Russian Chemical Reviews **73** (12) 1143 – 1172 (2004) © 2004 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2004v073n12ABEH000875

Modern analytical thermooptical spectroscopy

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Contents

I.	Introduction	1143
II.	General characterisation of thermooptical spectroscopy methods	1144
III.	Fields of application of analytical thermooptical spectroscopy	1152
IV.	Study of interfaces in condensed systems	1161
V.	Conclusion	1165

Abstract. The review surveys the main lines of research in thermooptical spectroscopy related directly or indirectly to analytical chemistry. The advantages and drawbacks of thermooptical spectroscopy methods are considered. Particular attention is given to the coupling of thermooptical spectroscopy to chromatography, flow analysis techniques, capillary electrophoresis, *etc*. Prospects for the development of analytical thermooptical spectroscopy are discussed. The bibliography includes 606 references.

I. Introduction

A pioneering study on analytical thermooptical spectroscopy [1] was published 25 years ago. In this time, the development of an analytical method is considerable and its status compared with other methods also change. The characteristic feature of the recent studies in the field of thermooptical spectroscopy is that researchers turn from the 'reproduction' of spectrophotometric procedures to a search for specific thermooptical methods of analysis.[2 – 17] It should be noted that not only the most commonly used thermal lens spectrometry but also such methods as mirage spectroscopy,[2, 5, 7, 8] the thermal prism technique,[4, 5, 16] photothermal refraction spectrometry [2, 4, 7, 8, 10, 11, 16] and photothermal interferometry [4, 17] have attracted increasing attention. In the period from 1997 to 2002, the distribution of methods used in studies in the field of thermooptical spectroscopy was as follows: thermal lens spectrometry, 43%; photothermal deflection, 27%; photothermal radiometry, 12%; photothermal displacement, 9%; photothermal interferometry, 4%; thermal lens microscopy, 4%; photothermal refraction spectrometry, 1%. Hence, it is evident that a new line of investigation, *viz*., analytical thermooptical spectroscopy, has evolved. There is a pronounced tendency to use thermooptical methods in fundamental studies, where their advantages as non-destructive highly sensitive methods of molecular light absorption spectroscopy are most obvious.[6, 15, 17, 18] In the period from 1998 to 2003, the number of studies devoted to thermooptical methods has steadily increased by approximately 300 papers *per annum* (Fig. 1).

In the present review, we analyse state-of-the-art thermooptical spectroscopy and its applications in analytical chemistry and related fields in the last 10 – 15 years. The coupling of thermooptical spectroscopy to other modern analysis methods (primarily, to chromatography, flow analysis methods, capillary electrophoresis, kinetic methods) enables one to extend the range of compounds that can be detected and to enhance the sensitivity of measurements. The review covers new fields of application of thermooptical spectroscopy in analytical chemistry and chemical analysis, such as the design of compact photothermal and photometric devices (chemical microchips and integrated microanalysis systems) on the basis of thermooptical detection, analysis of medical and biological samples and molecular analysis of surface- and volume-absorbing solid substances. In our opinion, the review of the main methods and applications of modern thermooptical spectroscopy will be of interest not only to analytical chemists but also to researchers in physical chemistry, biochemistry, surface chemistry and physics and laser chemistry.

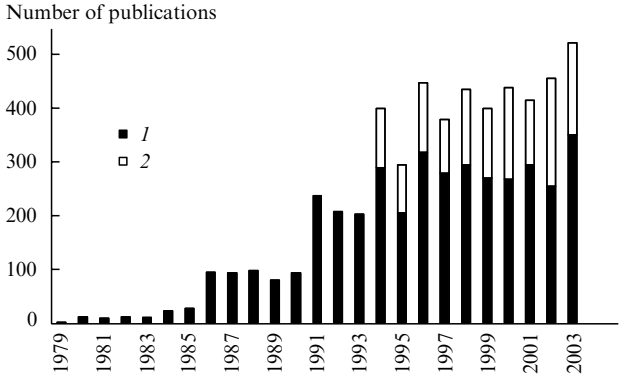


Figure 1. Changes in the number of papers (*1*) in the field of thermooptical spectroscopy in refereed journals in the period from 1979 to 2003 and changes in the number of abstracts of papers (*2*) presented at conferences on thermooptical and photoacoustic spectroscopy, analytical chemistry, chromatography, capillary electrophoresis and microanalytical systems in the period from 1994 to 2003.

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Received 22 September 2003
Uspekhi Khimii **73** (12) 1235 – 1268 (2004); translated by T N Safonova

II. General characterisation of thermooptical spectroscopy methods

1. Theoretical fundamentals of thermooptical spectroscopy

Methods of thermooptical (photothermal) spectroscopy are based on measurements of refractive index changes induced by electromagnetic radiation absorption (Fig. 2).[2–5,7,8]

All thermooptical methods are based on the conversion of absorbed radiation into heat. Initially, an irradiated sample absorbs radiation which is accompanied by transition of its atoms or molecules into the excited state. Then, the excited state relaxes back to the ground state. Relaxation can follow several paths. For purposes of thermooptical spectroscopy, radiationless non-radiative relaxation accompanied by the conversion of absorbed radiation into heat is of most interest. The spatial temperature distribution in an irradiated sample corresponds to the spatial energy distribution in incident radiation. The temperature distribution, in turn, gives rise to optical anisotropy, *viz*., a non-uniform spatial refractive index distribution. The refractive index distribution causes a change in the optical path length, resulting in the formation of an optical element. The characteristics of this element provide a basis of a photothermal signal.

For thermooptical spectroscopy methods, not only high intensity of laser radiation but also its mode composition, *viz*., a particular spatial energy distribution in the beam, is of considerable importance. In this case, the photothermal effect is regular. In a medium, which is isotropic before irradiation, this effect leads to the formation of an optical element similar in action to a lens, a prism, a diffraction grating, *etc*.[2,4,6,7] Data on thermooptical elements, measured signals, methods of their detection and the fields of application are given in Table 1.

The theory of thermooptical spectroscopy can be divided into three parts describing the following stages:[4]

(1) absorption of excitation radiation to form the temperature field;

(2) formation of the refractive index field in accordance with the temperature distribution;

(3) influence of the thermooptical element on transmitted radiation.

The key problem is to calculate the temperature change, which depends most substantially on the thermooptical properties of a sample and its thermal and optical structure. A calculation of the changes in the probe beam after it passes through a thermooptical element is a trivial problem. Methods for its solution have been developed in detail.[4]

Let us consider a finite thickness sample irradiated with a laser beam in the TEM_{00} mode (the Gaussian intensity distribution across the TEM_{00} mode), *i.e*., with the beam with radial symmetry of intensity. This beam is described by the expression[4]

$$I(r) = \frac{2P_e}{\pi\omega_{0e}^2}\exp\left(-\frac{2r^2}{\omega_{0e}^2}\right), \quad (1)$$

where $I(r)$ and P_e are the intensity at a distance r from the centre of the beam and the total power of the excitation beam, respectively, and ω_{0e} is the excitation-beam waist radius. The spatial heat distribution in the sample in the absence of radiation losses is defined by the three-dimensional differential equation of thermal diffusion

$$C_P\rho\frac{d}{dt}\left[\Delta T(r,z,t)\right] - k\nabla^2\left[\Delta T(r,z,t)\right] = Q(r,z,t). \quad (2)$$

Here C_P is the heat capacity, ρ is the density of the medium, k is the thermal conductivity coefficient, $\Delta T(r,z,t)$ is the change in the sample temperature with respect to the initial level (the temperature of the environmental medium), z is the coordinate along the axis coinciding with the beam propagation direction, t is the time, $Q(r,z,t)$ is the heat released upon absorption of laser radiation in the TEM_{00} mode per unit of volume in a unit of time

$$Q(r,z,t) = 2\pi\alpha(z)I(r)r\mathrm{d}r, \quad (3)$$

where $\alpha(z)$ is the linear absorptivity of the sample.

Various other processes can easily be taken into account by introducing additional terms in the thermal diffusion equation. For a particular experiment, the characteristic features are specified by the boundary conditions necessary for solving the heat transfer equation. By choosing appropriate conditions, one can reduce the dimensionality of the thermal diffusion equation. The solution of this equation is the spatial and time dependences of the temperature rise in the excitation region $\Delta T(r,z,t)$. The solution of the thermal diffusion equation is expressed in terms of Green's function formalism.[4] In studies with the use of pulse lasers, the heat transfer is often ignored because the time of thermal wave propagation is substantially longer than the laser pulse duration. In this case, the spatial temperature distribution in the sample is assumed to be exactly consistent with the spatial energy distribution in the incident pulse.[4] In experiments using a continuous radiation source, the signal is, on the contrary, formed predominantly through heat transfer.

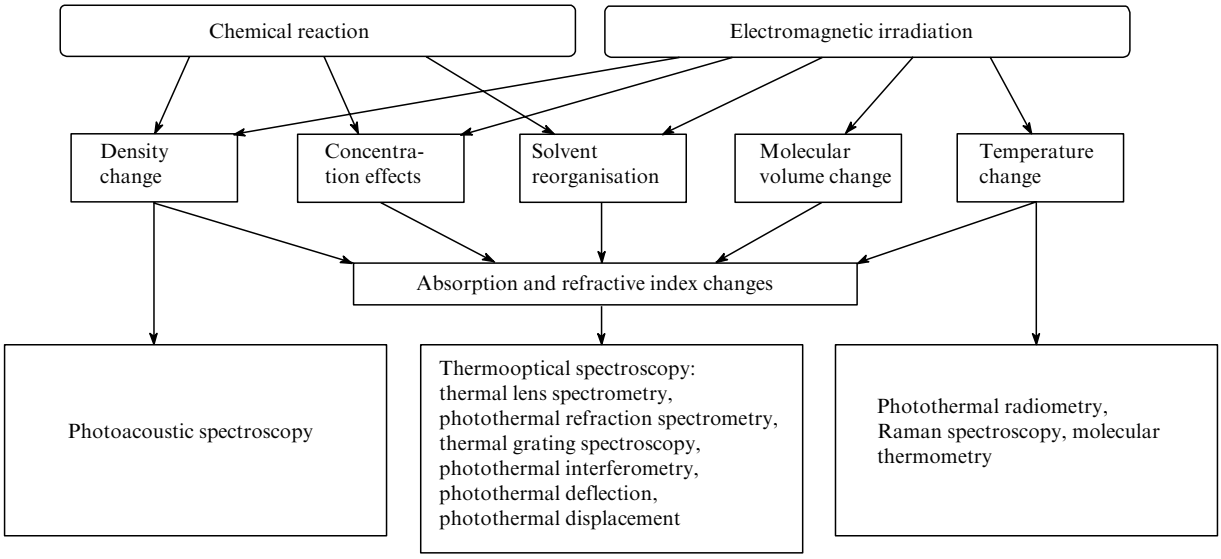


Figure 2. Main photothermal effects, which occur in condensed media irradiated with a laser, and methods for their detection.

Table 1. Main thermooptical methods and their characterisation.

Method	Thermooptical element	Signal	Detector	Objects; fields of application
Thermal lens spectrometry	divergent spherical lens	changes in the probe beam divergence (lens focal distance)	photodiode, photoelectron multiplier or multichannel photodetector	analytical determination of microamounts, detectors in chromatography, remote probing
Time-resolved thermal lens spectrometry	divergent spherical lens	slope of a time evolution curve of a thermal lens	photodiode, photoelectron multiplier	liquids and gases; a detector in chromatography
Photothermal refraction spectrometry	divergent cylindrical lens	changes in the probe beam divergence (lens focal distance)	photodiode, photoelectron multiplier or multichannel photodetector	liquids; probe analysis, analysis of small-volume samples (10^{-12}–10^{-14} litre), detectors in chromatography and capillary electrophoresis
Photothermal deflection (mirage effect)	pseudoprism in a medium in direct contact with a sample	probe-beam deflection	position-sensitive detector	gases, surfaces of condensed media; detectors in capillary electrophoresis
Photothermal displacement	mirror (bending of the sample surface)	spatial probe beam displacement	the same	surface and subsurface flaw detection
Photothermal radiometry	temperature fluctuations on the sample surface	surface thermal radiation	IR detector, lock-in amplifier	remote probing of surfaces, studies of fast processes
Photothermal microscopy	changes in refractive index distribution	amplitude and phase of the probe beam or thermal lens signal	scanning photodetector	microscopic analysis of surfaces, biological cultures and tissues, *in situ* analyses
Thermal grating spectroscopy	spatial diffraction grating	diffraction pattern in probe beam	the same	condensed media; studies of reaction mechanisms
Photothermal interferometry	changes in refractive index distribution	amplitude and phase of probe beam	Mach–Zehnder, Fabry–Perot, Jamin–Lebedev interferometers	flow rate measurements, surface absorption measurements, studies of DNA and proteins

The refractive index distribution $n(r,z,t)$, *i.e.*, the thermooptical element as such, is generally described by the following approximate equation:[19]

$$n(r,z,t) \approx n_0 + \frac{\mathrm{d}n}{\mathrm{d}T}\Delta T(r,z,t), \tag{4}$$

where n_0 is the refractive index of the non-excited sample. In the simplest case, the optical-path length change depends only on the refractive index (for example, in liquids). However, for solid samples, an additional increase in the optical path length due to expansion on heating is sometimes taken into account. In this case, the thermal expansion profile of the sample in the excitation region corresponds to the intensity profile of the incident radiation. This effect is described by a general equation of the optical path length (s) [17, 20]

$$\frac{\mathrm{d}s}{\mathrm{d}Q} = \frac{1}{\rho C_P}\frac{\mathrm{d}s}{\mathrm{d}T}. \tag{5}$$

The temperature dependence of the optical path length is related to the refractive index change $n(T)$ and the sample elongation $l(T)$ by the equation

$$s(T) = n(T)l(T).$$

The distribution of the optical-path length change (or the refractive index change) determines the phase shift of probe electromagnetic radiation passing through the excitation region. The phase shift is accompanied by a change in the radiation intensity distribution in the detector plane. Changes in the probe beam intensity in the detector plane are most accurately estimated by methods of diffraction optics. In this approach, the precise solution is found by solving the Huygens–Fresnel superposition integral. The direct solution of the system of Eqns (2)–(5) is very complex and cumbersome. The simplest expressions can be obtained with the use of the Fresnel and Fraunhofer approximations in diffraction processes, which involve detection in the near-field and far-field regions, respectively. Along with the diffraction model for the photothermal signal, simpler models, for example, a parabolic model [19] and a paraxial aberration model,[4] are sometimes used in thermal lens spectrometry.

