Thermal-lens spectrometry for studying molecular layers covalently bonded to a flat glass surface

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The molecular layers of the Reactivrot B5A dye covalently bonded to flat quartz glass surfaces was studied by thermal lensing in combination with electron-probe microanalysis.

Studies of the structure of chemically bonded molecular layers are of importance in the chemistry of surface compounds.¹ A small contribution from the layer mass to the total sample mass does not allow methods traditionally used for solving the problems of three-dimensional chemistry to be applied. Therefore, the composition and structure of bonded molecular layers on porous substrates with high specific surface areas are usually studied. In the case of developed surfaces, the mass fraction of a bonded layer can reach 10%, which is sufficient for elemental microanalysis, IR, UV, and EPR spectroscopy *etc.*² However, in the case of a chemical modification of the surface of flat substrates, the study of the bonded layer becomes a complicated problem. We applied thermal lens spectrometry (TLS) to study chemically modified flat surfaces of quartz glasses.

Thermal lensing is a thermooptical method commonly used in analytical practice.³ This method is based on detecting heat effects due to the non-radiative relaxation of molecules that absorbed electromagnetic radiation.^{3,4} In thermal lensing, an equilibrium redistribution of temperature in the irradiated sample results in a Gaussian profile of refractive index determined by the spatially Gaussian form of the excitation laser beam. This profile can be treated as an optical element similar to a lens with the focal distance being a function of the absorbance of the test sample.³

Thermal lensing has such features as (i) high instrumental sensitivity, which makes it possible to detect absorbances in liquid samples down to 10^{-7} – 10^{-8} , to determine concentrations down to 10^{-12} mol dm⁻³, to analyse volumes down to 10^{-15} dm³ and to detect hundreds of molecules in such volumes; (ii) the possibility to use all the variety of methods and approaches of conventional spectrophotometry; and (iii) non-destructivity, which makes it possible to apply TLS to a wide range of test substances.^{3–5} Usually, thermal lensing is applied to determine substances like dyes or metal chelates absorbing the radiation of an excitation laser in liquids.^{3–5}

However, the sensitivity of the method is sufficient to measure the concentration of a dye on a nonporous glass surface. Shimosaka *et al.*⁶ studied the Acridine Orange dye adsorbed on glass using total-internal-reflection thermal lensing. The aim of this study was to examine the uniformity and surface concentration of a bonded layer.

A dual-laser parallel-beam (collinear) thermal lens spectrometer was used.⁷ The thermal lens was excited with an INNOVA 90-6 argon-ion laser (Coherent, USA) with $\lambda_e = 514.5$ nm (TEM₀₀ mode); the maximum power at the sample was 180 mW. The probe was a SP-106-1 helium–neon laser (Spectra Physics, USA) with $\lambda_p = 632.8$ nm (TEM₀₀ mode). The signal (the intensity at the centre of the probe beam) was measured with an FD-7K photodiode. Next, the signal was amplified, and it entered an ADC–DAC board of an IBM PC/AT computer. The measurement was synchronised using the special software.⁷ The optical parameters of the spectrometer are summarised in Table 1.⁸ The beam waist location and waist spot sizes of laser beams were measured using an 818-SL digital power meter (Newport Corp., Fountain Valley, CA, USA) according to Snook and Lowe.⁵

Electron-microscopic images were taken on a CamScan 44 scanning electron microscope with a thermal-emission tungsten

Table	1	Parameters of the dual-beam thermal lens spectrometer.
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Excitation laser	Wavelength λ_e (nm)	514.5	
	Focussing lens focal length (nm)	300	
	Confocal distance (mm)	19.5	
	Laser power at cell (mW)	180	
	Spot size at the waist (µm)	60±1	
Probe laser	Wavelength $\lambda_{\rm p}$ (nm)	632.8	
	Focussing lens focal length (nm)	185	
	Confocal distance (mm)	3.1	
	Laser power at cell (mW)	4	
	Spot size at the waist (µm)	25±1	
Other parameters	Cell length (mm)	2	
	Sample-to-detector distance (cm)	200	
	m in equation (2)	2.0±0.1	
	V in equation (2)	3.1±0.1	

cathode. Due to the very low conductivity of the samples, measurements were made at low acceleration voltages at the equilibrium point (2 kV or lower). At this potential, the total secondary current is equal to the primary electron current. For each sample, the equilibrium points were selected to eliminate charging effects on the images. At this potential, photographs were made every 2 min during 20 min (the images did not change). Focussing was performed at low magnifications (×25) to prevent charging. Secondary-electron images were obtained with a magnification of 200 to 1500.

