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Diffuse reflectance measurement using gas absorption spectroscopy

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ABSTRACT

A precise method for the measurement of diffuse reflectance by using gas absorption spectroscopy technique with an integrating sphere is demonstrated. A quantitative relationship between the diffuse reflectance and the gas absorption spectrum is formulated, which has been further validated by experiments. The precision of the reflectivity measurement depends on the diameter and port fraction of the integrating sphere as well as gas concentration, and it increases linearly with the magnitude of the reflectivity. A high precision of 0.005% was achieved at the reflectivity of 0.98844(5).

1. Introduction

Diffuse reflectance measurement is important in many studies, such as evaluation of the quality of compounds, element and crystal [1–3], thin films and surface structure of the materials [4]. As a powerful tool, it is employed in fields of physics, chemistry, biology and medicine [5–7]. Traditional method for diffuse reflectance measurement uses a spectrometer to measure the reflected light intensity. The precision of this traditional method depends on the precision of the spectrometer and the stability of the light source. The angle of incidence and the detection angle may also lead to systematic error. For practical applications, especially for the measurement of some parameters of materials, which are sensitive to the reflectivity, more precise methods are always in demand. At present, the improvement on the precision of diffuse reflectance measurement is usually based on higher precise spectrometer or more sensitive device. We show here that this purpose can be achieved by more sensitive detecting techniques. Gas absorption spectroscopy, especially tunable diode laser absorption spectroscopy, can provide precise and highly reliable absorption spectrum. The physical quantities relating to the spectrum can be obtained from spectral analysis [8–11]. When using integrating sphere as a gas absorption cell for gas concentration measurement, the diffuse reflectance of a material coated in the inner surface of integrating sphere can be directly correlated with the gas absorption spectrum. This correlation allows us to derive the diffuse reflectance from gas absorption spectrum analysis. Most reported papers about using integrating sphere were about gas concentration measurement [12,13]. In this paper, a novel high precision measurement method for diffuse reflectance has been developed by employing gas absorption spectroscopy with an integrating sphere. A theoretical model of the relationship between the diffuse reflectance and gas absorption spectrum based on the integrating sphere theory and Beer–Lambert law was formulated, which has been validated by experiments. The new method can achieve a precision of 0.005% at the reflectivity of 0.98844(5).

2. Theory

Many integrating sphere theories have been reported before [14–18]. For the convenience of building the relationship with the Beer–Lambert law, here we only consider the total intensity change in the integrating sphere. For a good quality commercial integrating sphere with standard spherical cavity geometry, the radiance from a given point is a constant in any direction, and after a single pass, the irradiance is perfectly uniform over the inner surface of the sphere. The average path length for a single pass through a closed integrating sphere is equal to two thirds of the diameter [19]. According to the Beer–Lambert law, the intensity in the integrating sphere after the first reflection can be written as:

$$I_1 = I_0 \rho \exp\left(-\alpha N \frac{2}{3} D\right), \quad (1)$$

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where D is the diameter of the integrating sphere, ρ is the diffuse reflectance, I_0 is the single incident beam intensity, α is the gas absorption cross section and N is the number density of the target gas in the integrating sphere. For the first transmission, the intensity of the laser is decreased by gas absorption and the reflection loss. From the second to the nth transmission, laser intensity is also decreased by the ports of the integrating sphere. It is convenient to use port fraction f to describe open ports ratio, which equals to the sum of all open ports area divided by the total internal surface area. After the second reflection, the intensity in the integrating sphere is:

$$I_2 = I_0\rho^2(1-f)\exp\left(-\alpha N\frac{4}{3}D\right) \tag{2}$$

It follows that after the nth reflection, the intensity in the integrating sphere becomes:

$$I_n = I_0\rho^n(1-f)^{n-1}\exp\left(-\alpha Nn\frac{2}{3}D\right) \tag{3}$$

Because the laser is continuously incident into the integrating sphere, the total intensity in the integrating sphere is the intensity sum from the first to the nth reflections. Expanding the total intensity into an infinite power series, and given the fact that $\rho(1-f)<1$, Eq. (3) reduces to a very simple form:

$$I = I_0\frac{1}{\frac{1}{\rho\exp(-\alpha N2/3D)}-(1-f)} \tag{4}$$

Eq. (4) indicates that a uniform light field is formed inside the integrating sphere. The total input light intensity in the integrating sphere is higher than the instantaneous input intensity due to the superposition of multiple reflections inside the cavity. It follows that the intensity per unit area on the sphere inner surface is given by

$$I = \frac{I_0}{\pi D^2}\frac{1}{\frac{1}{\rho\exp(-\alpha N2/3D)}-(1-f)} \tag{5}$$