From the above it follows that the mathematical apparatus of thermooptical spectroscopy is very complex. Hence, it is generally impossible to deduce an exact, simple and clear expression for a photothermal signal in analytical form. In practice, numerical methods are often used for simulation of a signal.

The theory of thermooptical spectroscopy of solid substances and heterogeneous materials differs substantially from the theory of thermooptical spectroscopy of homogeneous samples. Heat propagates in different layers or regions of solid matter and can also go to the gas or liquid surrounding the sample. To describe the resulting temperature change, it is necessary to simulate thermal diffusion.[4]

The complexity of three-dimensional thermal diffusion and the temperature and refractive-index changes taking place in solid samples forced researchers to search for alternative way to describe of a photothermal signal.[4] It is assumed that, first, spatial anisotropy of the refractive index, responsible for a photothermal signal, is not necessarily determined by the source intensity but depends much more substantially on the anisotropy of the sample. Second, it is generally impossible to obtain an exact solution of the thermal diffusion equation for a given geometry of the optical scheme.[4] To the contrary, this geometry is determined by the heterogeneous nature of the sample and the excitation source. In the next step, the chosen scheme can be used for studying thermal diffusion and the resulting temperature and refractive-index changes according to a standard procedure.[4] The three-dimensional structure of the material under study is revealed using experimental data and information, which is obtained by solving

the equation for specially chosen geometric conditions, rather than by solving thermal diffusion equations for a specific geometry of the optical scheme, which is usually done in studies of homogeneous samples.[4]

2. Thermal lens spectrometry

Of all the thermooptical methods, thermal lens spectrometry has gained the widest acceptance.[1–18, 21–71] This method is based on the periodic formation of a lens-like element in a medium that absorbs laser radiation with the TEM_{00} mode. The focal distance of the resulting thermal lens depends on the absorbance of the sample. The main advantages of this method are as follows: first, it allows one to study samples in different aggregate states and perform remote measurements and, second, it requires relatively simple equipment. The thermal lens signal depends on the temperature gradient of the refractive index and the thermal conductivity coefficient of the medium. The strongest thermal lens effects are observed in non-polar and low-polarity organic liquids.[3] It should be emphasised that this is also typical of other photothermal effects. Physical models of the thermal lens effect have been developed in detail.[54–60]

In conventional thermal lens spectrometry, two laser beams are coaxial (a spherical lens). The scheme of formation and detection of a thermal lens signal is presented in Fig. 3. If the formation of the thermal lens is completed, the stationary thermal lens signal (ϑ) is calculated as either a change in the probe beam intensity at the detector

$$\vartheta \equiv \frac{I_p(0) - I_p(\infty)}{I_p(\infty)}, \tag{6}$$

where $I_p(0)$ is the intensity at the centre of the probe beam reaching the detector at the initial moment $t = 0$, before the formation of the thermal lens; $I_p(\infty)$ is the intensity at the centre of the probe beam after completion of the formation of the thermal lens ($t \to \infty$), or as a relative broadening of the probe beam in the detector plane

$$\vartheta = \frac{\omega_{2p}^2(\infty) - \omega_{2p}^2(0)}{\omega_{2p}^2(\infty)}. \tag{7}$$

Time evolution of the thermal lens in a sample during one cycle of operation of a chopper (a modulator) of the excitation beam (or a single laser pulse) is described by a time-resolved thermal lens signal, which is the instantaneous relative intensity of the probe beam at the centre of the detector, $I_p(t)/I_p(0)$. The probe beam absorption in a sample is assumed to be negligible.

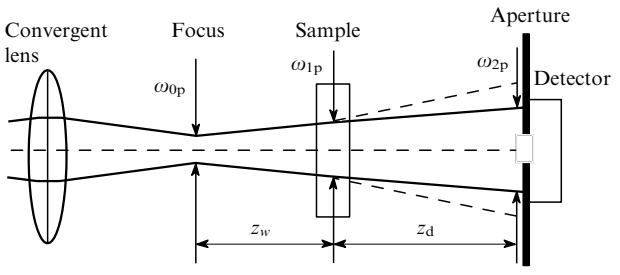


Figure 3. Diagram showing propagation of the probe beam; ω_{0p}, ω_{1p}, ω_{2p} are the radii of the probe beam in the waist, at the sample and in the plane of the detector, respectively; z_w is the distance between the probe laser waist and the sample; z_d is the distance between the sample and the plane of the detector.

In the case of liquids and isotropic solid substances, the thermal lens signal is usually described using the diffraction theory, in terms of which the relation between the thermal lens signal and the absorbance of the sample is expressed as follows:

$$\vartheta = (1 - 2.303AE_0P_eB)^2 - 1, \tag{8}$$

where A is the absorbance of the sample, P_e is the power of excitation radiation, E_0 is the thermal-lens enhancement factor (an increase in sensitivity compared to conventional spectrophotometry) for a unity power of excitation radiation

$$E_0 = -\frac{dn/dT}{\lambda_e k}, \tag{9}$$

(dn/dT is the temperature gradient of the refractive index, λ_e is the wavelength of the excitation laser, k is the thermal conductivity coefficient), B is the geometrical constant of a thermal lens spectrometer

$$B = \frac{1}{2}\operatorname{arctg}\left(\frac{2mV}{1 + 2m + V^2}\right), \tag{10}$$

V is the distance between the probe beam waist and the cell with a sample (in units of confocal distances of the probe laser)

$$V = \frac{z_\omega}{z_{cp}} + \frac{z_{cp}}{z_d}\left[\left(\frac{z_\omega}{z_{cp}}\right)^2 + 1\right], \tag{11}$$

m is the area ratio of the cross-sections of the probe and excitation beams in the sample

$$m = \left(\frac{\omega_{1p}}{\omega_{0e}}\right)^2 = \left(\frac{\omega_{0p}}{\omega_{0e}}\right)^2\left[1 + \left(\frac{z_\omega}{z_{cp}}\right)^2\right]^2, \tag{12}$$

where ω_{0e} and ω_{0p} are the waist radii of the excitation and probe lasers, respectively, z_{cp} is the confocal parameter of the probe laser.

For non-isotropic solid substances, the diffraction model of the thermal lens effect is inapplicable, because an analytical expression for neither a time-resolved lens signal nor a stationary thermal lens signal can be deduced.[72]

Quantitative measurements of the thermal lens effect enable one to evaluate the absorbance up to $y \times 10^{-8}$ and the concentration up to $y \times 10^{-12} - y \times 10^{-10}$ mol litre^{-1} (see Refs 6, 13, 21–43, 58, 62–71, 73–93). On the whole, the sensitivity of thermal lens spectrometry is 2–4 orders of magnitude higher than that of conventional spectrophotometry.

For isotropic samples, the time-resolved thermal lens signal is described in terms of the diffraction model by the following expression:

$$\frac{I_p(t)}{I_p(0)} = \left(1 - \frac{2.303E_0P_eA}{2} \times \right. \tag{13}$$

$$\left. \times \operatorname{arctg}\left\{\frac{2mV}{[(1 + 2m)^2 + V^2]t_c/2t + 1 + 2m + V^2}\right\}\right)^2 +$$

$$+\left(\frac{2.303E_0P_eA}{4}\ln\left\{\frac{[1 + 2m/(1 + 2t/t_c)]^2 + V^2}{(1 + 2m)^2 + V^2}\right\}\right)^2,$$

where t_c is the characteristic time constant of the thermal lens

$$t_c = \frac{\omega_{0e}^2}{4D}, \tag{14}$$

D is the thermal diffusivity of the sample.

Time-resolved thermal lens spectrometry is based on the time evolution of the focal distance of the thermal lens. The response time of the method is 0.1–1 ms, which is approximately an order of magnitude shorter than that achieved in stationary thermal lens measurements.[78, 94–98] Time-resolved thermal lens spectrometry is used for the detection in chromatography or studies of kinetic processes.

Presently, a differential (dual-cell) modification of thermal lens spectrometry is under development. In this method, the background signal is compensated by the formation of a thermal lens in two cells placed sequentially. The second cell containing a reference solution is placed symmetrically in front of the excitation laser waist.[30, 99–105] The thermal lens signal formed in this cell [see Eqn (6)] is proportional to absorption of impurities responsible for the background signal. The thermal lens signal in the second cell can be represented as the sum of the thermal lens signals of the analyte component and the background. The divergent thermal lens formed in this cell can be considered as a superposition of two thermal lenses, whose focal distances depend on absorption of the analyte components and impurities. Hence, the thermal lens effect in the first cell compensates for broadening of the probe beam, which occurs due to absorption of impurities in the second cell containing the solution analysed. In this case, the signal depends only on absorption of the component analysed in the second cell. Advantages of two-cell measurements over the conventional single-cell method is evidenced by the fact that the detection limit of iron(II) by its reaction with 1,10-phenanthroline is five times lower (20 nmol litre^{-1}), and the minimum quantifiable concentration is almost ten times lower (40 nmol litre^{-1}).[99]

3. Photothermal refraction

Crossed-beam thermal lens spectrometry or photothermal refraction is based on the optical scheme of thermal lens measurements, in which the excitation and probe laser beams are mutually perpendicular (a cylindrical lens).[49, 106–111] Although the sensitivity characteristics of this method are analogous to those of thermal lens spectrometry, photothermal refraction makes it possible to detect absolute amounts as low as several tens of molecules of absorbing substances in the volume from $y \times 10^{-18}$ to $y \times 10^{-15}$ litre (a crossing region).

Due to a high spatial resolution, photothermal refraction is used in capillary chromatography, capillary electrophoresis methods and local analysis of liquids.[49, 106–117] However, equipment required for the optical schemes of photothermal refraction are more cumbersome compared to that used in the parallel-beam scheme, and these optical schemes are characterised by a substantially more complex mathematical model, which describes the relationship between the signal recorded and the geometric parameters of the optical scheme. Besides, this mode of recording the thermal lens signal is inconvenient for performing analyses in a volume larger than 0.1 ml, because the energy of the excitation laser beam reaching the crossing region substantially decreases as the absorbance of the sample and the optical path length increase, resulting in narrowing of a region of the linear dependence of the refractometric signal (a linearity region).[118]

The use of the thermal lens detection in the near-field region (the sample-to-detector distance is 10 cm) gave additional impetus to the development of photothermal refraction.[109–111] Further investigation demonstrated that detection under these conditions corresponds to detection in capillaries, because the edge effects caused by interference of the probe laser beam at capillary walls are eliminated, and the measurement reproducibility is substantially improved. In addition, this approach employs compact apparatus, which made it possible to create a detector prototype for capillary electrophoresis (Fig. 4).

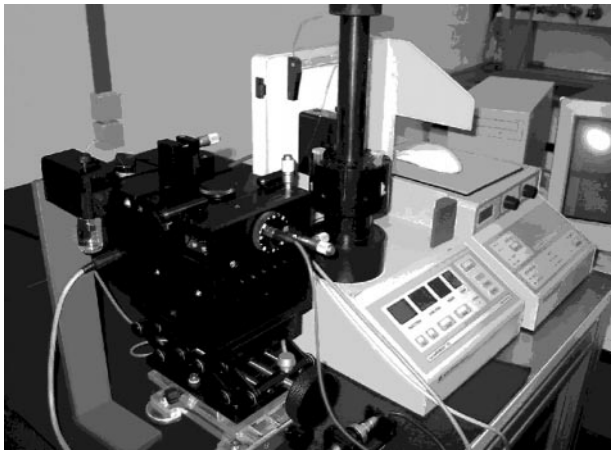


Figure 4. Photograph of a detector prototype for capillary electrophoresis based on photothermal refraction spectrometry.
The photograph courtesy of Drs W Faubel (Karlsruhe Research Centre, Germany) and U Puell (Marburg University, Germany).

4. Total internal reflection thermal lens spectroscopy

Thermal lens spectrometry under conditions of total internal reflection [an analogue of total internal reflection fluorescence spectroscopy] is a powerful tool for studying interfaces (liquid–liquid, liquid–solid, *etc.*) when nanogram amounts of reagents are used.[119, 120] However, this method has little use. The method is based on providing conditions under which the laser beam inducing a thermal lens undergoes total internal reflection from the interface. This allows the detection of photothermal effects, which appear virtually only at the interface. Taking into account that thermal lens spectrometry as a method of molecular absorption spectroscopy is suitable for a larger number of compounds compared to fluorescence, this method has great potential although it is still in its infancy.

5. Photothermal deflection and photothermal displacement

Mirage-effect spectroscopy (thermal deflection spectroscopy, thermal prism)[5, 51, 121–153] and photothermal displacement spectroscopy (thermal mirror)[154–170] are the next most commonly used methods after thermal lens spectrometry. These methods are most widely employed in a purely thermal modification using excitation with IR radiation, which is associated primarily with investigations of semiconducting and polymer materials. These methods are only partially used in experiments on selective excitation in the optical range.

These methods are based on the changes in the optical characteristics of the surface and subsurface layers of the medium caused by heating of a sample with an excitation laser (Fig. 5). In a liquid or gaseous medium, which exists in direct contact with the sample, the thermooptical element is formed. The latter acts as a prism on the radiation propagating along the sample surface. This process is accompanied by thermal deformation of the irradiated surface, resulting in its bending. The probe laser beam, which passes parallel to the surface (a mirage effect) or is incident on the surface at a particular angle (a thermal mirror), is deflected by the thermal prism at a definite angle from the initial direction or is

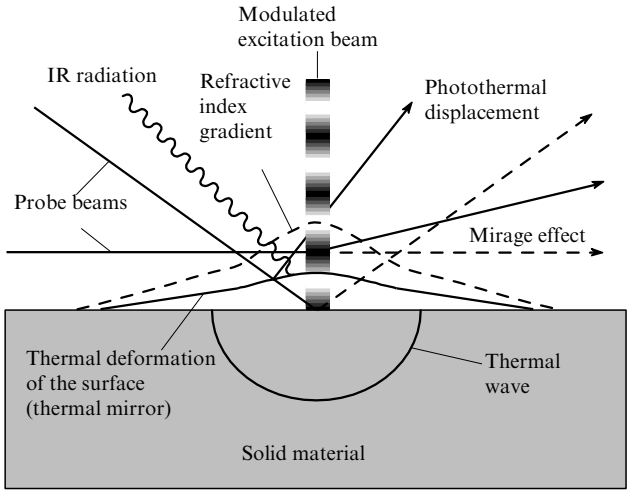


Figure 5. Thermooptical effects under laser excitation of the surface.

reflected from the bent surface and broadened. The perturbations caused by heating are associated with the absorbing ability and thermal properties of the surface under study and depend on the thermal properties (heat capacity, thermal conductivity) of the environmental medium. The scheme of the appearance of the above-described photothermal effects is shown in Fig. 5.

