====== ARTICLES ======

Potentials of Thermal Lens Spectroscopy for Polymethacrylate Optical Sensors

N. V. Saranchina[a], A. V. Sukhanov[a], D. A. Nedosekin[b], N. A. Gavrilenko[a], and M. A. Proskurnin[b]

[a] *Department of Chemistry, Tomsk State University, pr. Lenina 36, Tomsk, 634050 Russia*

[b] *Department of Chemistry, Moscow State University, Moscow, 119991 Russia*

Abstract—The sensitivity of the earlier proposed procedures for the determination of iron(II, III) with 1,10-phenanthroline, silver(I) with dithizone, mercury with copper(II) dithizonate, copper(II) with lead diethyldithiocarbamate, and ascorbic acid with 2,6-dichlorophenolindophenol using polymethacrylate optical sensitive elements for solid phase spectrophotometry is enhanced through the use of thermal lens spectrometry as the most sensitive method of molecular absorption spectroscopy. The limits of detection for all photometric reactions in the polymethacrylate matrix are reduced by an order of magnitude (to 10 nM) without substantial changes in the experimental conditions.

Keywords: thermal lens spectrometry, photothermal spectrometry, solid-phase spectrophotometry, polymethacrylate matrices.

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In the contemporary analytics, the use of reagents immobilized on solid matrices acquires elevated importance. Among the advantages of such systems are the stability of the immobilized reagents, the convenience of the utilization of such combination in analysis, and no need in toxic solvents. Immobilized reagents are used to develop sensors for solid-phase spectrophotometry [1, 2], visual tests [3], and optical fiber sensors [4]. An evident interest for the immobilization of reagents is also represented by transparent polymer materials. The transparency and absence of an intrinsic coloration of the reagent matrix make easy the visual and instrumental evaluation of the color change of the sorbent upon its contact with an element to be determined.

Earlier we proposed transparent polymethacrylate matrices (**PMM**) for the immobilization of reagents [5–12]. This allowed us to combining in one solid phase the ability to immobilize reagents without the loss of the matrix transparency and the ability of reagents to give analytical reactions with analytes, and also to preconcentrate and quantify them in the solid phase by spectrophotometry using standard equipment.

The wide use of spectrophotometry is determined by its simplicity and reliability. Spectrophotometry is one of the most important methods for controlling reactions between substances in solution and for determining compound composition and structure [13]. Recently spectrophotometry has approved itself in solid-state studies. Unfortunately, the method has insufficient sensitivity and selectivity. A proper selection of an organic reagent for a photometric reaction on an adsorbent can improve of the selectivity of the, while its sensitivity can be enhanced using methods of molecular absorption spectroscopy. Thermal lens spectrometry (**TLS**) is a thermal optical method of molecular absorption spectroscopy based on the optical measurement of the amount of energy that releases in the radiationless relaxation of the absorbed, most frequently laser, radiation [14]. In the first approximation, thermal lens spectrometry can be considered as an analogue of spectrophotometry, as signals in both cases obey the basic law of light absorption [14, 15]; however, it is a more sensitive method allowing the reliable registration of absorption at a level of 10^{-6} absorbance units [16].

The aim of this work is to use the earlier developed procedures for the solid-phase determination of Hg(II) [6], Cu(II) [7], Fe(II, III) [8], Ag(I) [12], and ascorbic acid [11] using reagents immobilized into a polymethacrylate matrix without their substantial change with thermal lens detection for the enhancement of the sensitivity of determination.

