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Fast lifetime and amplitude determination in luminescence exponential decays

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ABSTRACT

In this work a novel algorithm for the fitting of an exponential decay luminescence curve is proposed. It is based on the integration of the luminescence intensity over two or three temporal windows in different states of the sample: steady state with and without optical excitation and during the whole luminescence intensity decay. These measurements allow to obtain the amplitude of the signal, the offset and the lifetime respectively, not only for single exponential decays, but also for multiple exponential behavior, if averaged values are considered. The proposed approach does not require a very fast instrumentation, since the width of the integration windows are fixed to values much higher than the expected lifetime of the sample, which represents a clear advantage over other window-based methods for the determination of luminescence lifetime. In addition, no previous knowledge of the expected lifetime is necessary. Specifically, this algorithm is applied for the fitting of the luminescence curve of an oxygen sensor based on PtOEP, and implemented on a very reduced and simple electronics, consisting basically on a digital color detector of 12-bits resolution that allow to define integration times high enough for measurements of the intensity using this approach. Good results are achieved, proving the benefits of the method.

1. Introduction

In the last years, optical sensing is gaining more and more acceptance over electrochemical detection due to the advantages that it offers regarding flexibility, remote sensing through fiber optics, response time or its non-invasive character [1–4]. Optical sensing is based on the monitoring of one or several optical parameters of the sensor response including but not limited to luminescence intensity [5], wavelength shift [6], color change [7], absorbance [8], reflectance [9] or luminescence lifetime [10]. The chemosensors based on luminescent indicators are particularly promising due their high sensitivity and versatility [11,12]. Among the different types of luminescent highlight those based on attenuation of luminescence intensity and/or lifetime by the target analyte. In consequence, both parameters luminescence intensity and lifetime are susceptible to be related to the concentration of the analyte for its determination [13]. From the point of view of photostability and immunity to stray optical signal interference, decay time measurement seems to be more advantageous than intensity [14,15]. Furthermore, using lifetime methods there is no dependence in the measurements of the detector sensitivity, sensing layer thickness or indicator concentration. Nevertheless, studies where the luminescence intensity is measured have been also reported since the instrumentation for this strategy is much simpler due to the steady nature of the intensity [16–18].

Time-resolved measurements of luminescence lifetimes, where the lifetime refers to the rate of luminescence decay after optical excitation, are applied in medicine, biology and physics [19]. The decay time of the luminescence can be determined with different methods such as time-domain techniques that require high speed and complex instrumentation such as time-correlated single photon counting [20] or phase modulation techniques which utilizes the frequency-domain to determine lifetimes with relatively simple hardware and signal-processing, thus making this technology available for many new applications [21].

Most of the luminescence decay curves follow a single or multiple exponential form [22], and many studies have been published where different algorithms and methods are exposed for the fitting of the curve parameters amplitude and decay time [23,24]. Other strategies consist of the direct reading of the decay time, instead of its calculus from secondary measurements, such as the implemented in reported handheld portable instrumentation [24,25].

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In this work, the authors propose a new simple method to obtain both the amplitude and the decay time or lifetime in a luminescence emission when it can be fitted to a simple or multiple exponential functions, using a time domain analysis technique. This new algorithm consists of the integration of the luminescence intensity emitted by the sample in both steady state and during the whole signal decay. This method allows a fast calculation of the decay amplitude and lifetime, with no requirements about fast instrumentation or previous knowledge of the estimated value of the lifetime, as it will be shown in the following section.

In Section 3, this method is tested on a case study where an oxygen sensor is calibrated using a very simple electronics that allow to fully characterize the curve decay.

2. Theory

A luminescence process is produced from molecules excited to higher energy states – some vibrational levels of the excited electronic state – by the absorption of energy.certain. The excited molecule can return to the ground state directly by emitting a photon, which is known as fluorescence, or in a two-step process composed by the transition to the triplet state and the later emission of a photon, called phosphorescence [26]. The lifetime of an excited singlet state is approximately 10^{-9} to 10^{-7} s and therefore the decay time of fluorescence is of the same order of magnitude. As phosphorescence originates from the lowest triplet state, it will have a decay time approximately equal to the lifetime of the triplet state, that is, from 10^{-6} s to minutes.