In mirage and photothermal displacement spectroscopy, optical position-sensitive detectors, for example, photodiode matrices and video cameras, are generally used. The angle ϕ (or a distance) at which the probe beam is deflected can serve as an analytical signal. This signal is called the amplitude signal, because it characterises the displacement amplitude of the probe beam relative to the non-excited state of the surface.

There are a number of equations describing the photothermal deflection. The form of these equations depends on the aim of a particular study and the phase state of the medium under study. In investigations of the surfaces of solid materials and gaseous media, the following equation is used:[5]

$$\phi = -\frac{\mathrm{d}n}{\mathrm{d}T}\frac{\alpha l P_\mathrm{e}}{\pi^2\psi\rho C_\mathrm{P}\omega_{\mathrm{e}0}^2}\left(-\frac{2x_0}{\omega_{\mathrm{e}0}^2}\right)\exp\left(-\frac{x_0}{\omega_{\mathrm{e}0}^2}\right). \qquad (15)$$

This equation is valid if the excitation and probe beams are mutually perpendicular (Scheme 1). In studies of weakly absorbing media, the propagation directions of the excitation and probe beams in samples form an acute angle (Scheme 2). In this case, the following equation is valid:[4]

$$\phi = -\frac{\mathrm{d}n}{\mathrm{d}T}\frac{\alpha l P_\mathrm{e}}{2\pi k x_0}\left\{2\exp\left[-\frac{2x_0^2}{\omega_{\mathrm{e}0}^2(1+1/\psi t_\mathrm{c})}\right]- \qquad (16)$$

$$-\exp\left[-\frac{2x_0^2}{\omega_{\mathrm{e}0}^2(1+2/\psi t_\mathrm{c})}\right]-\exp\left(-\frac{2x_0}{\omega_{\mathrm{e}0}^2}\right)\right\}.$$

Here α is the linear absorptivity of the sample layer giving rise to a photothermal signal; l is the thickness of the absorbing layer; ψ is the chopper frequency; x_0 is the so-called interaction distance, *viz*., the distance between the surface of the sample and the parallel-arranged probe beam (displacement of the probe beam) for Scheme 1 or the distance between the optical axes of the beams for Scheme 2.

The refractive index field induced by heating is responsible for the phase change of the displaced beam relative to the incident beam. The observed phase difference is called the phase signal. This signal is recorded by a lock-in amplifier connected to a position-sensitive detector. The spatial resolution of measurements is related to the size of the beam cross-section of the excitation laser, which, in turn, is limited by the wavelength of the excitation beam.

These methods have some specific features. For example, the mirage effect appears in the surrounding medium rather than in the sample. In this connection, measurements by the mirage spectroscopy are not carried out *in vacuo*. The possibilities of determining the concentrations of solid substances in gases, in particular, in air, are limited by their thermooptical characteristics. Hence, an auxiliary liquid possessing appropriate thermooptical properties is often applied on the surface to strengthen the thermal prism. However, this approach has drawbacks associated with the difficulty of choosing such liquids (it is necessary to exclude completely an interaction of the liquid with the material under study).

Of all theoretical models of the formation of a photothermal signal, the model of the mirage effect has been best developed. In the method of photothermal mirror, simulation of the thermal deformation of the surface is a much more complicated problem. In addition, the probe beam deflected by the deformed excited surface can be additionally deflected due to the presence of the refractive index field in the surrounding medium (if measurements are carried out not in vacuum). As a result, calculations become even more complicated.

Nowadays, mirage spectroscopy is one of the most convenient and commonly used thermooptical methods for studying surfaces with very high or very low light absorption. Generally, this method is used for microscopic studies and flaw detection in semiconductors,[171] metals[172,173] and various optical materials.[174–176] Mirage spectroscopy is rarely employed in analytical chemistry as a highly sensitive method of molecular absorption spectroscopy.

Mirage spectroscopy is used in immunoassay adsorption analysis with isolation of a specially coloured antigen–antibody complex on the surface of a solid substrate followed by detection of surface absorption.[177–179] This method is used also in thin-layer chromatography for detection of the absorption profile along the elution profile.[180–182] The new application of mirage spectroscopy for analysis by thin-layer chromatography[183] is limited to measurements with the use of non-selective excitation. However, mirage spectroscopy is not considered as a solo analytical method for the detection of surface absorption. The study[183] was aimed only at estimating the deep concentration profile in the chromatographic zone based on the determination of the surface properties by several thermooptical methods, including mirage spectroscopy. Besides, mirage spectroscopy is used in capillary chromatography.[149–153,184]

6. Photothermal radiometry

Photothermal radiometry is based on measurements of IR radiation from the sample surface after its irradiation with a laser beam (see Fig. 5).[185–214] The amount of emitted energy is proportional to the absorptivity of the sample. In photothermal radiometry, the rate of time evolution of the signal is substantially higher than that in mirage spectroscopy and the thermal-mirror technique, because the time required for evolution of surface deformation and the temperature gradient in the surrounding medium is longer than the thermal relaxation time determining the onset of emission of IR radiation from a heated sample. Semiconducting energy-dispersive detectors are used for rapid and highly sensitive measurements of emitted IR radiation. The possibilities of photothermal radiometry are most evident in studies of semiconducting materials and in IR tomography of biological tissues, including *in vivo* studies. The advantages of photothermal radiometry are the possibility of remote probing, simplicity of experimental equipment and, what is most important, high time resolution (10^{-7}–10^{-8} s). The latter fact allows one to measure absorption spectra of intermediates and study fast processes. Photothermal radiometry is used for determining the absorptivities of thin films, coatings and biological tissues of living organisms.[191,199–206] Theoretical models for photothermal radiometry are constructed on the basis of one-dimensional heat transfer and the law of blackbody radiation. However, the majority of real systems show substantial deviations from the model approximations, which complicates the interpretation of experimental data. These approximations are best suitable for analysis of semiconductors using laser radiation, whose wavelength is larger than the semiconductor band gap. In this case, the signal (thermal radiation) is generated by a plasma wave rather than by a thermal wave, and experiments correspond closely to the model of blackbody radiation.

7. Photothermal microscopy

Photothermal microscopy has been created in the course of the development of thermal lens spectrometry. In this case, the optical set-up of a thermal lens spectrometer is included in the scheme of measurements of an optical microscope.[178,215–232] Photothermal microscopy is used primarily in biological studies as a non-destructive method for investigating cell functioning and in medicine for diagnostic purposes. Depending on the conditions (virus activity, impairment of cellular functions, *etc*.), the optical

characteristics of cytoplasm can differ from those of cell nuclei, which are easily detected with a photothermal microscope.

Photothermal microscopy enables one to study the characteristic features of reaction pathways with the use of nanogram amounts of reagents. This method can be combined with microflow analysis and microchromatography. The further use of the results of these investigations is directly associated with the development of microflow injection analysis, microelectrophoresis and, on the whole, integrated microanalysis systems.[216–231] Photothermal microscopy can also be used for studying reactions under conditions of integrated microanalysis systems (detection of trace concentrations, investigations of mirochannels, microflows, *etc*.) and as a detection method.

8. Photothermal interferometry

Another group of thermooptical spectroscopy methods includes photothermal interferometry and related methods.[189, 233–245] In these methods, a three-dimensional pattern (an amplitude and a phase) of the probe beam recorded on an interferometer (Mach–Zehnder, Fabry–Perot or Jamin–Lebedev) serves as an analytical signal.[239, 246, 247] These methods allow one to determine the local absorption distribution on the surface and in subsurface layers. The sensitivity of photothermal interferometry is the highest of all thermooptical methods (the weakest signal is determined by quantum noise of an interferometer, the absorbance is $y \times 10^{-10}$) and allows the determination of highly absorbing compounds in amounts up to individual molecules. In addition to chemical analysis, photothermal interferometry is employed to study the hydrodynamics of liquids and gases, determine the rates of microflows with high precision, and establish nucleotide sequences in DNA and amino acid sequences in proteins.[242, 245] The amplitude signal in photothermal interferometry is calculated by the equation

$$\phi = \frac{\pi^2}{2}\sqrt{\frac{D}{\psi}}\,\frac{\omega_{e0}^2}{\lambda_p}\,\frac{\partial n}{\partial T}\,\frac{\alpha l}{k}\,P_e\left|\mathrm{erfc}\left(\sqrt{\frac{\psi}{D}\,\frac{\omega_e^2+\omega_{e0}^2}{8}}\;e^{i\pi/4}\right)\right|, \qquad (17)$$

where λ_p is the probe beam wavelength.

Photothermal spectroscopy holds promise for measuring ultralow light absorption in solid materials for laser and fibre-optical techniques, which was confirmed by studies.[239, 240, 248–251] To measure the rates of liquid and gas flows with a sensitivity up to $y \times 10^{-6}$ cm s^{-1}, an optical thermal anemometer was devised.[249–251] An apparatus was created for separate measurements of the bulk and surface light absorption in materials for power optics. This apparatus is successfully used for monitoring low absorption ($y \times 10^{-5}$ cm^{-1}) in ZnSe and ZnSe-based optical elements.

9. Thermal diffraction spectroscopy

Thermal diffraction spectroscopy is based on the spatial periodic refractive index change in a medium caused by the photothermal effect, which is induced by absorption of the excitation beam energy.[252–261] In this case, the thermooptical element behaves as a diffraction grating, and the diffraction pattern produced by the probe beam serves as a signal. This method requires very complex equipment and is used for solving special problems, in particular, for testing the quality of laser optics (spatial distribution of microelements in optical materials) and for studying fast processes (energy transfer in crystals, photochemical processes, structural vibrations of crystal lattices).[254, 257, 260, 262–267]

One promising line of investigation for the use of thermal diffraction spectroscopy is concerned with chemical kinetics and reaction mechanisms. The method allows one to separate diffusion processes and chemical reactions, because the total signal of these processes can be considered as a superposition of short-lived and long-lived diffraction gratings.

A modification of the thermal diffraction method, *viz*., photothermal IR microspectroscopy, employs a microthermometer as a probe, which is used in atomic-force microscopy and thermal microscopy.[268, 269] In a photothermal microscope (unlike an atomic-force microscope), a probe of this type serves both as a thermometer and a heater, which allows the simultaneous detection of surface samples and samples of subsurface layers.[262] The instrument can be use both for measuring photothermal spectra at a given point (region) of samples based on the results of surface scanning in the mode of atomic-force microscopy and for obtaining photothermal samples, in which the signal is proportional to the concentrations of substances that absorb at the excitation wavelength. An important feature of photothermal IR microspectroscopy employing a thermoprobe is that this method, unlike other photothermal methods, is not restricted by the diffraction limit of spatial resolution.[267] Interestingly, photothermal measurements, scanning thermal microscopy, thermomechanometry or thermocalorimetry can be combined in the same instrument, because all these studies are carried out with the use of a Wollaston thermoprobe.[270] Photothermal microscopy provides better spatial resolution compared to conventional measurements using Fourier-transform IR spectroscopy.[267] Such photothermal measurements are used for studying composite materials, biological samples (hair, cells), in particular, for examining microprobing of drugs and the influence of antioxidants on cell functioning.[267–270]

10. Characteristic features of thermooptical spectroscopy methods

The characteristic features of thermooptical spectroscopy methods can be divided into six main groups.

The first group includes characteristics related to high sensitivity. Modern methods for recording the absorbed energy allows the determination of the temperature, volume or refractive-index changes corresponding to absorption of $y \times 10^{-8}$–$y \times 10^{-10}$ absorbance units, which is 4–6 orders of magnitude lower than the sensitivity of conventional spectrophotometric methods.[1–10, 46, 59, 74, 86] In addition to high instrumental sensitivity, thermooptical spectroscopy is characterised by a wide linear dynamic range of measurements (for thermal lens spectrometry, this range is up to 6–8 orders[4, 6, 11, 18, 90]). However, highly sensitive analytical methods have drawbacks, which are associated primarily with the purity of reagents and solvents, the problem of test experiments, laborious sampling, sample preparation, *etc*.

The second group includes characteristics reflecting the distinguishing features of thermooptical spectroscopy as a method of molecular absorption spectroscopy. The advantages of the latter are diversity of substances (including organic compounds) which can be detected, the possibility of investigating samples in different aggregate states, well-developed methods and numerous procedures for sample preparation and non-destructive determination (which allows one to analyse biological samples, for example, living cells), the possibility of performing remote analysis[21] and determinations in flow.[8, 10, 42, 43, 46, 178] However, thermooptical spectroscopy has all drawbacks of conventional spectrophotometry (primarily, spectral non-selectivity).

The third group includes the parameters of thermooptical spectroscopy as calorimetric methods. The common feature of these methods is the extraction of information on the composition and properties of the analyte by recording absorbed radiation and taking into account the attendant changes in the physical and (or) thermodynamic parameters. The absorbed energy can be measured using various modes of detection: acoustic (acoustic wave formation, gas pressure changes), interferometric, refractometric (refractive index changes), optical (measurements of the intensities of transmitted or absorbed radiation), thermometric (contact temperature control), direct calorimetric (direct detection of thermal radiation) or extensometric (changes in the sample size).

The fourth group includes the characteristics of thermooptical spectroscopy, such as power characteristics (the signal is proportional to the incident radiation intensity) and geometric characteristics (the signal depends on the geometry of the optical scheme).

These properties are not unique (recall photoacoustic spectroscopy). The advantage is that the dynamic range can be even more extended (up to 8 – 10 orders of magnitude) by varying the power of the radiation source.[27 – 33, 91 – 93, 271] However, the strong dependence of the thermal lens signal on the geometric parameters (positions of the laser beam waists, cells containing samples and the detector) leads to a serious problem of measurement reproducibility.[55, 58, 59, 80, 272, 273] In addition, not only sensitivity and reproducibility but also the linear range of the signal depends on the geometric parameters of the optical scheme.[59, 274 – 279]

The fifth group of parameters, which characterise the main distinguishing features of thermooptical spectroscopy, is associated with the use of lasers as powerful intense sources of monochromatic coherent radiation. As a result, the number of effects induced by interaction of radiation with an absorbing medium sharply increases. In addition to sample heating, researchers face the photochemical effects (which can play both positive and negative roles), the simultaneous manifestation of the photothermal effect and luminescence, *etc.*[3, 6, 280 – 284] It should be noted that the influence of laser radiation on samples in thermooptical experiments is poorly understood.