This equation can be used to predict the intensity received by any point inside the integrating sphere for a given input intensity I_0. Eq. (5) is purposely written into the product of two parts. The first part describes the initial incident intensity uniformly distributed over the entire inner surface of the integrating sphere. The second part of the equation is dimensionless, which can be defined as the sphere multiplier M,

$$M = \frac{1}{\frac{1}{\rho\exp(-\alpha N2/3D)}-(1-f)} \tag{6}$$

It means that the superposition of infinite number of diminishing reflecting light intensity can be regarded as M times the initial incident light intensity. As mentioned above, the average path length for a single pass through a closed integrating sphere is equal to two thirds of the diameter. So the effective optical path length L_{eff} of the light in the integrating sphere can be expressed as follows:

$$L_{\mathrm{eff}} = \frac{2}{3}D\frac{1}{\frac{1}{\rho\exp(-aN2/3D)}-(1-f)} \tag{7}$$

Thus, the relationship between the diffuse reflectance and the effective optical path length L_{eff} is established. The diameter D and port fraction f in Eq. (7) can be measured directly. If the gas concentration N is known, the reflectivity will be directly related to the effective optical path length. In principle, the theoretical effective optical path length of the integrating sphere can be set as a path length, which can be obtained from an absorption spectrum of a gas with the same concentration N in Eq. (7) by using integrating

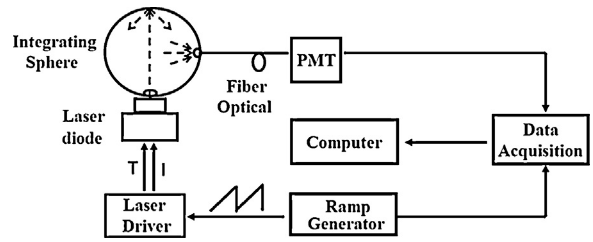

Fig. 1. Schematic diagram of the reflectivity measurements configuration.

sphere as a gas absorption cell. According to the Beer–Lambert law, the transformation formula is as follows:

$$L_{\mathrm{eff}} = -\frac{1}{aN}\ln\frac{I}{I_0} \tag{8}$$

Hence, the only thing needed is to obtain the effective optical path length from the gas absorption spectrum measurement, then, the reflectivity can be derived from Eq. (7). The first derivative of Eq. (7) can be used to analyze the precision of the diffuse reflectance measured using this method:

$$\frac{d\rho}{\rho} = \left(1-\rho(1-f)\exp\left(-\alpha N\frac{2}{3}D\right)\right)\frac{\Delta L_{\mathrm{eff}}}{L_{\mathrm{eff}}} \tag{9}$$

3. Experimental validation

Experiments at room temperature and atmosphere pressure have been carried out to validate the theoretical model. As shown in Fig. 1, an integrating sphere with a diameter of 83.8 mm (Labsphere. 3P-GPS-033-SL) and port fraction of 0.002 was used as the gas absorption cell (including two ports: input port and output port). The coating material in the integrating sphere is Spectralon reflectance material, which is a thermoplastic resin, it has high reflectivity of 99% at 764 nm as the manufacturer provided. Atmospheric oxygen was used as test gas. A tunable diode laser (Laser Components. Single Mode VCSEL 763 nm TO46) with a center frequency of 764 nm was used as the light source. A laser beam was input into the integrating sphere through the input port, and by adding a 10 Hz saw-tooth waveform with the amplitude of 360 mV to the injection current, its center frequency was tuned across the P_{11} line of oxygen at 764 nm. A photomultiplier (Hamamatsu, PMTH-S1-1P28) was used as the receiver to detect the output optical signal from the output port of the integrating sphere and transformed the optical signal into electric signal. The electric signal was collected by a data acquisition card and transmitted to a computer. A data analyzing program based on LabVIEW™ can automatically record the data and calculate the gas absorbance, which corresponds to the term $-\ln I/I_0$ in Eq. (8).

4. Results and discussion

The validity of this method depends on the correctness of Eq. (7). We made numerical calculations for the absorbance of oxygen P_{11} line variation with different concentrations according to Eq. (8) under the same experimental conditions. Eq. (7) was used to calibrate the optical path length of the integrating sphere. The absorption cross section of P_{11} was obtained from HITRAN-2008 database. The numerical data are represented by the cross points in Fig. 2. The experimental results of absorbance at different concentrations are shown in Fig. 2 marked by triangle points, which show excellent agreement with the numerical modeling result. This result confirmed that the optical path length can be described by Eq. (7). These results were also compared with the numerical modeling result with a constant optical path length of 436 cm for a single pass cell, which was the optical path length of the integrating