EXPERIMENTAL

Processing of experimental data. The thermal lens measurements provide a sequence of cyclic switches on and off of an inducing laser, i.e., the formation and
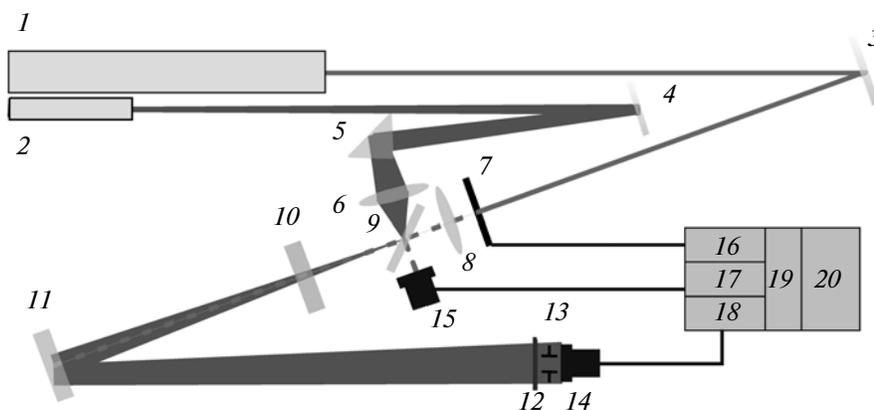
Principal scheme of the coaxial two-beam thermal lens spectrometer II. *1*, inducing laser; *2*, probe laser; *3*, dichroic mirror of the ZR-88 type; *4*, *9*, *11*, dichroic mirrors of the ZR-100 type; *5*, quartz prism; *6* and *8*, focusing lenses; *7*, chopper (trigger); *10*, sample under investigation' *12*, broadband filter; *13*, diaphragm; *14* and *15*, photodiodes of the L-3DP3C type (Panasonic); *16*, *17*, and *18*, analogue amplifiers of signal and converters of current into voltage; *19*, analogue-to-digital and digital-to-analogue converter; *20*, PC 1.

dissipation of a thermal lens, which creates a series of signals θ [14, 16]:

$$\theta = \frac{1}{B}\left(\sqrt{\frac{I_{\text{off}} - I_{\text{on}}}{I_{\text{on}}} + 1} - 1 \right), \quad (1)$$

where I_{off} and I_{on} are intensities in the middle of the probe beam with no thermal lens and at the fully developed thermal lens, respectively, and B is the so-called geometrical parameter [17]. The theoretical enhancement of the sensitivity of absorbance measurements S_{theor} in going from conventional spectrophotometry to thermal lens spectrometry is calculated as follows:

$$S_{\text{theor}} = \theta / A = 2.303 E_0 P_e, \quad (2)$$

where P_e is the power of laser radiation at the wavelength λ_e inducing the thermal lens [16], E_0 is the sensitivity factor of thermal lens measurements, i.e., the increase in sensitivity in comparison to spectrophotometry at the power of the inducing radiation 1 mW,

$$E_0 = -\frac{dn/dT}{k\lambda_p}, \quad (3)$$

Where dn/dT is the temperature gradient of the refraction index, k is the coefficient of thermal conductivity of the medium, λ_p is the wavelength of the radiation probing the thermal lens. The calculation of the parameters of the thermal lens effect in liquids was described in [14].

To compare the experimental growth of the sensitivity of determination in going from spectrophotometry to thermal lens spectrometry in contrast to the theoretical growth S_{theor} according to (2), we calculated the ratio of detection limits for spectrophotometry and TLS:

$$S_{\text{exp}} = \frac{c_{\text{min, SF}}}{c_{\text{min, TLS}}}. \quad (4)$$

Instruments. On the basis of the previous studies on the registration of the thermal lens signal [17], we assembled a coaxial two-laser thermal lens spectrometer (see figure). The duration of heating and cooling the sample was determined by the attainment of the signal a constant value, i.e., in the so-called reverse synchronization mode. The thermal lens was induced with an Innova 90-6 argon ion laser (*1*) (Coherent, United States) with the generation wavelengths 488.0 and 514.5 nm (TEM$_{00}$-mode, the maximum output power of the radiation $P_e \approx 1.5$ W). The probe laser (*2*) was an HRP020 helium−neon laser (ThorLabs, United States) operated at $\lambda_p = 632.8$ nm (TEM$_{00}$-mode, the output power of the radiation 2.0 mW).

