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Direct estimation of the standard error in phase-resolved luminescence measurements. Application to an oxygen measuring system

Carlos Medina-Rodríguez [a], Santiago Medina-Rodríguez [a,b,*], Ángel de la Torre-Vega [a], Alberto Fernández-Gutiérrez [b], Jorge F. Fernández-Sánchez [b]

[a] Department of Signal Theory, Telematics and Communications, CITIC-UGR, University of Granada, C/ Periodista Rafael Gómez 2, E-18071 Granada, Spain
[b] Department of Analytical Chemistry, Faculty of Sciences, University of Granada, Av. Fuente Nueva s/n, E-18071 Granada, Spain

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ABSTRACT

Phase-resolved luminescence measurements provide accurate estimations under low illumination conditions and/or low signal-to-noise ratio. However, the accuracy of these measurements is limited by noise. In this article we propose a procedure, based on spectral analysis of noise, for the statistical characterization of the noise affecting the luminescent signal and the determination of the standard errors affecting the modulation-factor and the phase-shift estimates. This way, in addition to the phase-resolved luminescence measurements, we provide information about the uncertainty of these measurements. The standard errors are directly estimated from the recorded signal and the procedure only requires a FFT computation, which makes it fast and easy to be implemented. The proposed method was successfully applied to an oxygen measuring system based on phase-resolved luminescence. At each single measurement, it provides, in addition to the oxygen partial pressure, the corresponding standard error. Experiments show that the standard errors estimated from FFT using one signal are coherent with the standard deviations and the root mean square errors observed from a collection of measurements.

1. Introduction

In the recent years, optical chemical sensors have achieved great popularity in many areas related to environment, industry, biotechnology and medicine [1–4], and a variety of measurement methods, sensing materials and optical devices have been developed showing the advantages of optical sensing over other transduction methods [5–8]. Some of these advantages are the availability of low-cost miniature optoelectronic light sources and detectors, the versatility of formats and materials for the development of optical sensing phases, the absence of electromagnetic interferences and the flexibility for designing multi-analyte array-based sensors or for integrating optical chemical sensors into sensor networks [8]. Currently, the most commonly techniques employed in optical chemical sensors are optical absorption and luminescence [1,6]. In this work, we focus on luminescent chemical sensors based on the measurement of luminescence lifetime.

Lifetime-based measurements are preferred in luminescence spectroscopy since they are less susceptible to errors than direct intensity measurements [1,9,10]. The luminescence lifetime can be determined by time-resolved methods or phase-resolved methods [1,11–13]. Unlike time-resolved methods, phase-resolved methods do not require advanced instrumentation, and allow the use of low-cost, simple, and miniature light sources and optoelectronic devices [4,9,14,15], making this technology attractive for many new applications [7,8]. Consequently, phase-resolved methods are preferred for designing cheap, reliable and robust luminescence lifetime-based chemical sensors [16–19].

To date, a wide variety of measuring systems based on phase-resolved techniques have been reported in the literature for working with light sources modulated at one or several modulation frequencies [4,11,13,20]. These systems utilize the frequency domain to determine the phase-shift and/or the modulation-factor at the modulation frequency from the excitation and emission signals [11,14]. The values of phase-shift and modulation-factor (or the apparent lifetimes calculated from them) are directly correlated with the analyte concentration to be determined, and therefore

* Corresponding author at: Department of Signal Theory, Telematics and Communications, Research Center for Information and Communications Technologies of the University of Granada (CITIC-UGR), C/ Periodista Rafael Gómez 2, E-18071 Granada, Spain.
E-mail address: smedina@ugr.es (S. Medina-Rodríguez).

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they can be used to obtain the corresponding calibration curves of a sensor [1]. This approach has allowed the development of luminescent chemical sensors with high sensitivity, selectivity and robustness, fast response times and low cost [9,11,21].

An important problem affecting whatever measuring system is the uncertainty associated to the measurements. In phase-resolved luminescence chemical sensors, this uncertainty is mainly associated to noise affecting the luminescent signals, particularly when the measurements are acquired under low illumination conditions or under low signal-to-noise ratio (SNR) [17,22].

In this work we propose a procedure for the direct estimation of the standard error in phase-resolved luminescence measurements based on the In-phase/quadrature (IQ) method [9,11,17,23,24]. It is based on the spectral analysis of the noise in a spectral band around the modulation frequency. By assuming that the noise affecting the luminescent signal at the modulation frequency can be statistically characterized from the spectral analysis around this frequency, the standard error affecting the modulation-factor or the phase-shift is estimated. From these standard errors, by applying error propagation theory and using the calibration curves, the standard error in the analyte determination can also be estimated. The procedure for estimating the standard error is fast and easy to be implemented since it only requires the computation of a Fast Fourier Transform (FFT) of the luminescent signal (and computation of FFT is very efficient even for very long signals).