The sixth group includes parameters reflecting the unique properties of thermooptical spectroscopy. In relation to this connection, let us mention several important factors.

1. In thermooptical spectroscopy, the laser mode structure is the most important characteristic of laser radiation. Due to regularity of this distribution for the observed photothermal effect, it is possible to construct the precise mathematical model, which relates the strength of the effect (for example, the focal distance of the resulting thermal lens) to the concentration of absorbing components of the system.[6, 55, 56, 239]

2. The solvent plays a decisive role in thermooptical spectroscopy because when a medium is heated its parameter change, for example, refractive index and density. For example, a particular (chemically inert) absorbing compound is characterised by photothermal signals in organic and aqueous media, which differ by several orders of magnitude.[271] Methods of thermooptical spectroscopy are successfully used for determining the above-mentioned characteristics of solvents.[285 – 291]

3. It should be emphasised that the photothermal effects are local in character. They do not cover the overall volume of the sample, but only a small region around the excitation laser beam. This gives rise to strong convection of the liquid, which can lead to blurring and periodic oscillations of the signal.[292] However, the period of convective oscillations can provide important information on the photothermal properties of substances.[293, 294] Another consequence of the local character of the photothermal effects is that chemical processes in the heated portion of the solution can be either accelerated or decelerated (due to heating, photochemical reactions, *etc.*), resulting in a change in the concentration gradient and the formation of diffusion flows of substances.

Evidently, the above classification of the characteristics is tentative, but it gives an insight into the problems associated with the development of analytical thermooptical methods. When describing the features of these methods and classifying these characteristics, we used the principle 'from general to special'. It should be noted that only the first three groups of characteristics were considered in the literature concerned with the problems, advantages and drawbacks of analytical thermooptical spectroscopy, although (strange as it may seem) these characteristics are not unique for thermooptical spectroscopy and are met with in other methods. The last three groups of characteristics are generally ignored considering their well-known drawbacks, which decrease the efficiency of the method, or regarding them as personal techniques used by researchers. As a result, the true place of thermooptical spectroscopy among analytical methods is actually an open question.

In our opinion, this view is incorrect, because specific effects manifested in thermooptical experiments, such as the simultaneous detection of several analytical signals, and the employment of photothermal effects as an active component of the analytical method rather than as a passive mode of detection will presumably provide the basis for a 'special line' of the development of analytical thermooptical spectroscopy. It is encouraging that virtually all most important recent studies have been aimed at developing or, at least, searching for new approaches to methodology, sample preparation and measurements of the signals.[9 – 18, 50 – 54, 58, 112 – 117, 119, 120, 216 – 232, 239, 274, 282, 295 – 297]

11. Apparatus for thermooptical measurements

Dual-laser (dual-beam) optical set-ups have gained wide acceptance in thermooptical spectroscopy. In these schemes, a thermooptical element is formed in a sample under the action of one beam (the excitation beam), and the change in the characteristics of the second (probe) beam serves as an analytical signal.[4 – 10, 54 – 71, 184, 298 – 309] Correspondingly, the excitation laser wavelength is chosen at the absorption maximum, and the probe beam wavelength is, on the contrary, chosen at the absorption minimum. Since thermooptical methods belong to power methods, powerful continuous wave lasers (argon ion, krypton ion, helium cadmium, *etc.*) or pulsed lasers (Nd : YAG, CO, nitrogen, eximer, *etc.*) are used for excitation. It should be noted that thermooptical methods are not limited to the use of laser radiation. However, the use of laser radiation allows one to substantially enhance the effects, which, in fact, appear upon any interaction of radiation with matter. Sources of IR, UV and visible radiation with a continuous spectrum (xenon lamps) are also employed.[295] In this case, the regularity of the intensity profile of excitation radiation is achieved by using absorbing spatial filters.

The basic diagram of thermooptical measurements is shown in Fig. 6. Various methods employ radically different systems for beam focusing and convergence. In all thermooptical methods, the signal depends on the geometry of the optical set-up. Hence, careful adjustment and calibration of a thermooptical spectrometer are required before experiments, and the parameters should be frequently monitored during the course of measurements. A system for synchronisation, which provides synchronisation of the onset of the formation of a thermooptical element and the onset of signal accumulation, most commonly consists of either a mechanical or electromechanical chopper (for beam modulation of an excitation continuous wave laser), a controlling block (a lock-in amplifier or a sampling integrator) and a photodiode. The function of the reference signal is to record the current power of the excitation laser and normalise the signal.

The uniqueness of a thermooptical spectrometer is that the signal contains information only on light absorption of a sample, but the measurement technique allows one to use this instrument simultaneously as, for example, a nephelometer or a refractometer. Hence, a thermooptical spectrometer is a multipurpose instrument, which can provide much more information compared

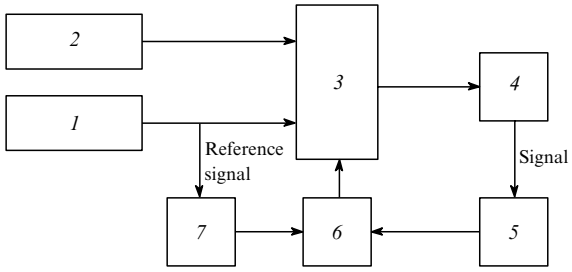


Figure 6. Basic diagram of thermooptical measurements.
(*1*) An excitation laser, (*2*) a probe laser, (*3*) a system for beam modulation, focusing and convergence, (*4*) a sample, (*5*) a photodetector for analytical signal, (*6*) a system for synchronising and recording, (*7*) a photodetector of a reference channel.

to its spectrophotometric analogue. As an example we refer to thermal lens fluorimetric procedures for the determination of picogram amounts of transition metal complexes and a combined thermooptical refractometric detector for liquid chromatography. The merit of the latter is that it can be used for the simultaneous determination of compounds of different nature at nanogram levels (for example, the determination of metal chelates and polysaccharides without their preliminary derivatisation).[239, 248]

Let us consider a typical thermal lens spectrometer[58, 59] (Fig. 7). A thermal lens is induced in a cell with an Innova 90-6 argon ion laser *1* (Coherent, USA) with a lasing wavelength of 514.5 nm (TEM_{00} mode, the maximum power is 1.5 W). An SP-106-1 helium neon laser (Spectra Physics, USA) is used as the probe laser *2* with a lasing wavelength of 632.8 nm (TEM_{00} mode, the power is 10 mW). The beams of both lasers are initially vertically polarised. After an optical rotator *3* (model 310A, Spectra Physics, USA), the horizontally polarised excitation laser beam passes through a mechanical modulator (chopper) *4*. A part of the beam energy is directed to a FD-7K power monitoring photodiode *6* using a plate *5*. An amplifier *7* converts the current from the photodiode into a voltage and directs the signal to the second channel of an analogue-to-digital converter and a digital-to-analogue converter (ADC–DAC) board *8* installed on an IBM PC/AT *9*. To synchronise the detection system with the operation mode of the modulator, a part of the radiation energy of the excitation laser is allocated to a lock-in photodiode *11* using a plate *10*. The signal passes to a synchronisation block *12*. The latter forms a pulse, which coincides with the moment of the opening of the chopper. The pulse passes to the ADC–DAC board of the computer. This pulse corresponds to the onset of the formation of a thermal lens in the cell and serves as a signal for the beginning of a new cycle of data reading. The chopper is controlled by a computer through a converter *8* and a synchronisation block *12*. The excitation laser beam, which is focused by a lens *13*, passes through a plane-parallel plate *14* (which is used for fine tuning of the beams in the cell) and a Glan prism *15* and is directed to a cell *16*. The probe laser beam is sent through a system of mirrors *17* and *18* and a focusing lens *19* to the Glan prism, where it is reflected and goes to the cell. A dichroic mirror *20* serves for the preliminary separation of the excitation and probe laser beams and makes it possible to get rid of an additional thermal lens, which could be induced by a highly absorbing filter *21*. The helium neon laser beam, which bears information on light absorption by the sample, passes through an 2-mm aperture *22* located on an optical axis of the system and falls on a FD-7K photodiode *23*. The signal from the photodiode is converted by an amplifier *24* and goes to an ADC–DAC converter of the computer.

Photothermal detectors for capillary electrophoresis on the basis of photothermal refraction in the near-field region (Fresnel diffraction) have been extensively developed in recent years. A prototype of such detectors for high-performance capillary electrophoresis was devised at the Karlsruhe Research Centre (Germany)[113, 114, 310, 311] (see Fig. 4).

The scheme of a typical instrument for mirage spectroscopy[112–115] is shown in Fig. 8. This instrument consists of a probe monoblock equipped with a position-sensitive recording system (Phototherm Dr. Petry Gmbh, Germany). Excitation is performed with a Nd : YAG laser (ADLAS DPY 321, Germany) at wavelengths of 1064 and 532 nm; the maximum radiation power is 50 mW. A helium neon laser (Melles Griot, USA) with a power of 5 mW and a wavelength of 632.8 nm is used as the probe laser. The scanning system allows one to study samples of sizes of 2×2 cm at 1 μm resolution. The chopper frequency of the excitation source varies from 10 to 1000 Hz, which corresponds to heating of a sample layer with a depth from 1 nm to 1 μm. The signal recording system is equipped with a position-sensitive detector and a lock-in amplifier. The deflection amplitude (the amplitude signal) and the path difference (the phase signal) of the probe beam are recorded.

Photothermal IR microspectroscopy employs a modified Fourier-transform IR spectrometer. To ensure thermooptical measurements, the modulated beam from an IR spectrometer heats a sample. Heating is detected by a thermal probe. The output signal from the spectrometer returns to the input of the spectrometer, which makes it possible to record photothermal interferograms. In the scanning mode, a thermal probe is mounted on a positioning system (most often on an atomic-force microscope).[262]

As mentioned above, the main idea of photothermal interferometry consists of measuring the optical path length changes caused by a photothermal modulation of the refractive index. Compared to other photothermal methods used for detecting thermal perturbations of the optical parameters of a medium, *viz.*, photothermal deflection spectroscopy and thermal lens spectrometry, the phase method provides higher sensitivity and stability of measurements. However, in spite of substantial potential advantages, the phase method has little practical application. This is associated with the fact that commonly used Michelson and Mach–Zehnder interferometers are rather complex instruments, which are very sensitive to the environmental conditions and require tedious tuning. A photothermal detector on the basis of polarisation and fibre-optic interferometers, which has been

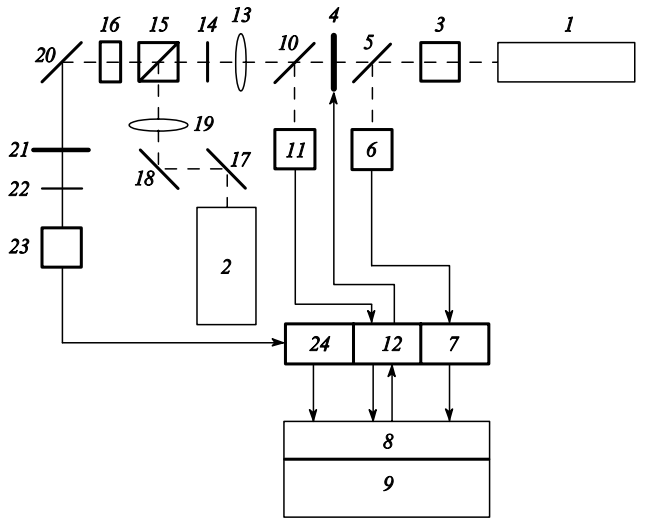


Figure 7. Block diagram of a dual-laser thermal lens spectrometer (for notations see text).[58, 59]

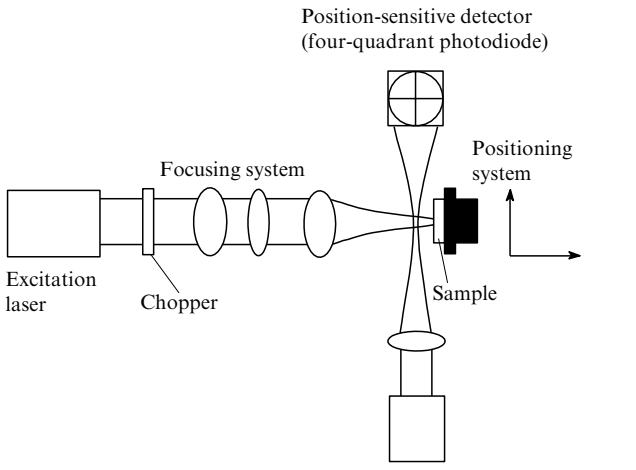


Figure 8. Scheme of a mirage spectrometer.[112–115]

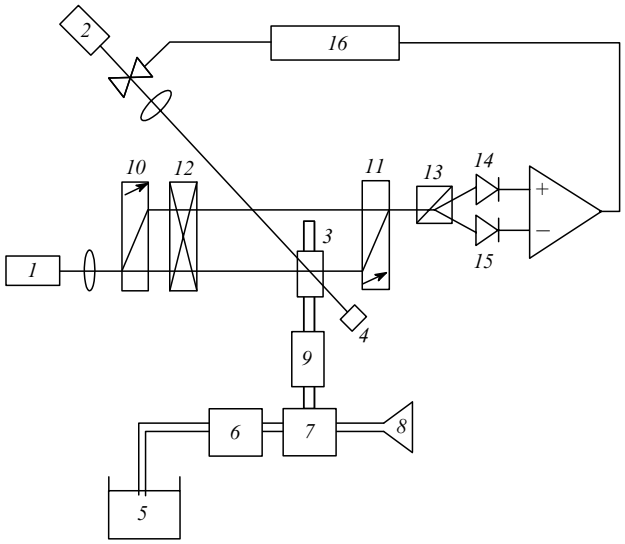


Figure 9. Scheme of a thermooptical polarisation interferometer equipped with an HPLC detector.[239, 240, 248]
(*1*) A probe laser, (*2*) an excitation laser, (*3*) a cell, (*4*) a power metre of an excitation laser, (*5*) an eluent, (*6*) a chromatographic pump, (*7*) an injector, (*8*) an injector port, (*9*) a chromatographic column, (*10*, *11*) Savart plates ($CaCO_3$), (*12*) a 90° optical rotator, (*13*) a Wollaston prism, (*14*, *15*) photodiodes, (*16*) a lock-in amplifier.