The radiation of inducing laser *1* after rotating mirror *3* passed through a mechanical modulator (chopper) *7*, then was focused by lens *8*, focal distance 330 mm, passed through the converging dichroic mirror of the ZP-100 type (*9*) and, after all, come to the sample *10*. Certain part of the beam reflected by mirror *9* was delivered to the photodiode of power control *15* (L-3DP3C type, Panasonic). The signal from the power control photodiode via the amplifier *17* converting current into voltage came to channel *2* of analogue-to-digital converter *19* connected to a PC *20*. To synchronize the detection system with the operation of the modulator, we used a control card *16* of an analogue-to-digital converter. The beam of the probe laser via a system of mirror *4* and prism *5* and also focusing lens *6* (focal distance 185 mm) came to the converging dichroic mirror *9*, from which it was reflected and then passed through the sample and thus probed the thermal lens generated by the inducing beam.

After the sample, both beams fell to dichroic mirror *11* of the ZP100 type. It served for the preliminary separation of inducing and probe beams and thus made unnecessary an extra thermal lens, which would

have been generated in strongly absorbing filter *12* (i.e., the OS-11 (2 mm) and KS-11 (2 mm) colored glasses). The beam of the probe laser carrying information was reflected by mirror *11* and passed through broadband filter *12*, which absorbed the residual radiation of the inducing laser, then through diaphragm *20* (diameter 4 mm) arranged on the optical axis of the system and came to the diode of signal registration *14* of the L-3DP3C type (Panasonic), from which the signal transformed by amplifier *18* was delivered to channel *1* of the card of analogue-to-digital conversion of a PC. The lenses *6, 8*, and the sample *10* could move along the beam with a minimal step of 0.5 mm, which allowed the variation of the positions of constrictions of both inducing and probe beams relative to the sample.

To control both spectrometers, we used an analogue-to-digital conversion card model c8051Fx-DK (Silicon Laboratories, United States) with the following parameters: a 16-bit analogue-to-digital converter; conversion time 2 μsec; number of channels (input), 2; number of channels for digit-to-analogous conversion, 2; frequency of data reading 1–5 kHz. The card made possible the registration of analogous signals starting from a precisely set moment (mode of external start from PC). The readings from the card were passed to a PC accessory program via an RS-232 interface. To collect and process the data of thermal lens measurements, a special algorithm was developed. The accessory program was written in the C++ language, version 5 (Borland Corp. United States).

The thermal lens spectrometer made possible the rearrangement of the geometry of the optical scheme and the power of the inducing radiation in wide range of parameters; this ensured the energy absorbed by the sample to vary in the range from 0.1 mJ to 20 J; power, from 1 to 200 mW; specific power, from 250 to 5×10^7 W/cm^2, and the time of radiation, from 0.01 to 10 sec.

The optical characteristics of polymethacrylate matrices with immobilized reagents before and after their contact with analyte solutions were registered against an unmodified polymethacrylate matrix on a Shimadzu UVmini 1240CE spectrometer.

To control the pH of solutions, an EV-74 universal potentiometer with a glass indicator electrode was used (calibrated at 25°C using buffer solutions with pH 4.0 and 7.0).

Solvents and reagents. The solutions of dithizone, sodium diethyldithiocarbamate, 1,10-phenanthroline and 2,6-dichlorophenolindophenol were prepared by dissolving precise loads in respective solvents: dithizone in a 0.005 M solution of NaOH, all others in water. A stock 2 M solution of mercury(II) was prepared by dissolving precise load of metallic mercury in dilute nitric acid. Stock solutions of metals (1 mg/mL) were prepared by dissolving precise loads of their salts according to the known procedures [18, 19]. Working solutions of metals with lower concentrations were

prepared by diluting the stock ones in day of experiment. The stock (1 mg/mL) and working solutions of ascorbic acid were prepared in day of experiment. All reagents were of chemical or analytical grade and used as purchased. The necessary pH values were created using solutions of HNO$_3$, H$_3$PO$_4$, HCl, and NaOH.

