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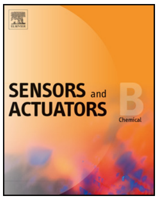

Real-time optimal combination of multifrequency information in phase-resolved luminescence spectroscopy based on rectangular-wave signals

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ABSTRACT

A method for optimally combining multifrequency information in phase-resolved luminescence spectroscopy using rectangular-wave signals is proposed to improve the accuracy in the determination of the analyte concentration. From the rectangular-wave signal, phase-shift- and modulation-factor-based apparent lifetimes are estimated at each harmonic independently, together with their corresponding standard errors. Both the lifetimes and their standard errors are estimated "on-the-fly" from the Fast Fourier Transform (FFT) of the excitation and emission signals and applying error propagation theory. Independent determinations of the analyte concentration and their standard errors are then optimally combined in order to obtain an improved determination of the analyte concentration. The combination, formulated in a statistical framework, is a weighted average of different determinations proportional to the inverse of the variance of each independent determination. The proposed method has been applied to an oxygen measuring system to evaluate its accuracy and demonstrate its applicability in real-time measuring instruments.

1. Introduction

To date, most measurement schemes based on phase-resolved luminescence spectroscopy [1] make use of sine- or square-wave modulated excitation sources [2,3], and phase detection is performed at one or several modulation frequencies by use of commercial lock-in amplifiers [4–6] or either simple analog [7,8] or digital [9,10] implementations.

In a recent article [11], we demonstrated some advantages of using short duty-cycle rectangular-wave modulated excitation signals in phase-resolved luminescence spectroscopy. Among others, the use of rectangular-wave signals allows to determine the analyte concentration independently for the different harmonics of the modulated signal. In that work, we also demonstrated that the combination of the information from different harmonics can significantly improve the accuracy of an oxygen measuring system. In a statistical formulation, the optimal combination of several independent estimates of analyte concentration is a weighted average of individual estimates, where such weights are inversely proportional to the variances of the estimates (i.e., an estimate with high uncertainty will have a lower weight than an estimate with low uncertainty). One of the problems encountered in the referenced work was the definition of a procedure for computing the variance of each estimate. In this work, the variances were determined from a collection of measurements recorded in the laboratory (i.e., from the same set of measurements used to calibrate the oxygen measuring system). The experiments using the variances computed with this procedure demonstrated that, theoretically, if we had an accurate estimation of the variances, the information from different harmonics could be combined to improve the accuracy of an oxygen measuring system. However, the procedure proposed for computing the variances cannot be implemented in a real instrument: On the one hand, it makes no sense recording N measurements for improving the accuracy of just one measurement, since it would increases the measuring time in a factor N. On the other hand, the variances cannot be previously estimated as a part of the calibration procedure, since the experimental conditions could strongly differ from the operation conditions [12].

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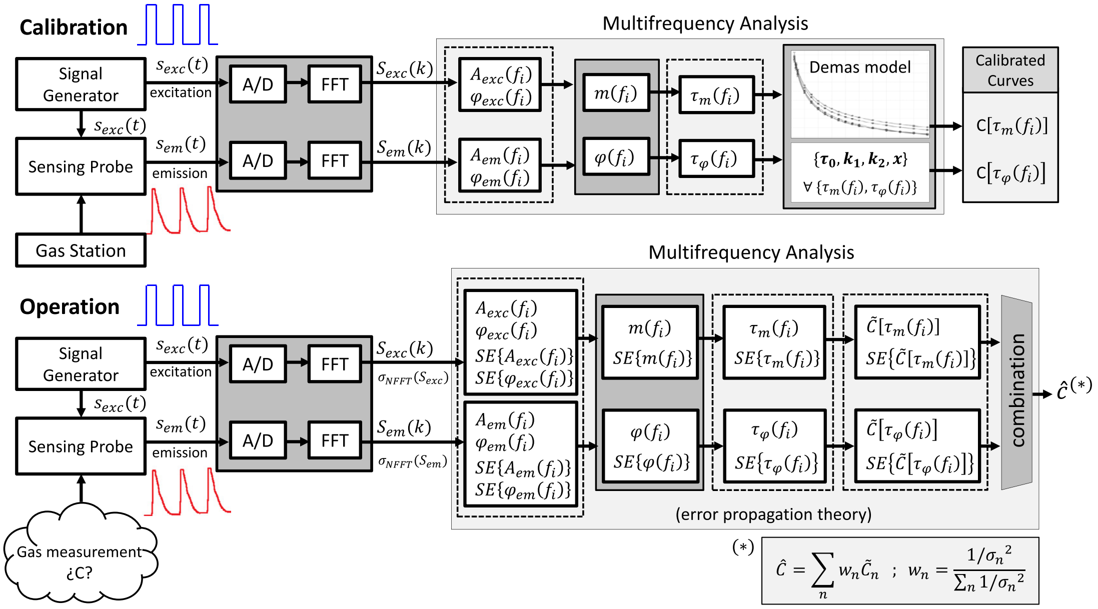

Fig. 1. Block diagram describing the calibration process in phase-resolved luminescence spectroscopy and determination of the analyte concentration in real operating conditions by combining multifrequency information using rectangular-wave signals to improve the accuracy in the determination of the analyte concentration.

