# INTERPRETATION OF DENSITOMETER RECORDS

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## Interpretation of Densitometer Records

When a spectroscopic record is obtained with the streak camera the intensity of light varies across the film because of changes in wavelength and along the film because of changes in time. E = exposure = intensity * exposure time, and exposure time is the same for all wavelengths and times. So E is proportional to I. If Intensity from the flash lamp is $I_1(\lambda, t)$, after passing through the samples it is reduced to:

$$I(\lambda, t) = I_1(\lambda, t) \, e^{-\alpha(\lambda, t) \, d(t)} \tag{1}$$

Where $d(t)$ is thickness of the sample. Exposure of the film and subsequent developing produces blackening (or greying) of the film. The degree of blackening is called the film density. To a first approximation the relation between film density and exposure is as shown in the accompanying sketch.
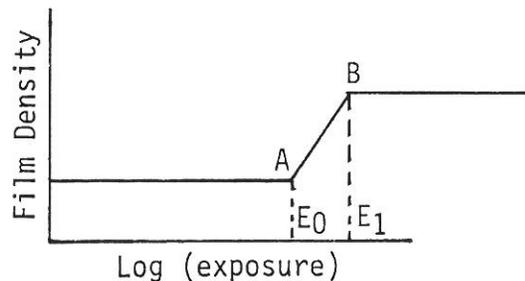


Exposure, E, will have its maximum value when absorption coefficient $\alpha$ is 0 and its minimum when $\alpha = \alpha_{max}$. In the ideal case, these 2 values would span the linear range, ie.,

$$D = D_1 \ \ \text{when} \ \ E = E_1, \alpha = 0.$$
$$D = D_0 \ \ \text{when} \ \ E = E_0, \alpha = \alpha_{max}$$

Since $I/I_1 = E/E_1 = \exp(-\alpha d)$ and, within the linear range,

$$D = \gamma \log \left[ \frac{E}{E_1} \right] + D_1 = \gamma \log \frac{I}{I_1} + D_1 \qquad (2)$$

then

$$D = -\alpha\, d\, \gamma \log e + D_1 \qquad (3)$$

Since:

$$D_0 = -\alpha_{\text{max}}\, d\, \gamma \log e + D_1$$

We can also write (3) as:

$$D = D_0 + (\alpha_m - \alpha)\, d\, \gamma \log e \qquad (3a)$$

When the developed film is placed in the densitometer and scanned with light of intensity $A_s$ at the film surface, the transmitted light intensity, $A$, is related to the film density as:

$$D = -\log \left[ \frac{A}{A_s} \right]; \qquad (4)$$

ie., larger values of $D$ produce smaller values of $A$. Combining (3a) and (4) yields.

$$D_0 + (\alpha_{\text{max}} - \alpha)d\, \gamma \log e = -\log \frac{A}{A_s}, \qquad (5)$$

so that $A$ increases with $\alpha$.

For the ideal case cited above where $\alpha = 0$ produces film density $D_1$ and $\alpha_{\text{max}}$ gives $D_0$, the corresponding ratio of transmitted intensities in the densitometer is:

$$\log \frac{A_0}{A_1} = \alpha_{\text{max}}\, d\, \gamma \log e \qquad (6)$$

The densitometer output is nominally linear with intensity, so $A_0$ and $A_1$ can be taken to be the numerical values extracted from the densitometer file. The analog to digital converter in the densitometer is limited to 8 bits, so the maximum value $A_1$ can have is 256. The minimum value of $A_0$ is zero, but this is not practically achievable because of noise on the film. For $A_0 = 10$, which might be achievable, $\dfrac{A_1}{A_0} \simeq 25$. Then the range of $\alpha$ d which can be recorded on a single film is:

$$\alpha_{max} d = \log \frac{25}{(\gamma \log e)} \tag{7}$$

For Kodak 2475 film, which we normally use for spectroscopy shots, $\gamma \approx 1$, though it varies with development. Then:

$$\alpha_{max} d \simeq 3.2 \tag{8}$$

More generally, the difference $(\alpha_2 - \alpha_1)d$ corresponding to a ratio $\dfrac{A_2}{A_1}$ is:

$$\begin{aligned}
(\alpha_2 - \alpha_1)d &= \log\frac{(A_2/A_1)}{(\gamma \log e)} \\
&\simeq 2.3 \log\left[\frac{A_2}{A_1}\right]
\end{aligned} \tag{9}$$

The absolute value of $\alpha d$ can be estimated for the non-ideal case from equations (3) and (4) provided $A_s$ is known:

$$\alpha \, d \, \gamma \log e = \log\left[\frac{A}{A_s}\right] + D_1 \tag{10}$$

For the Kodak 2475 film $D_0 \simeq 0.4$, $D_1 \simeq 2.2$, $\dfrac{E_1}{E_0} \simeq 100$.

The time dependence of the exponent $\alpha d$ results from changes in the electronic processes, which causes $\alpha$ to change, and changes in $d$ resulting from compression. Changes in the cell can be

better understood if $\alpha d$ is replaced by:

$$c \; n_{CS_2} \; \rho_{CS_2} \; d \; \sigma_t \; (\lambda, t)$$

where

$n_{CS_2} = $ number of $CS_2$ molecules per unit mass of $CS_2$

$c = $ volume fraction of $CS_2$ in mixture

$\rho_{CS_2} = $ mass density of pure $CS_2$ at ambient conditions

$\sigma = $ total cross-section of $CS_2$ molecules

Then $c \; n_{CS_2} \; \rho_{CS_2} = $ number of $CS_2$ molecules per unit mass of mixture and $d \; c \; n_{CS_2} \; \rho_{CS_2}$ is the number per unit cross-sectional area. This number does not change with time, except as reaction occurs. Then all the variation in $\alpha d$ occurs in the cross-section $\sigma(\lambda, t)$, which is directly related to the transition dipole moment.

If a more accurate relation between $A$ and $\alpha$ is required, deviations from the simplified relation between $D$ and log $E$ must be considered. This will require that the true relation be determined empirically for the existing conditions of the experiment. This is not a trivial matter. Interpretations of the measured values of $\sigma$ or $\alpha$ requires separation of the scattering and absorbtion contributions to $\sigma$. The former are not negligible and, in fact, may be dominant, as indicated by measured values of the reflection coefficient.