The thermal lens signal $\overline{\theta}_j$ for a single *j*-th measurement of a sample was calculated as the average of i = 50-100 signals of on-off thermal-lens excitation cycles resulting in a series of the relative change in intensity in the central part of the probe beam for a steady-state thermal lens $[\theta_{j1}, \theta_{j2}, \dots, \theta_{ji}]$. The values of θ_{ji} were calculated from the equation:^{3,4}

$$\theta_{ji} = \frac{I_{\text{off}} - I_{\text{on}}}{I_{\text{on}}},\tag{1}$$

where I_{off} is the time-averaged probe beam intensity without a thermal lens (excitation beam is off) and I_{on} is the timeaveraged probe beam intensity for a steady-state thermal lens (excitation beam is on) for a single cycle. Recalculation of the signal θ to absorbance A was made using the equation:^{3,5}

$$\overline{\theta}_{j} = \left[1 - \frac{\vartheta}{2} \arctan\left(\frac{2mV}{1 + 2mV + V^{2}}\right)\right]^{2} - 1$$
(2)

where $\vartheta = 2.303E_0P_eA$, P_e is the power of the excitation laser at the sample, *m* is the mode-mismatching factor and *V* is the distance from the probe waist to the sample normalised to the corresponding confocal length.⁵ The parameter $E_0 = (dn/dT)(\lambda_p k)^{-1}$ is the reduced enhancement factor for thermal-lens measurements, dn/dT is the temperature gradient of the refractive index, λ_p is the wavelength of the probe laser, and *k* is the thermal conductivity. In thermal-lens measurements, the following parameters were measured: an averaged signal of the sample for *j* subsequent cycles $\overline{\theta}_j$ and the measurement precision (deviation of the signal from cycle to cycle). For each test sample with the concentration of the test component *c*, the average signal $\overline{\theta}_n(c)$ was calculated for *n* replicate measurements. The repeatability of measurements was characterised by the relative standard deviation.



Scheme 1 Reactivrot B5A.

The value of ϑ is proportional to absorbance $A = \alpha l$, where α (cm⁻¹) is the absorptivity of the layer of the test compound and l (cm) is the sample depth. The absorptivity can be estimated as $\alpha = \varepsilon_s c_s$, where ε_s (cm mol⁻¹) is the surface absorption coefficient and c_s (mol cm⁻²) is the surface concentration of the absorbing layer. Taking into account the sufficient precision of measurements of beam radii at the sample (see Table 1), this makes it possible to calculate the surface concentration of the dye from the thermal-lens signal. In our experiments ($\lambda_e = 514.5$ nm), $\varepsilon_s = 9 \times 10^6$ cm mol⁻¹, $E_0 = 6.3$ W⁻¹, and $P_e = 0.180$ W.

The selection of the dye was dictated by its absorption-band parameters, by the absence of radiation losses under light absorption, and by the possibility of its chemical immobilization on the surface. We selected the Reactivrot B5A dye (Scheme 1). Modification of glasses with a sublayer of (3-aminopropyl)trimethoxysilane was made from a toluene solution in the presence of trace moisture according to Lisichkin et al.9 The dye was bonded to a (3-aminopropyl)trimethoxysilane sublayer under the conditions providing an incomplete surface coverage to reveal the possibility of detection of 'holes' in the bonded layer. A dye solution in dry methanol was used, and the reaction was carried out in a sealed ampoule at 70 °C for 16 h. Next, the ampoule was opened, and the sample was washed with dry methanol. The conditions of bonding the dye to aminated quartz glasses were selected from preliminary experiments with a porous silica substrate, Silochrom S-120. The dye was bonded by amino groups of (3-aminopropyl)trimethoxysilane as a modifier, which react with a SiO_2 surface (see Scheme 2).⁹

Thermal-lens studies of modified samples with the bonded dye showed that certain areas of a single glass plate are characterised by two significantly different signals. One of them is the response of the modified surfaces without the dye (a 'background' line in Table 2), which is mainly determined by background photothermal defocusing and light scattering. Another signal corresponds to the bonded dye and shows a curve with a plateau, and the signal of the plateau also corresponds to the thermal-lens signal of the modified surface before dye bonding (Figure 1). Subsequent measurements at the same sample position give the same signal.

The data obtained evidenced that the selected modification conditions result in 'holes' or sites without the dye. This is confirmed by the measurements of the same samples using scanning electron microscopy (see Figure 2). Thus, thermal lensing can be used for estimating the uniformity of the bonded layer in the scale corresponding the linear dimensions of the thermal lens (about 60 μ m in our case).

