Current-induced thermal lensing in chemical analysis

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Abstract. A novel spectroelectrochemical method based on the thermal-lens effect from electrolyte solution using regular Joule heat generation by current focussing in a small-sized channel is under development. Numerical calculations using finite-element modelling were used for a thorough estimation of experimental conditions (cell and electrode shape and size). The major interferring effects were estimated. A change in the analyte concentration near electrodes due to electrolysis is significant and is overcome by large-radius ring elctrodes and AC current. The calculations were confirmed by experiments. An advanced cell design with good reproducibility and the sensitivity of measurements down to 10^{-6} M is proposed.

1. Introduction

The overall sensitivity of quantification using thermal-lens spectrometry (TLS) depends not only on the effect strength, but rather on the regularity of the acting temperature field [1]. Nowadays, photoinduced (laser-induced, LITLS) thermal-lens effects are dominant. However, the nature of the excitation source in TLS is not restricted to lasers; the only requirement is a regular acting temperature field that can be related to the concentration of a component [2]. Previously [3], we showed that Joule heating can be used as a stable excitation source for conducting analytes in current-induced TLS (CITLS). Here, the action of the excitation laser [4] is replaced with a similar effect from an electric current, which is focused in a small volume [5]. Model experiments showed good sensitivity of CITLS. The aim of this paper is a more thorough selection of CITLS parameters based on interfering effects to increase the sensitivity and its experimental verification on a wider circle of analytes.

2. Experimental

The cell is a poly(methyl methacrylate) cylinder with a diameter of 60 mm and wall thickness of 5 mm with Teflon inserts (14 mm, diameter; 45 mm, length) with glass windows (Fig. 2). The cell is divided in the middle by an insulating Teflon membrane (thickness, 1 mm), which has a working channel with a radius of 1 mm. Each compartment has a platinum ring electrode (0.1 mm diameter); the distance between electrodes is 66 mm. A diode laser beam (DLU02, Velleman, 5 mW in the sample; the beam waist, 1 mm) with λ_p = 670 nm is directed through both windows and the channel center; and the changes in the beam divergence is measured by a far-field PMT (Russia) (sample-to-detector distance, 120 cm) with a KS-11 stained-glass bandpass filter and a 2-mm-diameter pinhole. Data collection is controlled by a personal computer through an ADC–DAC board and specially written software.
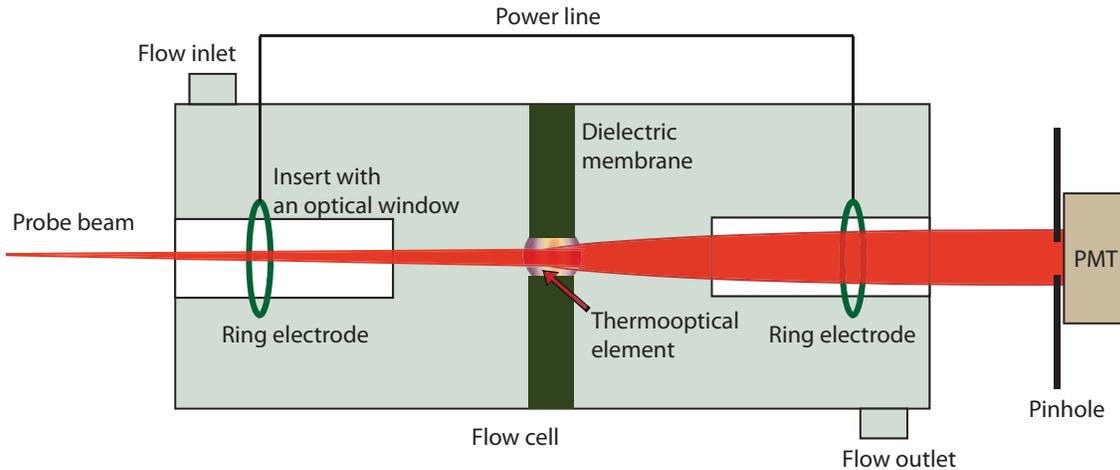
Figure 1. The schematics of the setup for CITLS measurements.