Figure 10. Photograph of a commercial thermal lens microscope for measurements in microfluid chips.[314]
The photograph courtesy of Prof. T Kitamori and Dr. M Tokeshi (University of Tokyo, Institute of Microchemical Technology, Japan).

devised in recent years, can be used in liquid chromatography and capillary electrophoresis.[239, 240, 248–251, 312, 313]

A diagram indicating the main features of a thermooptical interferometer based on a Jamin–Lebedev polarisation interferometer is presented in Fig. 9. Doubled-frequency radiation of a Nd:YAG laser *2* (532 nm, 25 mW) is used for excitation. A semiconducting laser *1* (680 nm, 10 mW) serves as a source of probe radiation. The diameter of the probe beam in cell *3* is 100 mm. The detector operates simultaneously in photothermal and refractometric modes. In the latter case, non-periodic changes in the refractive index of a liquid flowing through the detector are measured. The corresponding signal induced by changes in the mobile phase in a chromatographic system *5–9* is formed in a feedback system. In the photothermal mode, the presence of an absorbing analyte in the cell leads to a temperature rise and, consequently, to an increase in the refractive index, whose variations are proportional to the modulation frequency of the excitation beam. This gives rise to an additional phase signal, which modulates the polarisation state in the second Savart plate *11*. This modulation amplitude is analysed using a Wollaston prism *13* and is measured with the use of photodiodes *14* and *15*, which are connected to a lock-in amplifier *16* incorporated into the interferometer.[239, 240, 248, 250, 312, 313]

The results of studies confirmed that this model can serve as a basis for the construction of commercial detectors. The minimum absorbance detected with this instrument is 2×10^{-10}; the sensitivity is 1000–10 000 times higher than that of conventional spectrophotometers and is 10–100 times higher than that of thermal lens spectrometers; the detection limits are about a few picograms per millilitre; the linear dynamic measurement range is about five orders of magnitude.[239, 240, 248, 250, 312, 313]

The first commercial instrument based on integrated microanalysis systems, *viz*., an ITLM-10 thermal lens microscope (Institute of Microchemical Technology, Japan),[314] was specially designed for applications associated with chemical microchips (Fig. 10). The instrument employs a dual-beam parallel scheme of thermal lens measurements involving an excitation laser with a wavelength of 532 nm (50 mW) modulated with a frequency of 1 kHz and a probe laser with a wavelength of 670 nm (1 mW). A silicon photodiode connected to a lock-in amplifier serves as a detector. The dimensions of the instrument are $650 \times 280 \times 550$ mm and its weight is 25 kg. The provisional price of the instrument equipped with accessories (micropumps, microheaters, *etc*.) is ~ $70 000. The IMT Company (Japan) has designed about 300 modifications of glass and plastic chips for the determination of trace amounts of various substances. This instrument finds an ever increasing use in a combination of thermal lens spectrometry with chemical microchips.[314–319] Models for the simultaneous detection of a thermooptical signal and fluorescence and a portable thermal lens microscope are at the development stage.

III. Fields of application of analytical thermooptical spectroscopy

More than a thousand of papers, several monographs[2–5, 297] and numerous reviews[6–17, 115, 116, 220, 278, 279, 308, 320–322] concerned (in one way or another) with applications of thermooptical spectroscopy have been published. More than half of these publications were devoted to studies in the field of analytical and physical chemistry. Thermooptical spectroscopy has various applications regarding signal recording systems, purposes and subjects of investigation.

Analytical studies of gases by thermooptical methods are scarce.[111, 233, 323–336] Photoacoustic methods prove to be much more convenient, sensitive and fast in studies of gaseous media. Because of this, we do not consider this field of application in the present review. The possibilities of thermooptical methods in the determination of physicochemical parameters and the development of analytical applications are most evident in the analysis of condensed media.

Studies of volume-absorbing solids are limited to transparent substances. An important task is to search for and study new laser active media.[337–348] These studies dealt primarily with the balance between the appearance of fluorescence and the thermal lens effect in the solid matter that generates laser radiation. This problem has been considered in detail in several publications.[17, 320, 349]

1. Stages of the development of analytical thermooptical spectroscopy

There are three stages of the development of thermooptical spectroscopy, each next stage being performed at a higher qualitative level and their role in analytical chemistry being increased.

The publication of the classical study [1] can be considered as the beginning of the first stage. It is characterised by the simplest way of using thermooptical spectroscopy in analytical chemistry. In this stage, the available spectrophotometric procedures were simply extended to the thermooptical detection of absorption. During a long period of time, this approach prevailed, because it combined reliable conventional spectrophotometric procedures and high instrumental sensitivity of thermooptical instruments.[2, 7, 8, 272, 350] Nowadays, more than half of thermooptical procedures for analysis are still based on this approach. This approach is very fruitful both for determining various compounds from their own absorption and in the situation where the detection limit cannot be improved due to instrumental characteristics of a spectrophotometric instrument (Refs 1, 4, 7, 8, 21, 22, 63, 73–82, 272, 273, 295, 350–357).

However, by the late 1980s, evidence showed that the available photometric procedures could not be used for detecting compounds, whose concentrations were 2–4 orders of magnitude lower than those, for which these procedures have been designed.[2, 4, 23–26, 83–87] In addition to a serious problem associated with the purity of reagents, it is necessary to take into account changes in the conditions of complex formation and real redox potentials.[18] These changes can give rise to new side processes, which affect the reaction pathway.[4, 7, 27–38, 87–93] Hence, a demand arose for modifications of spectrophotometric methods. This gave impetus to the second stage of the development of thermooptical spectroscopy, which reached its peak in the early 1990s. The main aim of studies carried out at this stage was to enhance the sensitivity by both modifying chemical systems and optimising the optical set-up of an instrument. At the same stage, researchers began to design combined methods (primarily, chromato-thermooptical methods).[4, 16, 23, 36–40]

The modern stage began in the late 1990s. This stage is characterised by the development of unique applications (not necessarily photometric), which employ the combined influence of laser radiation and thermooptical effects on the system under study. The development of this approach is accompanied by an increase in the fraction of applied combined analytical (chromatographic,[41, 42] kinetic,[43, 44] electrophoretic [45, 46]) and non-analytical (for example, highly precise measurements of flow rates or sizes of colloidal particles [47–49]) methods. Growing interest in this line of investigation is evidenced by a large number of studies (in 2003, it reached a record value) and research groups working in this field (about 76 groups in 25 countries, Fig. 11) as well as by a qualitative change in the aims of studies. In 1986, journals publishing research papers in the field of analytical chemistry contained primarily studies devoted to instrumental characteristics of thermooptical measurements, mathematical processing, *etc*., whereas 75% of present-day publications are devoted to applied aspects (Table 2) and are based on specific features of thermooptical spectroscopy.[9, 13, 16, 50–53] In the following sections, we will try to explain the factors responsible for such substantial changes.

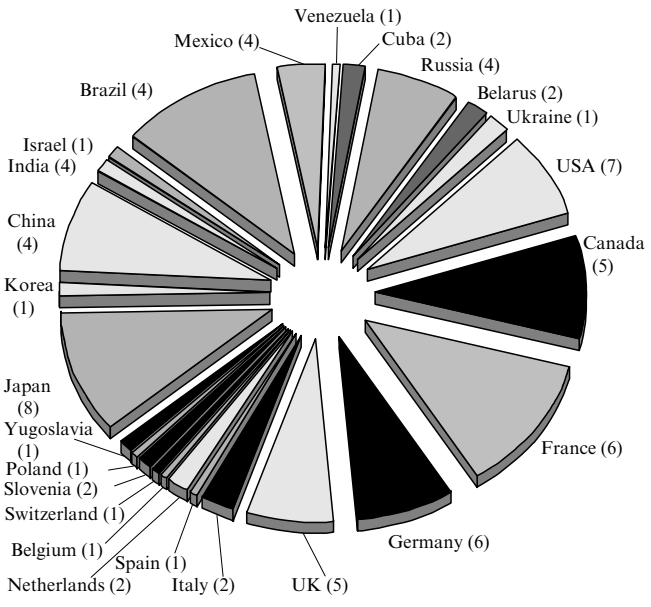


Figure 11. Diagram of the distribution of studies in the field of thermooptical spectroscopy by country in 2002.
The numbers of research groups working with this problem are given in parentheses.

Table 2. Distribution (in %) of studies in the field of thermooptical spectroscopy by main lines of investigation.

Line of investigation	Year		
	1986	1997	2000
Design and optimisation of instruments	39	11	17
Development of methods for analysis	23	41	27
Combined analytical methods	18	22	31
Other applied studies	20	26	25

2. Use of spectrophotometric procedures

Thermooptical spectroscopy allows one to determine optical densities at levels as low as 10^{-8} (see Refs 4–6 and 297). For most compounds, the detection limits are 10^{-10}– 10^{-9} mol litre^{-1} (the absorbance is from $y \times 10^{-7}$ to $y \times 10^{-6}$).[21, 22, 38, 76, 77, 353, 354] Even higher sensitivites (detection limits are from $y \times 10^{-12}$ to $y \times 10^{-10}$ mol litre^{-1}) were achieved in some studies.[355, 356, 358–360] The main advantage of thermooptical methods is the possibility of measuring absorption of ultrasmall amounts of substances in volumes of about $y \times 10^{-15}$–$y \times 10^{-9}$ litre due to small diameters of focused laser beams.[72, 112–116, 167, 189, 191, 239, 261, 321, 322, 361–375] In studies by crossed-beam thermal lens spectrometry, the detection limit of iron(II) involved in the complex with 1,10-phenanthroline was 120 molecules in a volume of 0.2 pl, which was determined by the crossing region of the laser beams in a cell.[356] In addition, a series of recent studies were devoted to the use of thermal lens microscopy in microflow analysis of substances and for the detection in capillary electrophoresis, where the detection limits were as low as zepto- (10^{-21} mol) and yoctomolar (10^{-24} mol) levels (in other words, individual molecules were detected) (Refs 178, 215–227, 296, 325, 376, 377).

Numerous studies were concerned with compounds, which served as models for either estimating the instrumental sensitivity of spectrometers (or signal recording systems),[1, 3, 6, 272, 350–354, 356] or examining the influence of solvents on the thermal lens effect.[1, 73–75, 273, 352–354, 357] For this purpose, the following simple and stable compounds, which are resistant to laser radiation, were chosen: a solution of molecular iodine in carbon tetrachloride,[73, 272, 351, 355, 357, 358, 378] aqueous solutions of presynthesised copper(II) complexes with EDTA [272] and acetylacetone,[77] iron(II) complexes with 1,10-phenanthroline [22, 78, 79, 272, 273, 357] or its analogues [273, 352] and cobalt(II) complexes with 1-(2-pyridylazo)-2-naphthol [77] and ethylenediamine.[73, 351]

Some researchers attempted to apply known spectrophotometric procedures without modifications to thermooptical spec-

troscopy,[22, 26, 85, 108, 354, 356] which led to a decrease in the detection limits, but did not allow the researchers to gain the most benefit from the method. The successive formation of a thermal lens under irradiation at two or more wavelengths made it possible to determine microamounts of compounds, whose maxima of absorption bands differ by 10–20 nm, in the case of their simultaneous presence in the sample.[61, 62, 81]

Thermooptical spectroscopy methods were used for determining various organic compounds, primarily, those containing nitrogen or sulfur.[32–36, 69, 71, 184, 379] In addition to studies of artificial mixtures serving for comparison of different modes of chromatographic separation, several studies were devoted to analysis of natural substances,[21, 26, 36, 37] in particular, to analysis of industrial and household dyes,[306] and examination of the possibility of controlling products of organic synthesis.[25] Studies dealing with the determination of proteins at a level of 1–100 ng[26, 38, 66, 76, 85, 304, 379] and amino acids at concentrations of $y \times 10^{-15}$–$y \times 10^{-12}$ mol litre^{-1} also deserve attention.[108, 301, 380, 381] Procedures were developed for the thermal lens detection of nanogram amounts of particular high-priority biological and medical samples (theophylline,[88, 89] phenols,[382] acetyl choline,[383] *p*-aminophenol[384–386]).

Modifications of the known spectrophotometric procedures taking into account the characteristic features of thermal lens spectrometry is the most rational way of devising analytical thermal lens procedures for the determination of different classes of compounds. In recent years, studies of real substances have become typical of analytical chemistry.

Many studies in the latter field associated with a combination of the thermooptical detection and the known separation and concentration methods are considered below. Here let us mention the following applications of thermal lens spectrometry: the determination of iron(II) in blood plasma using bathophenanthroline at a concentration of $y \times 10^{-7}$ mol litre^{-1};[373] the evaluation of the total concentrations of soluble organic compounds in sea water;[34] the determination of iron(III) and aluminium in natural waters[387, 388] and pesticides in waters, vegetables and food;[389, 390] and the detection of P-, Si-, S- and N-containing compounds in real substances.[54]

Investigations of the characteristic features of the photometric determination of phosphorus and silicon from the formation of heteropoly compounds and application of intracavity thermal lens spectrometry made it possible to detect these elements in various substances (inorganic acids of special purity grade, semiconducting materials, *etc.*) at a level of 50–100 pg ml^{-1}.[2, 24, 86, 87, 298, 353] Procedures were developed for the detection of cobalt, nickel and iron with the use of nitrosonaphthol,[90] dimethylglyoxime[91] and 1,10-phenanthroline.[92] A combination of reliable photometric methods and a universal methodology for devising thermal lens procedures made it possible to achieve the detection limits of 0.2–10 pg ml^{-1} and the quantifiable concentration ranges from 3 to 5 orders of magnitude.

The development of a methodological basis of measurements, a consideration of thermodynamic and kinetic factors, which affect the selectivity and sensitivity of the detection and minimisation of test experiments substantially improve the metrological characteristics of thermal lens procedures for the detection of various compounds.[228, 229, 232, 274, 276, 283, 382, 391–406] These procedures were used for determining molybdenum[27] and copper[401] in sea water, cobalt,[90] nickel[91, 93] and iron[92, 93] in highly pure water, bismuth[28] and cobalt[90, 93] in highly pure metals and nickel in nickel-containing heteropoly compounds, which are used as active compounds in chemical sensor elements for the detection of ammonia in the atmosphere.[407] The use of thermal lens spectrometry allows one to reduce the number of stages of analysis of heteropoly compounds and increase the accuracy of the determination of nickel.