Therefore, the proposed method provides, for each single measurement, not only the analyte determination but also the corresponding standard error, which is a significant add-on for phase-resolved luminescence measuring systems (since, conventionally, the estimation of standard errors would require the acquisition of several measurements). The proposed method has been applied to an oxygen measuring system based on phase-resolved luminescence. The results show that the standard errors estimated with the procedure (for each single measurement) are coherent with standard deviations and root mean square errors (RMSE) observed from a collection of samples at different conditions.

2. Theory

2.1. IQ method

The IQ method [23] has been used in phase-resolved luminescence for the estimation of the amplitude and the phase of the excitation and emission signals involved in the luminescence measurements [9,11,17,24]. Let's suppose a sinusoidal discrete signal $x(t)$ with T samples ($t = 0, 1, \ldots, (T-1)$), at a sampling frequency f_s, with amplitude A_x, phase φ_x and frequency f_0:

$$x(t) = A_x \cos\left(\frac{2\pi f_0 t}{f_s} + \varphi_x\right) \tag{1}$$

The in-phase and quadrature components of the signal can be estimated, respectively, as:

$$I_x = \frac{2}{T}\sum_{t=0}^{T-1} x(t)\cos(2\pi f_0 t/f_s)$$

$$Q_x = \frac{2}{T}\sum_{t=0}^{T-1} x(t)\sin(2\pi f_0 t/f_s) \tag{2}$$

and from I_x and Q_x, the amplitude and the phase of the signal can be estimated as:

$$A_x = \sqrt{I_x^2 + Q_x^2}, \qquad \varphi_x = -\arctan(Q_x/I_x) \tag{3}$$

2.2. Effect of noise in the IQ domain

If the signal is contaminated with an Additive White Gaussian Noise (AWGN) $n(t)$ with standard deviation σ_n, then the noisy signal is $y(t) = x(t) + n(t)$, and the in-phase and quadrature components of the noisy signal will be:

$$I_y = I_x + I_n, \qquad Q_y = Q_x + Q_n \tag{4}$$

where I_n and Q_n are the in-phase and quadrature components of the noise, which are independent Gaussian random variables with null mean and standard deviation $\sigma_{nIQ} = \sigma_n \cdot \sqrt{2/T}$ (see Supporting Information, SI, for details).

2.3. Estimation of σ_{nIQ} from the FFT

The estimation of the noise level affecting the signal is based on the Discrete Fourier Transform (DFT) of the noisy signal (DFT is usually implemented with the FFT algorithm). Let $N(k)$ (with $k = 0, 1, \ldots, (T-1)$) be the FFT (or equivalently the DFT) of a white Gaussian noise $n(t)$, defined as [25,26]:

$$N(k) = \sum_{t=0}^{T-1} n(t)\exp(-j2\pi kt/T) \tag{5}$$

As a consequence of the orthogonality of the transformation, the real and imaginary parts of each spectral component are independent Gaussian random variables with null mean and standard deviation $\sigma_N = \sigma_n\sqrt{T/2}$ [27]. The standard deviation of the noise in the IQ domain can therefore be estimated from the FFT as (see SI for details):

$$\sigma_{nIQ} = \frac{2}{T}\sigma_N \tag{6}$$

where σ_N^2 is the variance of the real and imaginary parts of the FFT components:

$$\sigma_N^2 = \frac{1}{2T}\sum_{k=0}^{T-1}\left[Re(N(k))^2 + Im(N(k))^2\right] \tag{7}$$

Since the signal $n(t)$ is not available, the standard deviation σ_N must be estimated from the signal $y(t)$ or its FFT, $Y(k) = X(k) + N(k)$. Therefore, not all the frequency components in $Y(k)$ can be used for estimating σ_N, because of the presence of the signal of interest at the frequency f_0. There also could be other signals in addition to the AWGN noise (interferences), or the noise could be colored. For this reason, σ_N should be estimated from a restricted set of frequencies $\mathcal{S}$ (with K_S spectral components), including components around f_0 (in order to estimate σ_N consistently with the power spectral density around f_0 for the case of colored noise) but excluding f_0 (since this frequency contains the signal of interest with more spectral power than the noise):

$$\sigma_N^2(\mathcal{S}) = \frac{1}{2K_S}\sum_{k\in\mathcal{S}}\left[Re(Y(k))^2 + Im(Y(k))^2\right] \tag{8}$$

and then the standard deviation of the noise in the IQ domain is estimated as $\sigma_{nIQ}(\mathcal{S}) = \sigma_N(\mathcal{S})\cdot 2/T$.

2.4. Removing the bias associated to interferences

Real signals are usually contaminated with interferences (for example, the 50/60 Hz line interference and its harmonics). The frequency f_0 is usually selected to avoid them, but avoiding the presence of interferences in the set of selected frequencies $\mathcal{S}$ is more difficult. Interferences with spectral power below that of the noise are not relevant, but those with spectral power above the noise will