

# LIMITS OF DIFFUSE LIGHT SCATTERING MEASUREMENTS

SZ. BÖRÖCZ and L. LÁNG

Institute of Physics, Section of Physics for Chemical Engineering,  
Technical University, H-1521 Budapest

## Summary

This paper describes a short investigation on the optimum condition of a reflection spectrometer and a quantity ( $Z$ ) is suggested which is characteristic of the signal/noise ratio.

Whenever optically diffuse scattering systems are measured one of the main problems is the meagre light intensity. So the minimum valid signal emerging from the noise is to be detected.

Restrictive factors are the lamps, the detector, the slit, the optical system collecting the light scattered by the sample, the electronics attached to the detectors, the method for data acquisition, and data processing.

Our measurements are carried out by a Unicam SP 700 monochromator to which the electronics prepared by ourselves is attached. Measured data are evaluated by a microcomputer.

According to the optical schema of the monochromator (double-beam) to enhance the quality of the measurements 2 spectra are measured:

First a calibration is carried out by memorizing a spectrum with a white standard as sample. Second, a spectrum of a sample is memorized, but all data are corrected by the similar data of the calibration. So the reflection:

$$R = \frac{\frac{S}{R}}{\text{calibration}}$$

where  $S$  is the sample signal

$R$  is the reference signal

The calibration corrects the deviations of the optical elements, as well. However, to simplify our model the calibration is uniformized by memorizing a value of 7000 at every point of the spectrum. That is why the random alterations of the calibration are neglected.

However, the general expression for the intensity of the remission is

$$R = \frac{I_S}{I_W} = \frac{\frac{I_S - I_D}{I_R - I_D}}{\frac{I'_W - I'_D}{I'_R - I'_D}} \quad (1)$$

at every point of the spectrum, where

$I_S$  is the remission intensity of the sample,  
 $I_D$  is the dark current,  
 $I_R$  is the a referential intensity.

The quantities distinguished by prime are measured during the calibration procedure.

$I_W$  is the remission intensity of the white standard.

$D$  is a quantity for the noise [1], and

$$Z = \frac{D}{\frac{\sum_{i=1}^n Y_i}{n}} = \frac{\sqrt{\sum_{i=1}^n (Y_{i+2} - 3Y_{i+1} + 3Y_i - Y_{i-1})^2}}{\sqrt{18(n-1)} \frac{\sum_{i=1}^n Y_i}{n}}$$

where  $n$  denotes the the number of data and  
 $Y_i$  the  $i$ -th data measured

is divided by the mean signal value, so the quantity  $Z$  is independent of the amount of the signal.

Our lamps are stabilized-power W and D<sub>2</sub> lamps. It is investigated how much time it takes to diminish the noise of the lamps. Measurements are carried out 10, 30 and 60 minutes after the lamps are on. It takes only 10 minutes for the W lamp to get into steady state condition. For the D<sub>2</sub> lamp  $Z$  is observed to decrease almost constantly.

*Turn on table*

$t$ (min)	10	30	60	
W	1.12	1.40	1.11	visible region
D	1.44	1.28	1.19	UV-region

$Z \cdot 10^3$

In case of a PM it is well known, that to increase the voltage by 100 V, the current response is doubled, while the incident light is the same. However, the noise is increased, as well. The question arises whether the maximum PM voltage is optimal or not.

Slit width (mm)		0.35			0.50	
PM voltage (V)	1000	950	900	900	850	800
Reference light beam	1083	758	508	1106	722	471
$Z \cdot 10^3$	1.3	1.35	1.19	0.80	0.87	1.46

According to the measurements  $Z$  is not affected by the  $PM$  voltage. However, when  $I_R$  is meagre, extinction is large, the differences and the quotients are more sensitive to the noise, that is why the maximum  $PM$  voltage is suggested.

It should be taken into consideration that a calculation limit exists as well: when the light beam in certain conditions is meagre, the sample and the reference values are near the value of the dark current. However, when in (1) the differences and the quotients are calculated, the measurements show high uncertainty.

But what  $Z$  value is the suggested during a measurement? This depends on whether the spectrum structured (fine structure) or not. In remission measurements, in general, there is no fine structure, so higher  $Z$  values are possible. Naturally the narrower the slit width the less the  $Z$ .

As an example a remission spectrum of a white surface is recorded at a minimum slit width (0.04 mm) within the range of 26 000–20 000  $\text{cm}^{-1}$ . Next the reference beam as well as the sample beam is diminished by a factor of 10. The value of  $Z$  is increased.

$\nu (\text{cm}^{-1})$	21 000	22 000	23 000	24 000	25 000	26 000
$Z \cdot 10^3$	0.14	0.22	0.41	0.51	1.2	1.8
$I_R - I_D$	1800	1700	1500	1200	800	300

Light attenuated by a factor of 10

$Z \cdot 10^3$	1.84	2.52	3.76	4.32	4.48	—
$I_R - I_D$	250	200	170	110	75	38

What is the upper limit of  $Z$  where the spectra are still evaluable? To show the different values of  $Z$  at a given spectrum a flat spectrum was recorded in the UV and visible regions. The regions are segmented, and  $Z$  is calculated in the segmented regions. In the regions where system response is poor,  $Z$  increased enormously. Our opinion is that the upper limit of  $Z$  is  $Z = 10^{-2}$  in remission spectra.

This problem is solved in certain instruments. The spectrum is recorded many times and memorized data are accumulated until the spectrum emerges from the background noise.

Another solution: the spectrum recorded at very low speed, and the data are accumulated at every point. But this method is problematic when the long range stability of the system is not sufficient.

Some measurements are described to monitor the conditions of a reflection spectrometer and to assess how the parameters of a system should be

Table 1

Values of $Z \cdot 10^3$ within the spectrum segments			
Visible region			
$\nu$ ( $\text{cm}^{-1}$ )	$Z \cdot 10^3$	$\nu$ ( $\text{cm}^{-1}$ )	$Z \cdot 10^3$
14 000	1.79	20 000	0.58
15 000	0.50	21 000	0.57
16 000	0.44	22 000	0.95
17 000	0.32	23 000	1.39
18 000	0.37	24 000	2.92
19 000	0.39	25 000	3.28
UV-region			
$\nu$ ( $\text{cm}^{-1}$ )	$Z \cdot 10^3$	$\nu$ ( $\text{cm}^{-1}$ )	$Z \cdot 10^3$
27 000	0.67	34 000	1.24
28 000	0.62	35 000	0.77
29 000	0.80	36 000	1.35
30 000	0.87	37 000	1.19
31 000	0.76	38 000	1.22
32 000	1.00	39 000	1.74
33 000	1.08	40 000	2.01

tuned to gain the optimal result. This process is more important in reflection spectroscopy because the absorption spectra are recorded within an extinction range  $10^4:1$ , but in reflection spectroscopy the extinction range is  $10^6:1$ .

Prof. László LÁNG }  
 Dr. Szilárd BÖRÖCZ } H-1521 Budapest