In recent years, new possibilities of thermooptical spectroscopy have attracted considerable attention. Besides, pioneering studies were carried out within the framework of conventional photometric experiments. For example, the advantages and drawbacks of photometric thermooptical measurements compared to classical spectrophotometric measurements were considered by researchers from the University of Lyon (France) (Refs 9, 57, 364, 367, 371, 373, 408–411). In addition to high instrumental sensitivity, thermooptical spectroscopy is characterised by having a substantially smaller dependence on light scattering and the possibility of detecting trace amounts of elements in samples. It should be noted that a photothermal spectrum does not coincide with the corresponding classical absorption spectrum (in particular, in the case of rare-earth metals),[412] which provides the basis for developing more selective and sensitive procedures for the detection of trace amounts of compounds. For example, procedures were designed to detect uranium(VI), neodymium(III) and praseodymium(III) at a level of 10^{-6}–10^{-5} mol litre^{-1} (Refs 24, 30, 413, 414).

Procedures for the determination of trace amounts, which cannot be used within the framework of conventional spectrophotometry (for example, for the determination of metals inolved in aqua complexes), deserve attention.[29, 43, 77, 86, 87, 353, 357] Studies devoted to thermal lens techniques for the detection of individual rare-earth metals and their mixtures[30, 31, 62, 70, 80] are of most interest. In this case, virtually no additional sample preparation is required, because absorption bands of aqua complexes of rare-earth metals are rather narrow, due to which they can be selectively determined in soils,[30] waters[80, 81] and uranium fuel[70] at a level of $y \times 10^{-7}$–$y \times 10^{-6}$ mol ml^{-1}. Dual-beam thermal lens spectrometry made it possible to determine the composition of a mixture of neodymium and erbium involved in aqua complexes at a level of $y \times 10^{-4}$ mol ml^{-1} against the background of a 50-fold excess of nickel glycinate.[62]

Accumulation of thermal energy in the sample under study was demonstrated to play an important role in the thermal lens detection of trace amounts of compounds, which adversely affect the accuracy of the determination.[32] Hence, it is necessary to optimise the set-up of a thermal lens spectrometer compared to the set-up of model measurements to provide the best sensitivity and reproducibility of thermooptical measurements of real samples.[32]

In recent years, successful attempts were made to extend the range of samples investigated by thermooptical spectroscopy. Procedures for the photometric determination of pyrogenic endotoxins from the main functional regions of their molecules (polysaccharides, lipids, the core region) were applied to the thermal lens detection of a total concentration of endotoxins in Pyrogenal and in an endotoxin sample from *E.coli* 0113 : H10, which is used for standardisation of biological assays. The detection limit of lipopolysaccharides is 70 ng ml^{-1}, which is comparable to the sensitivity of biological assays.[415–417] Let us also mention a method for the simultaneous evaluation of the concentration of hydroxy groups, the temperature and flow rate in the flame from the data of one experiment using thermooptical deflection spectroscopy,[418] where other methods do not work.[418]

a. Selectivity change

It is known that an increase in instrumental sensitivity imposes heavier demands upon the sample preparation. This problem, which is associated primarily with non-selective absorption, is typical of all highly sensitive methods. Hence, it is of first importance that the reagents and solvents be pure and the signal of the test experiment be low. However, a change in the reaction conditions in going to nanogram amounts of the reagents can lead to a substantial increase in selectivity of the thermal lens detection compared to the spectrophotometric method.

Let us consider several examples. It is known that the results of the spectrophotometric determination of bismuth by the iodide method are most affected by lead, tin, copper and antimony,[419–422] because poorly soluble iodides and sulfates of these elements are formed under the reaction conditions. The thermal lens detection of bismuth proved to be much more selective. Under new conditions, precipitates of poorly soluble compounds

are not formed and the selectivity is determined by absorption of metal iodide complexes.[423–425] The adverse effect of copper(II) on the determination of bismuth by the thermal lens method is much weaker than that in the case of spectrophotometric measurements and is manifested at concentrations four times as high as those in the case of monovalent copper ions. This effect can be due to the fact that the formation of copper(II) sulfate complexes cannot be ignored in dilute solutions containing sulfuric acid at a concentration of 0.02 mol litre^{-1}. These complexes inhibit reduction of copper(II) with iodide but do not hinder the detection of bismuth. Therefore, copper(II) is masked, which is manifested only in the determination of trace amounts of bismuth by the thermal lens technique.[403] The hindering effect of nickel, which is observed in the case of determination of iron with the use of 1,10-phenanthroline, also vanishes in going from micro- to nanogram concentrations of the reagents. This could be attributable to the fact that the nickel(II) complex is inert and is not formed in a sufficient amount during the sample preparation (20–25 min) at a level of $y \times 10^{-7}$ mol litre^{-1}.[392]

b. Sensitivity change

It is commonly assumed that sensitivity characteristics (detection limits, lowest quantifiable concentrations) depend primarily on the instrumental sensitivity of a thermooptical spectrometer (the laser radiation power and geometry of the optical scheme) as well as on the thermooptical characteristics of the medium [see Eqn (9)].[2, 4, 58, 276–279] However, a change in chemical interactions with decreasing concentration can enhance the sensitivity of the thermooptical determination of compounds in trace amounts.

For example, the lowest concentration of bismuth detectable by spectrophotometric and thermal lens techniques is 600 and 0.5 ng ml^{-1}, *i.e.*, the sensitivity increases by a factor of 1200.[18, 403] The thermal-lens enhancement factor E_0 is 160. The relatively low sensitivity of the spectrophotometric determination could be attributable to the fact that in the vicinity of the determination limit, an excess of potassium iodide is oxidised with atmospheric oxygen to form free iodine, which impairs the measurement reproducibility. In thermal lens measurements (because there is a large excess of ascorbic acid and a smaller amount of iodide), this fact can be ignored.[403]

The sensitivity of thermal lens measurements is additionally increased due to an increase in the degree of completeness of the analytical reaction at nanogram level. The real sensitivity coefficient of the thermal lens determination of phenols with the use of the azo-coupling reaction with *p*-nitrophenyl diazonium[382] increases by a factor of $\sim$100 compared to the spectrophotometric determination, and calculations according to Eqn (9) give an increase by a factor of 35–40. This is associated with the fact that the azo-coupling reaction is not completed under the conditions of spectrophotometric measurements (0.5 mg ml^{-1} of *p*-nitrophenyl diazonium, 0.1–1 μg ml^{-1} of the phenol); the yield of the product is $\sim$50%. Under the conditions of thermal lens measurements (0.01 mg ml^{-1} of *p*-nitrophenyl diazonium, 1–10 ng ml^{-1} of the phenol), the reaction is completed by 95%–99%, because the sensitivity of the determination is additionally increased by a factor of two.[382]

3. Determination of the fundamental characteristics of reactions at trace levels of components

A decrease in the concentration level of the reacting components is accompanied by a substantial change in the reaction conditions and different analytical effects.[27, 28, 32–36, 69, 71, 88–93, 184, 379, 400] This fact can be used for determining the reaction parameters, such as stability constants, acid dissociation constants, *etc*. It should be noted that measurements are carried in substantially more dilute solutions compared to those used in conventional spectrophotometry, which provides better measurement reproducibility.

Data on the thermodynamics and kinetics of the complex formation of nano- and picogram amounts of transition metal complexes with 1,10-phenanthroline, dioximes and diethyl dithiocarbaminates were collected based on the results of thermal lens experiments.[403–407, 426] The methods were developed for calculations of the overall and stepwise stability constants, characteristic rate constants, molar absorptivities (including those of intermediate complexes), acid dissociation constants and other characteristics obtained from thermal lens experiments.[18, 392, 403–407, 426] These studies showed that stability constants determined by thermal lens spectrometry have a higher accuracy, their values being one–two orders of magnitude lower than the stability constants determined by conventional spectrophotometry and potentiometry. When evaluating the stability constants by thermal lens spectrometry, one must take into account the changes in the kinetic characteristics of the reaction under study when changing from micro- to nanogram concentrations of the reacting components.[405, 406]

Thermal lens spectrometry provides a possibility of determining stepwise complexation constants (at concentration levels of components of $y \times 10^{-6}$–$y \times 10^{-8}$ mol litre^{-1}) in systems, where conventional methods do not work.[401, 402] In particular, the characteristic features of the complex formation in the bismuth(III)–iodide system can be judged at nanogram level from the stepwise stability constants evaluated by thermal lens spectrometry. In the case of copper(I) bis(1,10-phenanthrolinate), the stepwise stability constants can be determined by thermal lens spectrometry in more dilute solutions (large relative excesses of a competitive ligand, *viz*., acetonitrile, without changes in the composition of the medium).[401]

4. Kinetic applications

One of the modern trends in the development of thermooptical spectroscopy is the combination of thermooptical, kinetic and catalytic methods of analysis.[43, 44, 376, 427–447] The main advantage of this combination is the formation of a selective chemical analytical signal and its highly sensitive thermooptical detection. Also, the kinetic measurements have better reproducibility compared to stationary thermooptical measurements, because the accuracy of the determination is substantially improved.[44, 432] Another advantage of thermooptical spectroscopy is that it can be used for both the analytical determination and calculation of the kinetic constants.

Studies of the kinetics of interaction of metal ions with natural ligands (fulvic acids, humic acids, zeolites) and various photometric reagents in the presence of these natural ligands are among the most interesting applications.[387, 388] In these studies, procedures were designed for the determination of submicrogram amounts of copper, nickel, iron and aluminium in natural waters. These studies examined also the fundamental parameters of chemical interactions of the components in complex systems at trace levels. In particular, thermal lens spectrometry was used for measuring the characteristic rate constants with an accuracy of $\pm$0.001; the total absorbance change in the system was $>$0.003. The influence of light scattering on the thermooptical determination of metals and organic compounds was demonstrated [388] to be substantially smaller than that in classical photometric experiments. Studies of the reaction mechanisms of iron(II) tetrakis(4-sulfonatophenyl)porphyrin with carbon monoxide by photothermal deflection spectroscopy and the development of a procedure for the determination of carbon monoxide in biological samples[448] are interesting applications of thermooptical spectroscopy. The characteristic rate constants and activation enthalpies of the reaction were evaluated.

It should be emphasised that thermooptical spectroscopy can be used for studying both processes with very low quantum yields of fluorescence and processes characterised by substantial fluorescence of the products or reaction components. In the latter case, the results of thermooptical experiments supplement data

from luminescence spectroscopy, which allows one to characterise the reaction mechanism in much more detail and develop procedures for the simultaneous determination of several compounds in one experiment.[399] Undoubtedly, the main application of thermooptical spectroscopy is its use for enhancing the sensitivity of kinetic methods. The determination of nitrite ions and nitrate reductase by single-laser thermal lens spectrometry (argon laser, 514.5 nm, 800 mW) in an aqueous medium with a detection limit of 9 pg ml^{-1} (9×10^{-10} mass%) deserves attention.[43, 449] Compared to spectrophotometry, the detection limit was reduced by a factor of 20. The conditions of the thermal lens determination of *p*-aminophenol in paracetamol samples provide a detection limit of 100 ng ml^{-1}, which is an order of magnitude better than that obtained in most spectrophotometric and chromatographic procedures. Dual-beam kinetic measurements of a thermal lens signal (the excitation argon ion laser, 514.5 and 457.9 nm, 30 mW; the probe helium neon laser) were used for analysing binary gaseous mixtures.[61] The selectivity is provided by measuring the ratio of signals obtained at different wavelengths. The study,[442] in which the concentrations of heavy metals were determined in ancient animal remains, is yet another illustration of the possibilities of thermooptical spectroscopy.

The iron(II) complex with 1,10-phenanthroline (ferroin) is widely employed as a catalyst in the Belousov–Zhabotinsky oscillatory reaction.[450, 451] Bromide selective electrodes are most often used for monitoring the course of the oscillatory process.[452, 453] The bromate Belousov–Zhabotinsky oscillator, which was created on the basis of malonic acid as an organic substrate and iron(II) 1,10-phenanthrolinate as a catalyst and an indicator of the reaction pathway, was investigated.[391] The dependence of the physicochemical parameters of the reaction (the oscillation period, the lifetime of the system) on the starting concentrations of the reagents and the effect of additives of inhibiting ions on the system were examined. Under new conditions, the oscillation amplitude was demonstrated to increase compared to the oscillation amplitude under the conditions of spectrophotometric studies due to an increase in the fraction of ferroin involved in the reaction (the overall concentration of iron decreases), and the reproducibility of the oscillation period is improved.[391] The kinetics of the Belousov–Zhabotinsky reaction can be reliably monitored by thermooptical spectroscopy at iron concentrations of $y \times 10^{-6}$ mol litre^{-1} (which is impossible in studies using of most other procedures [454]), and the oscillation period can serve as an analytical signal.[391]

In recent years, a number of studies concerned with analytical applications of thermooptical spectroscopy have investigated of the enzyme kinetics. For example, a thermooptical biosensor for pesticides was designed on the basis of acetylcholine esterase.[389, 390] As a result, the time of analysis of organophosphate pesticides (paraoxon, chlorpyrifos, diazinon) and carbamate pesticides (carbaryl, carbofuran) was decreased to 15 min. The detection limits of pesticides were $y \times 10^{-7}$–$y \times 10^{-5}$ g litre^{-1}. The thermal lens method for the determination of pesticides was demonstrated to be rather inexpensive and does not require thorough sample preparation even for such complex substances as agricultural cultures.[390] In the study,[273] thermal lens spectrometry was used in combination with the enzymatic kinetic determination of dopamine with polyphenyl oxidase.

On the whole, the above examples demonstrate that a combination of thermooptical spectroscopy with kinetic methods of analysis holds promise. Particular new methods can be characterised as kinetic methods coupled with the thermooptical detection. In these methods, a detector plays a passive role. In applications which are not limited to the thermooptical detection of absorption, combinations of kinetic and thermooptical methods show unusual possibilities due to the use of thermooptical effects rather than their consequences (absorbance measurements). For example, new signals allow one to solve problems, which are otherwise impossible to solve.