Procedures. The polymethacrylate matrix as transparent sheets 0.60 ± 0.04 mm wide was obtained by radical block polymerization in accordance to the procedure described in [20]. Of the initial sheet we cut pieces of the size 6.0×8.0 mm and weight around 0.05 g.

The immobilization of reagents into the polymethacrylate matrix was performed by adsorption from solutions under batch conditions; the procedures were described in detail elsewhere [6–12]. To do that, 10–25 mL of a reagent solution was stirred with a matrix for 1–15 min. The immobilization of lead diethyldithiocarbamate and copper dithizonate was done in two steps. At the first step, the polymethacrylate matrices were treated in solutions of sodium diethyldithiocarabmate and dithizone, and then in solutions of lead(II) and copper(II).

The reaction of analytes with the reagents immobilized in the polymethacrylate matrix was conducted under batch conditions. A polymethacrylate matrix with an immobilized reagent (0.05 g) was put into 50.0–100.0 mL of an analyte solution of different concentrations and pH and stirred for 5–30 min.

Before the thermal lens measurements after the photometric reaction the sheets of the matrix were heated to 60°C through two subject glasses microscopy while gently compressing them with the glasses. heating was performed until the softening of the polymer surface layer began; the process was controlled visually. If necessary, the treatment was repeated.

In the thermal lens measurements, we scanned the surface at 10–30 points selected randomly or according to a preset algorithm. In each point, the thermal lens signal from the surface was registered at least 30 times (30 cycles of thermal optical heating and cooling). The erroneous values were rejected using the *Q*-test. The obtained thermal lens signal was compared with the one for a clear polymethacrylate matrix.

RESULTS AND DISCUSSION

Selection of photometric systems. As model solid-phase spectrophotometric procedures for studying the possibility for improving sensitivity using thermal optical spectrometry, we chose procedures based on various types of reactions in the solid phase: complexation reactions of Fe(II, III) with 1,10-phenantroline and Ag(I) with dithizone; complexation reactions with exchange adsorption between Cu(II) dithizonate and Hg(II), Pb(II) diethyldithiocarbamate, and Cu(II); and, finally, the redox reaction of the determination of ascorbic acid with 2,6-dichloroindophenol. The last system was selected because the method used is indi-

rect, i.e., absorbance goes down with an increase in the concentration of components to be determined and thus helped to evaluate the chances for the use of such type of procedures in TLS; this had not been reported before.

Preliminary thermal lens measurements. In contrast to the spectrophotometry measurements with a rather wide transmitting beam, in the thermal lens detection of the signal one has to reduce the scattering of the inducing light beam by PPM samples, because TLS is more sensitive toward the optical quality of the sample surface. The simplest solution for this problem converges to the gentle thermal pretreatment of the surface after the photometric reaction. For this purpose, the surface of sheets was heated to 60°C between two polished subject glasses for microscopy. The trick made possible the reduction of the relative standard deviation of the thermal lens determination for the same sheets from 0.5 to 0.02, and the relative standard deviation of the thermal lens readings for parallel measurements from 0.6 to 0.04 (for absorbance values 0.005−0.1). The absorbance of all sheet subjected to thermal pretreatment changed insignificantly.

The procedure of the thermal lens measurements of solid samples was identical for all photometric systems under consideration. The sample was introduced into a special holder of the spectrometer, and then the spectrometer was adjusted so as to attain the maximal orthogonality of surface to the inducing beam. If noticeable diffraction of probe beam after passing through the sample was detected even after its thermal pretreatment, such a sample was considered unfit for thermal lens measurements.

The relation of the thermal lens signal of all samples to the absorbance of PMM is linear in the range from 1×10^{-4} to 0.2 absorbance units; for the experimental conditions (100 mW) the calibration relation looks as follows:

$$\vartheta = (15.6 \pm 0.1)A - (1.00 \pm 0.01)$$
$$(r = 0.988, \ n = 16, \ P = 0.95). \tag{5}$$

The slope of this calibration function is in good agreement with the theoretically calculated sensitivity coefficient of thermal lens measurements Eq. (2), which makes 15.6. The variation of the experimental coefficient of the dependence $\vartheta = f(A)$ for the power of inducing radiation in the range 5−120 mW if given by a linear relation with the correlation coefficient equal to 0.999, which is indicative of the rather good accuracy of the registration of the thermal lens effect and absence of side or nonlinear effects.