When a luminophore is excited with a pulse of radiation, as a square pulse or an infinitely sharp pulse (δ-function), this results in an initial population n_0 of luminophores in the excited state. This population decays according to:

$$\frac{dn(t)}{dt} = (\Gamma + k_{n\Gamma})\, n(t) \tag{1}$$

where $n(t)$ is the number of excited molecules, Γ is the emissive rate and $k_{n\Gamma}$ is the non-radiative decay rate [27]. Solution of Eq. (1) results in an exponential decay of the excited population, which leads to a luminescence emission whose intensity is proportional to $n(t)$, that can be expressed as:

$$I(t) = I_0 e^{-(t/\tau)} + b \tag{2}$$

being I_0 the intensity at time 0, τ the lifetime or decay time and b the offset or baseline. In the following we are assuming that this baseline is negligible.

Most of the luminophores exhibits complex behavior with more than one decay time. For these molecules, the luminescence emitted cannot be fit to a single exponential function as the expressed in (2). In these cases, the intensity decay is typically fitted to the multi-exponential model:

$$I(t) = \sum_i I_i e^{-(t/\tau_i)} \tag{3}$$

where I_i and τ_i are the amplitude and lifetime of each single component of the luminescence intensity.

Numerous studies have been carried out in order to determine the amplitude and decay time in single and multiple exponential decays, and different methods have been reported both in time domain (TD) and frequency domain (FD) for this purpose [22,28,29]. In the following section a brief description of the main TD methods are exposed as a prelude for the introduction of the proposed approach. An extensive revision of the already developed algorithms in FD for exponential fitting can be found in [27,30].

2.1. Time domain lifetime measurements

Time domain measurements or pulse measurements are based on the registration of the luminescence emitted by a sample after optical excitation by a pulse of electromagnetic radiation, or simply light (visible radiation) in most of the cases. The analysis of the collected data allows to obtain the value or values of the decay time that characterizes the exponential decay expressed in (2) and (3) in order to be related to the concentration of a specific analyte. The main methods for obtaining this parameter are described below.

2.2. Numerical algorithms

Numerical methods of fitting the measured values to exponential equations make use of large sets of data resulting from a full measurement of the decay luminescence curve. The complete registration of the decay requires the use of fast and precise instrumentation. Measurements in a short time, as low as picoseconds are needed. All this make these approaches simple in theory but complex to set up.

The linear least squares (LLS) method is the simplest way to obtain the parameters of the mono-exponential form of the luminescence decay. It consists of taking the logarithm in both terms of Eq. (2) and if the resulting expression is applied to the intensity measurements X_n a linear form is obtained:

$$ln(X_i) = ln(I_0) - \frac{t_i}{\tau} \tag{4}$$

from where a linear least squares provides the value of I_0 and τ [31]. Although it is very simple, inaccurate results are obtained for low signal levels and if the background signal is too high [22].

The nonlinear least squares (NLS) algorithm is a usual tool for fitting a nonlinear function as the simple exponential form. In this algorithm, the discrete measured values of the intensity registered during the luminescence decay X_i are related to the values expected with the exponential model of (2) and (3):

$$r(t_i) = \sum_i \left(X_i - I(t_i)\right)^2 \tag{5}$$

The minimization of the residual r in Eq. (5) leads to identification of the parameters I_0 and τ [23,32]. This algorithm provides more accurate results, and it is also applicable to multi-exponential fitting.

The Prony method [33] utilizes a set of n equidistant intensity measurements to characterize multi-exponential decays in the form of Eq. (3). These intensity values lead to a set of equations expressed in (6):

$$\begin{aligned} &I_1 + I_2 + \cdots + I_m = X_0 \\ &I_1 e^{-(t_1/\tau_1)} + I_2 e^{-(t_2/\tau_2)} + \cdots + I_m e^{-(t_m/\tau_m)} = X_1 \\ &\vdots \\ &I_1 e^{-(n-1)\cdot(t_1/\tau_1)} + I_2 e^{e^{-(n-1)\cdot(t_2/\tau_2)}} + \cdots + I_m e^{e^{-(n-1)\cdot(t_m/\tau_m)}} = X_{n-1} \end{aligned} \tag{6}$$

For the resolution of this nonlinear problem, $2M$ equations are required. Prony proposed the polynomial:

$$\sum_{i=0}^{M} \alpha_i e^{-i\cdot(\Delta t/\tau_i)} = \prod_{j=1}^{M} \left(e^{-(t/\tau)} - e^{-j\cdot(\Delta t/\tau_j)}\right) = 0, \quad \alpha_0 = 1. \tag{7}$$

Since the experimental values X_n are known, the parameters α_n can be computed directly when $n = 2M$ or approximated via least squares when $n > 2M$ [23]. The Prony method is faster than