In the diagram showing formation of analytical signals presented in Fig. 12, the following three groups of sources of analytical information can be distinguished: (1) photometric [the formation of coloured products, a usual slope (α) of the initial region of the kinetic curve]; (2) thermooptical (changes in the thermooptical characteristics of the medium, convective oscillations, auto-acceleration of coagulation of colloidal products); (3) sources directly dependent on laser radiation (temperature effects, photoinduced effects, *etc*.). For example, we can go from simple photometric thermooptical measurements, which are described by the equation,

$$\vartheta(c) \propto A\,(c), \tag{18}$$

to

$$\vartheta(c) \propto E_0(c)A(c), \tag{19}$$

where the factor $E_0(c)$ [see Eqn (9)] reflects the dependence of the thermooptical properties of the sample on the concentrations of the reaction products. Hence, $\mathrm{d}E_0(c)/\mathrm{d}t$ is a new analytical signal.

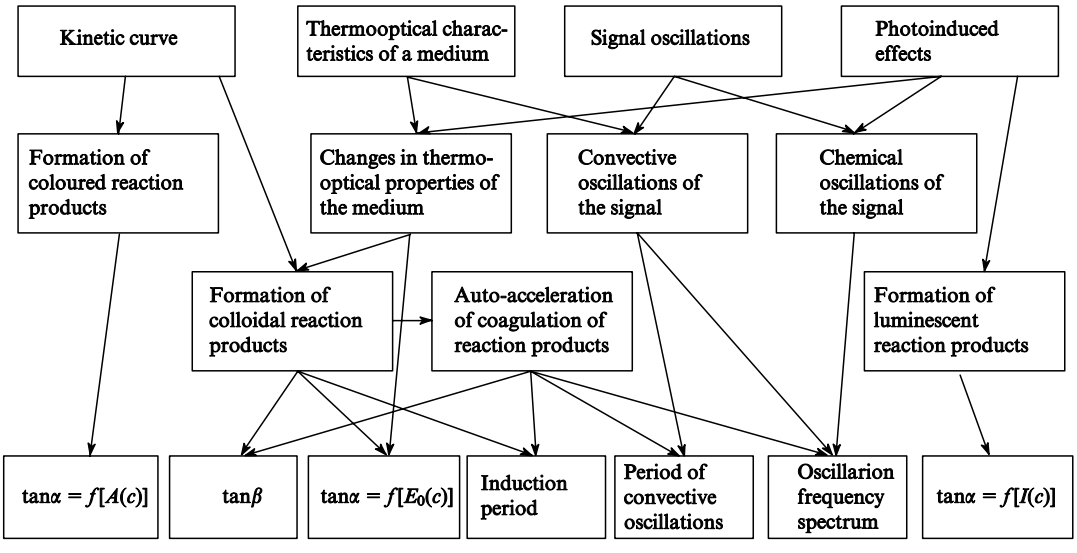


Figure 12. Scheme of formation of analytical signals in the kinetic thermal lens detection.
A is absorbance, α, β are slopes of kinetic curves.

In some cases, the thermooptical sensitivity $E_0(c)$ plays the major role. In particular, the spectrophotometric detection is inapplicable to the simultaneous determination of resorcinol and pyrocatechol by oxidation of bromate ions, because the molar absorptivity of the reaction products of resorcinol is no higher than 500 litre mol^{-1} cm^{-1}. Under the same conditions, the thermal-lens kinetic curves are characterised by good reproducibility and the detection limit of resorcinol in the absence of pyrocatechol is 5×10^{-5} mol $litre^{-1}$. Calculations showed that the factor $E_0(c)$ makes the major contribution to an increase in sensitivity of thermal lens measurements: the rate ratio $E_0(c)/dt : dA(c)/dt$ is 25 : 1. Therefore, the enhancement of sensitivity of thermal lens spectrometry due to changes in the thermooptical properties of the medium makes it possible to determine compounds, which cannot be detected by spectrophotometric methods.[283, 398, 399] In the case of the purely thermooptical detection, the kinetic equation takes the form

$$\vartheta(c) \propto E_0(c)A, \qquad (20)$$

where A = const. In other words, the equation is true if the reaction products do not absorb at the wavelength of the exciting radiation, and only thermooptical characteristics of a sample vary in the course of the reaction. In this case, the sensitivity of thermal lens measurements is provided by the addition of inert absorbing compounds. The range of compounds determined by kinetic methods can be substantially extended.

It was demonstrated that certain effects (changes in the thermooptical characteristics, auto-acceleration of coagulation of colloidal solutions of the reaction products in the region of thermal lens formation, a change in the period of convective oscillations of the thermal lens signal, *etc.*) can be used for determining the reaction components at trace levels. Components of mixtures can be determined by thermal lens spectrometry simultaneously (unlike spectrophotometric methods) due to the appearance of new analytical signals. In spite of an obvious complication of the system, the sensitivity of thermal lens measurements increases with no sacrifice in reproducibility.[384, 398]

Kinetic thermal lens measurements are used for measuring spectra of intermediate states. The changes in the enthalpies of the ketone and enol forms of 7-hydroxyquinone were evaluated by thermal lens spectrometry. The enol form was demonstrated to prevail in the ground state, whereas the ketone form prevails in the excited singlet state.[455] The quantum yield of the formation and the lifetime of the triplet state of pyridine in the liquid phase were measured [456] under two-photon excitation. In both cited studies, information was extracted from the analysis of the fast and slow components of the thermal lens signal after laser pulse absorption. The absolute quantum yield and the lifetime of singlet molecular oxygen sensitised by haematoporphyrin in ethanol were also estimated from the analysis of these components.[457]

Specific effects, which are directly associated with the nature of the thermal lens effect and, primarily, with the changes in the thermooptical and colloidal properties of the medium, are manifested in thermal lens measurements performed in systems involving an oxidiser (bromate or periodate ions), an organic reducing agent (aromatic amines or phenols), a catalyst (vanadium ions) and an activator (phenols, hydroxy acids).[458]

To conclude of this section, let us consider the kinetic effects observed only in thermal lens studies of known analytical reactions. Investigations of the stability of transition metal complexes with 1,10-phenanthroline by thermal lens spectrometry showed that the rate of formation of the iron(II) complex with 1,10-phenanthroline at pH 0–2 decreased substantially,[392] which was not observed in spectrophotometric studies.[459] Even more substantial differences in the results were found in studies of stability of iron(II) tris(1,10-phenanthrolinate) by thermal lens spectrometry and spectrophotometry. In spectrophotometric studies, the pH range for the formation of the complex coincides with the pH range of its decomposition, whereas at iron concentrations of $y \times 10^{-7}$ mol $litre^{-1}$ the complex decomposes at pH 1 only after one day, which differs from dissociation of ferroin at a concentration of $y \times 10^{-5}$ mol $litre^{-1}$.[460–462] A change in kinetic stability of the iron(II) complex with 1,10-phenanthroline at low pH can have an analytical application. Since the iron(III) complex is formed in an even more alkaline medium,[463] iron(II) can be determined in the presence of iron(III).

5. Use of thermooptical methods in flow analysis, high-performance liquid chromatography and capillary electrophoresis

Thermooptical spectroscopy holds considerable promise and is finding rapidly increasing analytical use for detection in HPLC, capillary electrophoresis, continuous flow and flow-injection analysis. The main advantage of this approach is the possibility of combining selective separation of the analyte components and their highly sensitive non-destructive detection in one instrument.

A large number of studies were devoted to the coupling of thermal lens spectrometry with HPLC (Refs 4, 6, 23, 36–43, 49, 106–111, 178, 377–379, 393, 408, 409, 464–480), capillary electrophoresis (Refs 45, 46, 112–116, 310, 311, 380, 381, 481–504) and various modes of flow-injection analysis.[73, 117, 389, 394, 395, 444, 505–510] Several reviews have dealt with these problems.[8, 10, 23, 84, 115, 220, 468, 471]

a. Flow analysis

Flow-injection analysis is an important area of application of thermal lens spectrometry.[73, 117, 394, 444, 505, 507–509] No universal detectors were designed for this analysis, and the choice of the detection method depends primarily on the purpose of a particular investigation. In flow-injection systems, the flow rates are generally 1–5 ml min^{-1}. In these experiments, peristaltic pumps are used instead of plunger pumps, which are employed in HPLC. Hence, noise, which is caused by flow pulsations and masks the thermooptical effect, is the most serious problem associated with the use of photothermal detectors. Nevertheless, due to the highly sensitive detection of absorption in automated analysis of solutions, thermooptical spectroscopy can be considered as one of the most promising detection methods in flow-injection analysis.

Models of changes in the thermal lens signal under flow conditions were proposed.[56, 58, 73, 78, 297] The thermal lens method was devised for the flow determination of Cu(II), Co(II), Fe(III), Bi(III), Nd(III), Pr(III), Al(III), Cr(III), Mn(II), Zn(II) and Pb(II) by the reaction with Xylenol Orange at pH 4.5 in aqueous solutions.[394] The influence of the reactor length and its temperature on the sensitivity and reproducibility of measurements was examined. The detection limits are $y \times 10^{-7}$ mol $litre^{-1}$, the quantifiable concentration ranges are $\sim$1.5 orders of magnitude.[394, 395] The absorbance can be measured in flow up to 1×10^{-6} using a dual-beam scheme (argon laser, 458 nm, 100 mW).[58, 59] The detection limit achieved in the colorimetric determination of iron(II) as a complex with 1,10-phenanthroline was 40 pg of iron in 100 μl of a sample at a flow rate of 0.5 ml min^{-1}. Organic dyes were detected at levels of $y \times 10^{-7}$ mol $litre^{-1}$ by flow-injection analysis coupled with photothermal refraction spectrometry.

b. High-performance liquid chromatography

A large number of combined analytical procedures employ thermooptical methods and HPLC. Universal spectrophotometric methods are widely used for detection in HPLC. In this case, the sensitivity is determined by the optical path length in a detector cell. The sensitivity of such detectors decreases substantially in going to capillary and microcolumn chromatographic systems. If a capillary is several micrometers in length, a conventional photometric detector actually does not work.

On the whole, thermooptical spectroscopy works well in HPLC. The main advantages of this method, *viz.*, high sensitivity and a small detectable volume, have been exploited in the majority of liquid chromatographic methods. As a rule, photothermal detectors decrease the detection limits by two–three orders of

magnitude compared to analogous methods employing the spectrophotometric detection.[11, 16, 58, 297]

A dual-beam optical scheme of thermal lens measurements with a coaxial arrangement of the excitation and probe beams in a detector cell is successfully employed in high-performance liquid chromatography. This method was used for determining various organic and inorganic compounds.[11, 389, 468, 469, 475, 505, 506, 511, 512] The sensitivity achieved in ion chromatography is more than three orders of magnitude higher than that of the photometric detection.[312, 313]

An attempt was made not only to create a model of a thermooptical detector for HPLC but also to devise algorithms of data collection and processing which are specific for the conditions of thermooptical detection in chromatography.[312, 313, 393, 397, 513] The optical set-up of a thermal lens spectrometer was optimised taking into account expert estimates,[274] according to which a substantial gain in spectrometer sensitivity is achieved for all optical schemes.

Most studies performed by thermal lens spectrometry coupled with HPLC were devoted to analysis of organic compounds. A combination of HPLC with the thermal lens detection was used to detect amino acids,[108, 474] nitro derivatives of aromatic compounds,[378, 514, 515] catecholamines[478, 479] and carotenoids (Refs 408, 475, 511). Thermal lens spectrometry, photothermal refraction spectrometry and other thermooptical methods are employed for constructing detectors for chromatographic analysis of organic compounds. The thermooptical detection in capillaries gives better results compared to those obtained with the use of standard cells due to the absence of liquid turbulence in the detection region. Dabsyl derivatives of amino acids were detected by reverse-phase HPLC coupled with photothermal refraction at a level of 10^{-15} mol litre^{-1}. In addition, thermooptical detectors are employed in analysis of dye compositions and for the quality control of products of industrial organic synthesis.

The detection of inorganic compounds has been studied less. After separation, cobalt(II), copper(II), manganese(II), nickel(II), iron(III), zinc(II) and lead(II) cations were determined by ion chromatography according to the post-column reaction with 4-(2-pyridylazo)resorcinol.[516] The influence of noise from a flow reactor on fluctuations of the thermal lens signal was examined.[517] A method was proposed for the determination of trace amounts of elements by HPLC coupled with the thermal lens detection. Procedures were developed for the detection of neodymium and uranium at nanogram levels.[518] Double-beam thermal lens spectrometry was used for detecting chromium(III) and chromium(VI).[42] In this case, pre-column derivatisation of chromium(III) with pyridine-2,6-dicarboxylic acid and of chromium(VI) with diphenylcarbazide was used. The detection limits of chromium(III) and chromium(VI) were 30 and 0.3 ng ml^{-1}, respectively.[42, 512, 519]

Various modifications of the thermal lens technique were used in combination with capillary liquid chromatography.[149–153, 184, 409, 473, 476, 477] In this mode of HPLC, crossed-beam thermooptical systems (photothermal refraction and mirage spectroscopy) are generally used for the detection. A prerequisite to the use of such systems in capillary liquid chromatography is the possibility of measuring the thermooptical characteristics of samples of very small volumes (as small as $y \times 10^{-9}$ litre). This method was used for detecting amino acids as dabsyl derivatives at femtomole levels (10^{-15} mol).[108] Other thermooptical spectroscopy methods were also employed in capillary liquid chromatography. For example, nitropyrene and dinitropyrenes were determined with the use of a pulsed photothermal refractometer as a detection system.[379]

In spite of the large number of studies devoted to applications of thermooptical spectroscopy in HPLC, there are no universal combined methods. Studies dealing with the complex and comprehensive examination of the possibility of combining HPLC with thermooptical detection methods are scarce. Nevertheless, taking into account the characteristic features of both methods,[112–117, 377, 464–467, 469, 472, 475, 480] their combination would be expected to provide a basis for devising a new analytical method.