3. Theoretical section

The signal is expressed as a probe-beam intensity change on a thermal lens [1]:

$$\vartheta \equiv I_p(0)/I_p(t) - 1 , \tag{1}$$

where $I_p(0)$ and $I_p(t)$ are intensities at the center of the probe beam at a distant detector plane before the formation of a thermal lens and at a moment t, respectively. The deduction of the equation for CITLS was made in a narrow cylindrical channel, in which the current is focused to a point heat source [3]. Under the following assumptions: (1) the resistance of the solution is much higher than that of electrodes; (2) the heat emerging at electrode surfaces is much lower than the heat dissipating in the channel; (3) current density in all the parts of the cell except the channel is negligible; (4) the membrane material is an ideal dielectric; and (5) the solution is dilute (equivalent conductivity Λ can be equaled to ion mobility), the expression connecting the signal with molar concentration c is [3]:

$$\vartheta_{CITLS} = B\lambda_p \cdot \left(\Phi_T U^2/r^2\right) \cdot t \cdot E_0 D_T \cdot \Lambda \cdot c , \tag{2}$$

where $B\lambda_p$ is the term combining all the geometry constants of the probe beam [6], Φ_T is a heat yield [1], U is the applied voltage, r is the channel radius, t is electrical pulse time, $E_0 = (-dn/dT)/\lambda_p k$ is the thermal-lens enhancement factor (dn/dT is the temperature gradient of the refractive index) [2]; D_T is thermal diffusivity and k is thermal conductivity. Eq. (2) predicts a linear dependence of the signal on the concentration of the target electrolyte. The signal is also proportional to the power density of the source U^2/r^2. The $E_0 D_T$ term, which gathers thermooptical parameters of the solvent, predicts the same level of influence of thermooptical properties on the amplitude and development of the signal in CITLS as in LITLS [3]. All the numerical estimations were made using COMSOL Multiphysics® v. 3.4 (COMSOL, Inc., MA, USA).

3.1. Numerical simulations of the cell parameters

To estimate the sensitivity of the setup, we used 1 mK as a minimum heating that can be reliably measured with a change in the divergence of the probe beam as a thermal-lens effect against other environmental factors affecting temperature and refractive index in solution [1]. The specific resistance providing a constant heating rate of 1 mK/s is 50 MΩ·cm, which corresponds to a concentration of 10^{-7} M of an electrolyte like NaCl. However, the real sensitivity of the method should be degraded due to the own specific resistance of water of 26.3 MΩ·cm [7]. Thus, concentrations that can be measured in an aqueous solution is about 10^{-6} M, unless a background-subtraction technique to compensate the solvent signal is used. This estimation can be used as a minimum limit of detection achieved with this simplest approach to a CITLS experiment with an electrolyte in water.
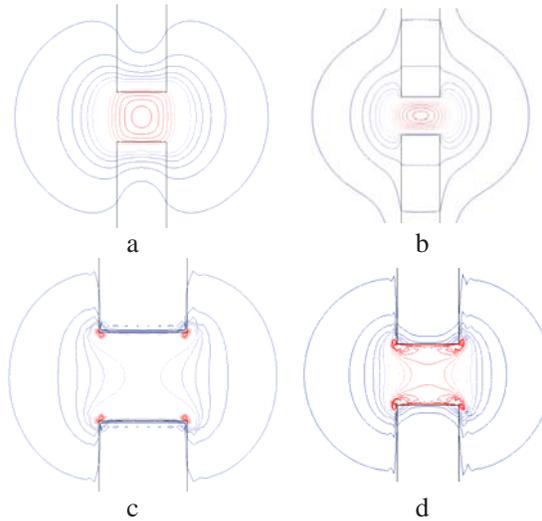
Figure 2. Relative distribution of temperature in the cell at 1 kV depending on heating time and membrane thermal conductivity (COMSOL Multiphysics®): a, 1 s, Teflon; b, 1 s, corundum; c, 1 ms, Teflon; and d, 1 ms, corundum.

To test the effect of heating time and thermal conductivity of the membrane on the signal, we calculated the temperature distribution for short (1 ms) and long, quasi-continuous (1 s) heating times and membranes made of Teflon (thermal conductivity twofold lower than water) and corundum (thermal conductivity is 100-fold higher). The results are shown in Fig. 2; the red color corresponds to higher heating.

Calculations for 1 s (Fig. 2, a and b) heating show that higher thermal conductivities increase the temperature gradient and should increase the signal. For 1 ms (Fig. 2, c and d), the heating at the channel edges is higher and it cannot be dissipated by the membrane material. Thus, in pulsed current excitation wide probe beams are disadvantageous due to the generation of inverse thermal-lens effect [1], which degrades the signal. Another conclusion for short excitation times is that the thermal conductivity of the membrane does not affect the temperature field, so the selection of the material may be dictated by other parameters.

