat generation and through heat conduction a temperature rise is obtained in the sapphire.
The resultant thermal expansion of the sapphire stresses the attached piezocrystal. The piezocrystal transforms the mechanical stress to a voltage which is amplified and processed in electric circuits. The incident light beam is chopped with a frequency in the range 1 to 1000 Hz. The above procedure is then repeated for each period resulting in a periodic signal from the piezocrystal.

Chopping the light is important for two reasons. First, variations in the ambient temperature will not affect the result. Second, only heat generated within a certain distance from the window contributes to the signal. This distance is known as the thermal diffusion length. Heat generated deeper in the sample is not transferred to the window during one period because heat conduction is a slow process. Values of the thermal diffusion length for some frequencies are shown in the table below.

<table>
<thead>
<tr>
<th>frequency (Hz)</th>
<th>thermal diffusion length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.21</td>
</tr>
<tr>
<td>10</td>
<td>0.068</td>
</tr>
<tr>
<td>100</td>
<td>0.021</td>
</tr>
<tr>
<td>1000</td>
<td>0.0068</td>
</tr>
</tbody>
</table>

Thermal diffusion length for water and for different modulation frequencies.

Now, for strongly absorbing samples the light intensity decays rapidly with distance from the surface. Thus most of the heat is generated within one thermal diffusion length and contributes to the signal. For weak absorption we have the opposite case with a slow decrease in light intensity. Only a small fraction of the light is absorbed within one thermal diffusion length resulting in a weak signal. By measuring the electrical signal it is thus possible to calculate the optical absorption coefficient of the sample. The absorption coefficient is usually proportional to the concentration of some chromophore giving the possibility to measure concentrations.
Optothermal spectroscopy has been applied to a wide range of measurement problems. The most frequently used clinical application is the measurement of Hemoglobin (Hb) in whole blood. This is done without dilution or other preparations of the sample, with the measurement of oxygen concentration in blood, sedimentation of red blood cells, and glucose concentration in plasma. Optothermal spectroscopy has also found application in the field of dermatology. For instance, hydration and penetration of drugs in the skin have been measured.

It is interesting to make a comparison between optothermal spectroscopy and other optical techniques. Transmission and reflectance spectroscopy are commonly used in clinical diagnosis. The absorption of optical radiation is common for all techniques. Thus all techniques rely on the fact that certain molecules absorb radiation of certain wavelengths. However, the detection of the absorption is different for the different techniques. In transmission spectroscopy the beam passing through the sample is measured. Very weak absorptions can be detected. The drawbacks are that no light-scattering can be allowed and that the thickness of the sample must be suitable and well-known. In reflection spectroscopy light reflected in the sample is collected and measured. This technique can be used for light-scattering samples however it is usually difficult to obtain quantitative information. Only if the sample is applied to a carrier with well-defined scattering properties it is possible to make quantitative measurement. Optothermal spectroscopy relies on detecting the light absorbed in the sample, thus the light not transmitted or reflected. This is an advantage since the signal is then proportional to the concentration to be measured. Optothermal spectroscopy is less sensitive to light-scattering than other techniques. It can therefore easily be applied to light-scattering samples without the need for any preparation of the sample. The measurement of Hb is a good illustration of this fact. The second advantage with optothermal spectroscopy is that the thermal diffusion length determines the thickness of the analysed volume (as long as the sample is thicker than the thermal diffusion length).
thermal diffusion length is determined by the thermal properties of the sample and by the chopping frequency. In conclusion one finds that optothermal spectroscopy can be applied to a large number of measurement problems. The result can easily be quantitatively interpreted and the sources for errors are few.

References
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