In electron-probe experiments, the stability of so called 'chemically labile' substances, *i.e.*, substances with low thermo- and electroconductivity, which may decompose under vacuum and electron-probe effects, is a very complicated problem that requires

Table 2 The bonding density of the dye to samples. Sample 1: (3-aminopropyl)trimethoxysilane was applied directly without a solvent. Sample 2: (3-aminopropyl)trimethoxysilane was applied from dry toluene. Sample 3: (3-aminopropyl)trimethoxysilane was applied from wet toluene. The bonding density of (3-aminopropyl)trimethoxysilane to Silochrom S-120 is about 1.6 group nm⁻². Blank sample is a glass treated with (3-aminopropyl)trimethoxysilane only (n = 15).

C 1 -	Average signal $\theta_n(c)$	Bonding density of the dye		Number
Sample		mol cm ⁻²	group nm ⁻²	of layers
Background	0.025 ± 0.002	_	_	_
Sample 1	0.022 ± 0.002	$(1.6 \pm 1.0) \times 10^{-10}$	1.0±0.6	0.87
Sample 2	0.018 ± 0.003	(3.2±1.4)×10 ⁻¹⁰	1.9 ± 0.8	1.74
Sample 3	-0.01±0.01	(1.6±0.5)×109	9±3	8.7
Silochrom S-120	_	8.3×10 ⁻¹¹	0.5	0.45



Scheme 2 The bonding of (3-aminopropyl)trimethoxysilane to a glass surface under dry conditions and in the presence of water traces.

special studies. Previously, we developed several approaches to the analysis of chemically labile samples, including non-conducting organic samples.^{10,11}

Especially important is the time dependence of the thermallens signal for areas with a bonded dye. As the temperature gradient of the refraction index for the used glass is positive, the signal ϑ increases with the concentration of the test substance on the surface (photothermal focussing). Thus, the term in parentheses in equation (2) and the signal θ increase with a decrease in the absorption of the bonded layer. Therefore, a reproducible increase in the signal for glass surfaces with a bonded dye is likely due to the decomposition of the dye under laser irradiation. This was confirmed by comparing electron-probe images of the plates before and after thermal lens measurements: the images show new 'holes' in dye covers with a round symmetry and a rough size of 60 µm. Under the same conditions, Reactivrot B5A in an aqueous solution is resistant to laser radiation. Probably, the rigid fixation of the dye on a solid substrate results in a decrease in its photostability. However, the residence time of the dye at the surface was much longer than the characteristic time of the thermal lens effect (~100 ms). Thus, it provided reliable thermal-lens determination of the dye by photodestruction kinetic curves (Figure 1).

The photodestruction curves showed that the process is complex. We suppose that TLS would provide data on the thermal stability of bonded molecular layers.

The surface concentrations of bonded dyes were found experimentally (Table 2). It is noteworthy that these data are not averaged through the whole surface and relevant only to the surface areas with the dye. Previously, it was shown¹² that the bonding of trifunctional silanes on porous substrates may result in the formation of polylayers. It is also known^{1,2} that the maximum bonding of monofunctional silanes to silica is limited by the area of the anchor group of a modifier, and it is 2.5 group nm⁻². Taking into account steric hindrances, the limiting density of a Reactivrot B5A monolayer is about 1.1 group nm⁻² (calculated using the PM3 method, WinMOPAC, Chem3D, CambridgeSoft). These calculations are in good agreement with the experimental data for Sample 1 (very close to the limiting density of a mono-



Figure 1 Thermal-lens measurements. Photodestruction of the Reactivrot B5A dye bonded to a glass surface. The curve corresponds to the photodestruction of the bonded dye, dashed line is the average signal of the surface modified with (3-aminopropyl)trimethoxysilane, solid line is the average signal of the initial unmodified glass surface. $\lambda_e = 514.5 \text{ nm}$, $P_e = 180 \text{ mW}$.



Figure 2 Secondary-electron image of a glass surface with the bonded Reactivrot B5A dye (acceleration voltage of 2 kV, magnification of 1500. Darker regions correspond to the bonded dye).

layer of the dye). If the bonding density exceeds this value, this unambiguously shows the formation of a polylayer, which is the case of Sample 3 in Table 2. However, if the experimental bonding density is lower than the theoretical value, it hardly gives an unambiguous answer. Nevertheless, the homogeneity of a monolayer can be estimated indirectly, *e.g.*, from the repeatability of TLS measurements at different sites of a sample.

The data (Table 2) suggest that the bonding density for the dye on a glass surface unambiguously correlates with the amount of water at the stage of surface modification with a (3-aminopropyl)trimethoxysilane sublayer. High amounts of water result in a developed structure of the modifier sublayer (see Scheme 2), which is in good agreement with the data of Fadeev and Lisichkin.² This leads to high concentrations of the dye bonded to the surface (Sample 3). The oligomerization of this trifunc-tional modifier was completely suppressed only in a pure modifier without a solvent (Sample 1).

Thus, thermal lensing combined with scanning electron microscopy is a promising approach to study chemically modified surfaces of non-conducting substrates.

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