The coefficients of equation $\vartheta = f(A)$ for different photometric reactions and equal powers of inducing radiation differ insignificantly, which shows that it is actually determined by the thermal optical effect, i.e., the thermal physical parameters of the medium, first of all, thermal conductivity and thermal permittivity, and is independent of the photometric system, and

also points to the good accuracy of the registration of the characteristics of PMM (we used 9 collections of matrices were used).

Thermal lens measurements using chosen photometric reactions. The performance characteristics of thermal lens measurements using the chosen photometric reactions are presented in the table. As it is shown, in using thermal lens spectrometry, the detection limits for all of the studied metals and ascorbic acid are reduced by an order of magnitude. Also is important that the previously reported [6−12] procedures for the solid-phase spectrophotometric determination of Fe(II, III), Cu(II), Hg(II), and ascorbic acid do not require changes in their conditions in going to thermal lens measurements.

In the determination of silver(I) by thermal lens spectrometry, one should reduce of the absolute concentration of the element in the polymethacrylate matrix, because at higher absorbance values, the linear relation between the thermal lens signal and absorbance is disturbed, which leads to the substantial worsening of performance characteristics of silver determination. The simplest way to reduce the signal is the reduction of the time of contact of the polymethacrylate matrix modified with dithizone with the solutions to be analyzed. The experiments showed that, under these conditions, no more essential corrections should be made in going from spectrophotometry to thermal lens spectrometry; therein, the sensitivity of the determination grows up by approximately an order of magnitude, as for the others reactions studied (see table).

It seems important that, for all reactions except for the one of iron(II) with 1,10-phenanthroline, the upper limit of the analytical range is not worse (for mercury it even exceeds) than the value obtained for conventional solid-phase spectrophotometry (see table). Herein, the lower limit of the analytical range for the thermal lens determination is substantially lower, which extends the analytical range for TLS.

Moreover, in the determination of mercury(II) by solid-phase spectrophotometry, the calibration relation is nonlinear in the concentration range of mercury(II) in solution $(1−100) \times 10^{-7}$ M, which necessitate the linearization of the calibration function on the logarithmic coordinates ($\log\Delta A_{490} - \log c_{Hg(II)}$), which can be considered a limitation of the procedure [6]. In similar experiments using thermal lens spectrometry at the concentrations below 1 μM, the dependence $\vartheta = f(c_{Hg})$ is linear, the coefficient of correlation is 0.9972, and no linearization of the relation of absorbance to the mercury concentration is required; this, finally, leads to the substantial extension of the analytical range; in fact, it makes 4 orders of magnitude for TLS against less than two orders for solid-phase spectrophotometry (see table).

The relative standard deviation for all four metals (RSD, %) belongs to the range of 2−20% (for absorbance in the range 0.5−5), which is somewhat lower

Analytical ranges and detection limits obtained by thermal lens spectrometry and solid-phase spectrophotometry for photometric reactions in a polymethacrylate matrix and their comparison