In another recently published study [13], we demonstrated that an algorithm based on the Fast Fourier Transform (FFT) [14] of the luminescent signal can be used to obtain the uncertainty associated with the phase-shift or modulation-factor measurements from a single recorded emission signal. This way, the uncertainties can easily be obtained from the recorded signal in real-time and under the operating conditions. Therefore, by applying error propagation theory, the uncertainly associated with the estimated apparent lifetimes or analyte concentration determinations can be estimated.

Taking into account the contribution of the two previous works [11,13], in this letter we propose the application of the FFT-based estimation of the uncertainty (extended to the case of multifrequency signals) to the optimal combination of multifrequency information in phase-resolved luminescence spectroscopy based on short duty-cycle rectangular-wave signals. This way, the combination of multifrequency information improves the accuracy in the analyte determination using exclusively the recorded signal involved in the current measurement, which provides a procedure that can be implemented in a real instrument and can operate in real-time. To the best of our knowledge, this is the first time that a multifrequency phase-modulation method with combination of information on-the-fly from more than one harmonic has been used in luminescence spectroscopy. The proposed approach has been applied to an oxygen measuring system based on phase-resolved luminescence, and experiments show that this method is able to optimally combine information from different harmonics in real-time (i.e., without requiring a calibration in the operating conditions).

2. Theory

2.1. Estimation of apparent lifetimes $\tau_m(f_i)$ and $\tau_\varphi(f_i)$ for each harmonic f_i

The use of short duty-cycle rectangular signals for excitation provides several harmonics with enough amplitude for allowing simultaneous measurements of phase-shift (φ) and modulation-factor (m) at several frequencies. For multifrequency analysis of the response, we apply an analog-to-digital conversion and subsequent processing of the recorded digital signals, which can easily be implemented via software in an ordinary computer or a microcontroller [4,10,11].

Let us suppose a signal $s_e(t)$, where the subindex e stands for excitation (exc) or emission (em) signals (see Fig. 1). If analysis of the digitized signal $s_e(m)$ is performed on a finite interval of M samples containing an integer number of cycles, then the amplitude (A_e) and the phase (φ_e) of the signal can be obtained for each harmonic f_i from the FFT [14]:

$$S_e(k) = \mathrm{FFT}\{s_e(m)\} = \sum_{m=0}^{M-1} s_e(m) \exp\left(\frac{-j2\pi km}{T}\right) \tag{1}$$

$$A_e(f_i) = \sqrt{[\mathrm{Re}\{S_e(k_i)\}]^2 + [\mathrm{Im}\{S_e(k_i)\}]^2} \tag{2}$$

$$\varphi_e(f_i) = -\arctan\left[\frac{\mathrm{Im}\{S_e(k_i)\}}{\mathrm{Re}\{S_e(k_i)\}}\right] \tag{3}$$

where k_i is the frequency component associated with the ith harmonic f_i. Taking into account the amplitude and phase of both signals (exc/em), the modulation-factor (m) and the phase-shift (φ) can be estimated at each harmonic f_i as [2]:

$$m(f_i) = \frac{A_{em}(f_i)}{A_{exc}(f_i)} \tag{4}$$

$$\varphi(f_i) = \varphi_{em}(f_i) - \varphi_{exc}(f_i) \tag{5}$$

The modulation factors and the phase shifts can be used to estimate modulation-factor- and phase-shift-based apparent lifetimes ($\tau_m(f_i)$ and $\tau_\varphi(f_i)$) from each harmonic f_i as [11]:

$$\tau_m(f_i) = \tau_0 \frac{m(f_i)/m_0(f_i)}{\sqrt{1 + (2\pi f_i \tau_0)^2 \cdot (1 - (m(f_i)/m_0(f_i))^2)}} \tag{6}$$

$$\tau_\varphi(f_i) = \frac{\tan[-\varphi(f_i)]}{2\pi f_i} \tag{7}$$

where τ_0 is the apparent lifetime at null concentration of the analyte and $m_0(f_i)$ is the modulation-factor at null concentration and frequency f_i.