To optimize the previously proposed setup [5], we calculated changes in gradients of temperature in the channel centre along and across the probe beam as functions of the cell parameters. As key parameters, we selected channel radius, the membrane length, the membrane thermal conductivity, electrode-to-channel distances, and the electrode shape and size. The calculations showed that the membrane length should be equal to the channel diameter, while the optimum channel diameter is a function of the probe-beam radius. Moreover, the signal increases with a decrease in the electrode-to-channel distances. However, it cannot be diminished beyond a certain value dictated by the cell geometry restrictions and the interfering effects (see below, subsection 3.2).

The dependence of the signal on the membrane thermal conductivity shows a broad peak from 2 to 10 W/m^3, with a maximum at 5 W/m^3. This range covers many dielectric materials and can be readily implemented. A numerical estimation of the heat yield for the selected geometry gives $\Phi_T = 0.7 \pm 0.1$, which is equal to the previous estimation [3].

It was found that rod-shaped electrodes should be shifted from the probe-beam axis to avoid the interfering effects (see below); however, it leads to an additional beam-deflection effect superposing with the thermal lens. This was confirmed experimentally. Thus, cylindrical or ring-shaped electrodes with the ring center coincidental to the probe-beam axis and the plane normal to beam direction should be used.

3.2. Numerical estimation of interfering effects

In a CITLS experiment, a number of interfering processes may occur. We studied the following interfering processes for DC generation: (i) the effect of double electrical layer on the electric current through the electrode-solution boundary, (ii) diffusion limitation of the current, (iii) local heating of the near-electrode space by the electric current, (iv) heating of the cell due to chemical reactions at electrodes; (v) the flow of the matter through the channel due to diffusion; (vi) the formation of stationary waves in the formed thermocline and (vii) the effect of the acoustic wave. It was shown that all of these effects are insignificant and can be neglected in a CITLS experiment: Diffusion current becomes significant after 220 s; the heating at electrodes gives 0.01 mK, which is 100-fold lower than

the thermal-lens effect; the diffusion flow through the channel is as low as 2×10^{-5}%, and a change in the refractive index due to current is 1×10^{-7}, which is less than 1% from the CITLS signal.

To the contrary, a change in the test substance concentration near the electrodes (about 2% per second) significantly affects the signal, thus, the ring electrode radius should be increased and AC generation of photothermal effects is advantageous.

4. Results and discussion

The reproducibility of measurements for the proposed cell design was investigated for 10 – 900 V AC and DC and showed that for the signal range of 0.04–15, the reproducibility RSD < 0.3, which is in agreement with the previous data [3]. The limits of detection (LOD) are summarized in Table 1. The linear ranges for all the test electrolytes cover four orders of magnitude, the upper LODs are at the level of 1×10^{-1} for all the electrolytes. The blank signal corresponds to the specific resistance 4 MΩ·cm, which is in satisfactory agreement with the value of specific resistance of the used distilled water. For potassium dichromate, it is possible to compare LITLS and CITLS under the same experimental conditions, and it was found that LITLS sensitivity is only 2.3-times higher than for CITLS, which is in agreement with calculations of the sensitivities of both methods using [1] for LITLS and Eq. (2) for CITLS (Table 1). For other electrolytes, the experimental slopes show good agreement with the theoretical calculations from Eq. (2). As a whole, the sensitivity parameters for all of the studied electrolytes are at the same level.

Table 1. Performance parameters for CITLS determination

Electrolyte	Cal. slope /M^{-1}	Theor. slope /M^{-1}	LOD, μM
HNO_3	800 ± 60	850 ± 10	2
KCl	400 ± 30	390 ± 10	5
K_2SO_4	700 ± 40	740 ± 10	2
$BaCl_2$	300 ± 30	310 ± 10	5
$Ce_2(SO_4)_3$	300 ± 30	310 ± 10	5
$K_2Cr_2O_7$	400 ± 30	410 ± 10	4

Thus, a more accurate approach to the estimation of the interfering effects and changes in cell design compared to [3] and [4] increased the sensitivity of CITLS. The sensitivity was increased by a factor of 10 compared to [3] and is comparable to common detectors used in conductivity detection. The correctness of Eq. (2) was successfully tested with a wider circle of analytes. As a whole, CITLS shows potential in chemical-analysis applications for conducting electrolytes as simple schematics of thermal lensing.

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