Photometric system	P_e, mW (TLS)	Analytical range, M		Detection limit, M		Ratio of sensitivity parameters	
		Spectrophotometry	TLS	Spectrophotometry	TLS	S_{theor}, Eq. (2)	S_{exp}, Eq. (4)
Fe(II, III)—1,10-phenanthroline	120	$(0.18–3.6) \times 10^{-5}$	$(0.010–1.0) \times 10^{-5}$	9×10^{-7}	1×10^{-7}	18.7	9
Hg(II)—dithizonate Cu(II)	100	$(0.1–7.0) \times 10^{-6}$	$(0.02–10.0) \times 10^{-6}$	1×10^{-7}	1×10^{-8}	15.6	10
Cu(II)—diethyldithiocarbamate Pb(II)	40	$(0.08–1.60) \times 10^{-5}$	$(0.01–1.4) \times 10^{-5}$	2×10^{-7}	2×10^{-8}	6.3	10
Ag(I)—dithizone	40	$(0.23–1.90) \times 10^{-6}$	$(0.02–1.5) \times 10^{-6}$	9×10^{-8}	1×10^{-8}	6.3	9
Ascorbic acid—2,6-dichloroindophenol	30	$(1.7–5.7) \times 10^{-4}$	$(0.2–5.0) \times 10^{-4}$	6×10^{-5}	5×10^{-6}	5.2	8.4

than that obtained for solid-phase spectrophotometry, 3–20%, and agrees well with the curves of instrumental error for both metals [21]. The parameter for the determination of ascorbic acid (4–30%) appeared a little worse than that in spectrophotometric measurements; we believe that the reason is that the procedure is indirect.

The use of thermal lens spectrometry in the indirect determination of ascorbic acid by reagents immobilized into a polymethacrylate matrix makes possible lowering of the detection limit by more than an order or magnitude with no changes in the reaction conditions; therefore, indirect measurements in TLS have no principal difference with the spectrophotometric ones from the viewpoint of the methodology of the experiment. This fact might be useful in future for the quantification of microquantities of various reductants and oxidants using redox agents immobilized into a polymethacrylate matrix and thermal lens detection, for which such indirect photometric reactions are basically utilized.

By comparing the sensitivity parameters for all systems (see table), one can find that, for the power of inducing radiation around 100 mW, the detection limits are worse that those expected from the thermophysical parameters of the medium, while for the power 30–40 mW, an opposite trend is observed: the limits of detection appear to be lower that those expected from the comparison of sensitivity coefficients. We suppose that this refers to the substantial fluidity of the taken PPMs and the presence of polyethylene glycol in them. As a result, the sufficient irradiation and, correspondingly, strong heating of the matrix by the focused

laser beam, irreversible transformations proceed in the irradiated matrix area, which significantly reduce the precision of measurements. This is supported by the fact that, with an increase of power up to 200 mW, quantitative measurements become impossible, and warming due to the thermal optical effect exceeds 40°C.

In contrast, at the lower power of the inducing radiation, the thermal consequences of the thermal optical effect are insignificant, and the detection limits become more and more sensitive to the effects mentioned above, i.e., the linearity of the calibration function is improved, and the thermal lens registration of absorbance becomes more precise in comparison to transmittance measurements at absorbance values below 0.001 [21]. Finally, the reduction of the detection limit appears stronger than the enhancement of the sensitivity coefficient. The result indicate that polymethacrylate optical sensors do not require powerful inducing lasers, and the high sensitivity of thermal lens measurements may be attained using diode lasers, which cost rather low. Therefore, compact and inexpensive thermal lens spectrometers can be created, and the sensitivity of absorbance registration can be enhanced using another principle of registration. Noteworthy, in thermal lens spectrometry, the amount of sorbent in which the analytical signal is generated, is reduced significantly. For solid-phase spectrophotometry, the necessary volume of the sorbent in spectrophotometer beam makes 1×10^{-5} cm^3 and the absolute amount of the substance in the beam, $n \times 10^{-11}$ mol. For thermal lens spectrometry, the size of the beam is 60 μm and the analyzed volume in the

beam of the spectrometer is 3×10^{-9} cm^3, the absolute amount of substance in the beam is $n \times 10^{-15}$ mol.

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Thus, the use of thermal lens spectrometry for polymethacrylate optical sensors necessitates minimal changes, or no changes at all, in the conditions of photometric reactions and may adopt rather simple ways for the elimination of optical defects and scattering by the matrix, as well as the selection of power for the inducing radiation. The detection limits for all tested systems in thermal lens spectrometry are lower by at least an order of magnitude in comparison to solid-phase spectrometry.

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