Thermooptical methods are also used for the highly sensitive detection required in thin-layer chromatography.[33, 500, 520] A photothermal detector for this chromatographic method was constructed on the basis of the mirage effect induced by pulsed laser radiation.[33]

c. Capillary electrophoresis

Nowadays, thermooptical spectroscopy is being extensively employed as a detection method in capillary electrophoresis.[108, 115, 116, 297, 301, 310, 380, 381, 473, 481–491, 493, 496–500] This combined method has a wide application in the detection of amino acids.[108, 116, 301, 380, 381, 482–488] The determination of amino acids as their dabsyl derivatives at a level of 10^{-12} mol litre^{-1} was described.[380] Unlike HPLC and flow analysis, not all detection methods are suitable for this separation method. Thermooptical methods (thermal lens spectrometry, photothermal refraction spectroscopy and the thermal prism method) are among the best detection methods in capillary electrophoresis. After the reaction with 4′-(dimethylamino)azobenzene-4-sulfonyl chloride, amino acids were determined at a level of several attomoles by probe capillary electrophoresis coupled with the thermooptical detection.[381, 501] Twelve amino acids were determined using the thermooptical detection during 13.5 min.[496] The detection limits were $\sim 10^{-7}$ mol litre^{-1} (or 100 fg in an injected volume of 0.6 nl). The authors of the cited study emphasised that the linearity range was substantially larger than that achieved in the spectrophotometric detection and covers more than four orders of magnitude. In the study,[521] traces of amino acids (tryptophane and phenylalanine) were detected without derivatisation at a level of tens of femtomoles by the photothermally induced capillary vibration method at the second harmonic wavelength of an argon ion laser (257.2 nm, 5 mW). In this study, the results of determination of vitamin B_2 were also reported; the detection limit at the excitation wavelength (476 nm) was 80 attomoles (the absorbance was 1.8×10^{-7}), which is three orders of magnitude larger than the detection limits reached with the use of alternative methods for absorption measurements.[521]

Methods of thermooptical spectroscopy are employed also for the detection of other organic and biologically active compounds, such as components of food additives,[466] proteins,[486] nucleotides,[485] metabolism products[492] and pesticides.[243] It should also be noted that thermooptical spectroscopy was used to determine the sequences of amino acids in DNA, peptides, *etc*.[522] In recent years, a number of studies were devoted to the determination of drugs, primarily, of antidepressants.[310, 523]

Methods of thermooptical spectroscopy are widely used also in inorganic analysis, for example, for the simultaneous detection of cations and anions (involved in coloured compounds) at levels of 10^{-12}–10^{-10} mol litre^{-1}.[493] In analysis of real samples, thermal lens spectrometry in the near-field region was employed for the determination of iron and nickel using 1,10-phenanthroline[311] and bathophenanthroline,[524] respectively. For iron, the detection limit was 4×10^{-8} mol litre^{-1}.[310]

As demonstrated above, the main processes attendant on the formation of thermooptical elements (heat transfer and the formation of the temperature profile of the refractive index) are directly related to the thermooptical characteristics of the medium (thermal conductivity, heat capacity, the temperature gradient of the refractive index). Changes in the latter provide the possibility to control the signal. For example, the sensitivity of thermal lens detection in capillary electrophoresis using an aqueous-acetonitrile mixture or an aqueous-methanolic mixture increases by an order or half-order of magnitude, respectively, compared to that achieved in the case of aqueous buffer solutions. The experimental data agree well with the results of calculations. Under the above-considered conditions, the detection limits of a number of organic compounds (phenol and aniline derivatives) are 10^{-8}–10^{-7} mol litre^{-1}.[310]

6. Microanalytical systems

A recent trend is to miniaturise instruments and equipment for chemical analysis and integrate all stages of analysis (sampling, sample preparation, separation, concentration processes, analytical reactions and measurements of an analytical signal) in one small (supercompact) device. Presently, such devices (called 'microanalytical systems' (micro-Total Analysis System, μTAS) or 'laboratories on a chip') are used for solving various problems of analytical chemistry, biochemistry, synthetic chemistry and biotechnology.[220,525] Chemical microchips are generally constructed with the use of state-of-the-art microtechnologies, and they often have a planar geometry. Glasses, quartz, various plastics, silicon and (more rarely) metals serve as materials for microchips. As a rule, a microchip scheme includes reservoirs for reagents, reaction circuits or microvessels, microcolumns or capillaries and communications with linear sizes of $y \times 10^{-9}$–$y \times 10^{-4}$ m.[232,443–445] In addition, micropumps, voltage sources and electrodes can be integrated into a microchip.[525] In some cases, a detector is also integrated into a microchip, although a microchip contains only a detection zone (generally optical) and an interface equipped with an external detector.[525]

A consequence of miniaturisation of analytical detection systems and their integration in a single device is a decrease in the volumes of samples (to $y \times 10^{-10}$ litre), reagents, solvents and wastes (to $y \times 10^{-6}$–$y \times 10^{-7}$ litre) and reduction of the analysis time compared to conventional analytical instruments. In addition, the principal distinguishing features of chemical microchips are that they differ (compared to macrosystems) in the conditions of heat and mass transfer and separation in microchannels, which provides the possibility to construct unique analytical devices and devise new procedures.

Due to a tendency to combine advantages of microchips (integration, compactness, the possibility of using the modern achievements of flow-injection analysis, capillary electrophoresis, HPLC, *etc*.) and detection by thermooptical spectroscopy (sensitivity, locality, high response rate), many studies devoted to microchips were performed with the use of thermooptical spectroscopy (Fig. 13), and the detection limits were declared to be several molecules or tens of molecules.[219,224,325,376,377]

The main fields of application of integrated microanalysis systems are as follows: (1) analytical chemistry (immunoassay methods, capillary electrophoresis, flow-injection analysis, extraction processes, enzymatic catalysis); (2) synthetic chemistry (transfer reactions at the liquid–liquid interface, influence of thermal, electrical and magnetic fields on reactions in microchannels, polymerisation); (3) studies in the field of cell biochemistry. Photothermal deflection spectroscopy, thermal lens microscopy and wavelength-tunable thermal lens microscopy are employed as the main instrumental approaches. The major achievements are associated with the detection of individual molecules, studies of the nanospace and spectroscopy of the liquid–liquid interface. Let us illustrate the above with typical example.

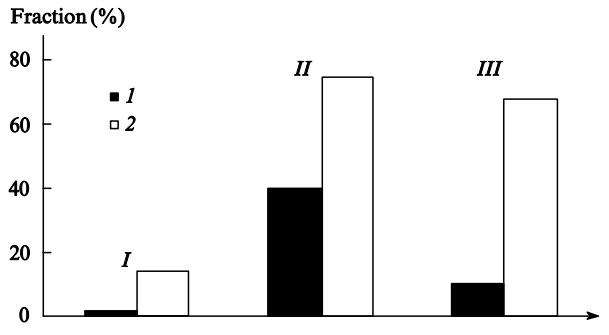


Figure 13. Distribution of studies in the field of thermooptical spectroscopy using macro- (*1*) and microsystems (*2*).
I — applied spectroscopy, *II* — analytical chemistry, *III* — commercial studies.

Methods of thermal lens microscopy were used in microflow-injection analysis of L-ascorbic and dehydroascorbic acids by reduction of iron(III) in the presence of 1,10-phenanthroline[228] and analysis of epinephrine and other catecholamines by their oxidation with sodium periodate.[526] The detection limit of ascorbic acid was 1×10^{-7} mol litre^{-1} (the absolute quantifiable amount of the compound was 3×10^{-20} mol), which is at least one-and-a-half orders of magnitude lower than the determination limit of this acid by capillary electrophoresis coupled with the electrochemical detection[527] and surpasses the known pharmacological method in sensitivity.[528] The procedure was used to determine ascorbic acid in urine and pharmaceutical samples.[228] The sensitivity of detection of catecholamines was as high as $y \times 10^{-6}$ g litre^{-1}, which allows one to use microflow analysis coupled with the thermooptical detection in clinical analysis. The method was employed for the determination of epinephrine, norepinephrine, dopamine and L-dopa in injection samples.[526]

An integrated microanalysis system equipped with a thermal lens detector and an additional IR laser was used for the rapid monitoring of enzyme reactions in flow.[444] Photothermal heating of a liquid flow in a small volume (5 nl) made it possible to heat and cool analyte solutions at rates of 50–60 K s^{-1}, which are an order of magnitude higher than that achieved in conventional heaters and 3–6 times higher than the heating rate of electrothermal microheaters. In enzyme reactions of hydrogen peroxide with 4-aminoantipyrine and *N*-ethyl-(*N*-oxy-3-sulfopropyl)-*m*-toluidine in the presence of horseradish peroxidase, the concentration of substrates can be determined by the thermooptical techniques with a time resolution of 0.6 s at a level of $y \times 10^{-4}$ mol litre^{-1}. In this case, the formation of reaction products depends completely on heating the flow with an IR laser beam and can be determined with high reliability.[444] The minimum reaction volume and the minimum quantifiable amount of the reaction products are 10 nl and 100 fmol, respectively.[445]

A microsystem equipped with a scanning thermal lens microscope deserves attention.[529] This microsystem was employed to study processes in a cell *in vivo*. It should be noted that nonfluorescent reagents can be used, and the detection does not require markers. The spatial resolution of the instrument is 1 μm, and the minimum absolute quantifiable amount of a compound (cytochromes in mitochondria) is 10^{-22} mol.[529]

A microimmunoassay analysis system coupled with the thermooptical detection was used for determining the oncofetal antigen, which serves as a marker of pancreatic cancer.[222] A specially designed microchip, was partially filled with polystyrene granules containing immobilised antibodies to this antigen. A sample of blood plasma with the marker under investigation and a solution containing free antibodies and antibodies immobilised on colloidal gold particles were passed through a microchannel. An interaction gave rise to complexes of the antigen with three antibodies immobilised on the surface of granules, whose concentration was measured on a thermal lens microscope. The determination limit of the oncofetal antigen was an order of magnitude lower than the limit achieved in an immunoassay (ELISA).[530] The results obtained in clinical tests were in good agreement with the results of the determination of the antigen by conventional methods. Analogously, an immunoassay combined with the thermooptical detection on chemical microchips was used for determining human immunoglobulin in blood[446] and gamma interferon.[481] In these experiments, the analysis time was halved due to the use of microanalytical systems. The time of determination of the oncofetal antigen was reduced from 24 to 1 h. In all cases, the detection is characterised by very simple procedures, which are presently under clinical tests.

The possibilities of thermal lens spectrometry coupled with microanalytical fluid devices are also well exemplified by studies of molecular transport in a three-phase water–cyclohexane–water flow system (in a microchannel, the thickness of the organic

phase sandwiched between two aqueous systems, was 64 μm).[510] Under these conditions, the distribution parameters of Methyl Red were determined.[510] Such experiments can be carried out only with the use of integrated microanalysis systems (under these conditions, an organic phase exhibits membrane properties). As in the above-described case, non-fluorescent compounds can be used, which substantially extends the scope of this method. In particular, a theoretical model of molecular transport through a liquid organic membrane under microflow conditions was proposed in the study.[531] This model can find use in biochemical investigations.

A number of recent studies have been aimed at designing microanalytical systems, which combined, for example, flow-injection analysis and immunoassays,[222, 481] capillary electrophoresis and the detection on a microchip by thermal lens microscopy [315] and the detection with the use of interferometer-based microsystems.[532]

Full spectrum lamps were used in the study [315] for inducing a regular thermooptical effect. In this case, a thermooptical element is formed not due to a spatial distribution of the intensity in the incident beam but due to formation of the heat outflow profile as a result of a specially chosen shape of a microchannel in a microchip. In this case, the thermooptical detection is the only possible way of forming an analytical signal, and a thermal lens detector is completely integrated in a microanalysis system.

A combination of thermooptical spectroscopy and integrated microanalysis systems is employed not only in analytical and bioanalytical investigations but also for the synthesis of compounds in a microflow with the thermooptical detection of the products in a real-time mode.[218, 219, 223, 316, 317, 533, 534] These methods are based primarily on two-phase systems under flow conditions giving rise to coloured reaction products at the interface and the thermooptical detection of the compounds in the organic phase. These methods are characterised by high selectivity of reactions at the interface and high sensitivity of thermooptical detection in organic media. In particular, this combination of methods was proposed for use in studies of azo-coupling reactions [218] and alkylation.[317]

Of analytical applications within the framework of this approach, a selective method for the detection of potassium and sodium ions is worthy of notice.[223] This method is based on the formation of a two-phase system in a microchannel. The organic phase in this system contains the ions under study, whereas the organic phase is composed of several solutions of ionophores added successively. The solutions contain also a lipophylic non-selective acid – base indicator. The ionophores selectively interact with the ions (in the case under consideration, valinomycin reacts with potassium ions, and dibenzo-16-crown-5 derivatives react with sodium ions). Interactions of ionophores with the ions lead to extraction of the latter into the organic phase, resulting in a change in the colour of the indicator, and the ions are detected using a thermal lens microscope.[219] In addition to high sensitivity of detection, this approach is fast, which is an obvious advantage over an optrode detector.[535] The thermooptical detection in microchannels is characterised by a short diffusion time and rapid response of the thermooptical detector (the overall time of analysis is 8 s).[219] In the case of an optrode, the system response is rather slow because of slow diffusion of the ions in the optrode membrane. In addition, a micromode of measurements allows one to use substantially smaller amounts of expensive reagents. In particular, the detection of subnanogram amounts of potassium and sodium necessitates 0.5 μl an organic solution of the reagent. For one test, 2 ng of ionophores and 3 ng of an indicator are required. On the whole, the thermooptical detection leads to an increase in the sensitivity of determination of sodium and potassium by an order of magnitude compared to that achieved with the use of an optrode detector.[535]

7. Specific fields of application of thermooptical methods

a. Role of the solvent. Non-photometric thermooptical spectroscopy

The highest sensitivity, *i.e.*, the maximum factor E_0 [see Eqn (9)], can be achieved by choosing a medium characterised by a high temperature refractive index and low thermal conductivity. In this respect, aqueous solutions are inferior to non-polar solvents (benzene, carbon tetrachloride, saturated hydrocarbons) as a medium for thermal lens measurements. For example, low concentrations of 9-nitroanthracene were determined in various solvents, and the detection sensitivity in n-pentane was demonstrated to be twice as high as that in methanol and 40 times higher than that in water.[536]

However, water has a number of advantages, because it is available, can be easily purified and serves as a convenient reaction medium. It should also be taken into account that fluctuations of the thermal lens signal in aqueous solutions are much weaker than those in organic solvents.[93] As a result, the determination limits in aqueous solutions are lower than those in organic solvents.[93, 271]

Aqueous-organic mixtures can be considered as solvents of choice for thermooptical measurements. On the one hand, convenient conditions for both the sample preparation and the photometric reaction in an aqueous medium are provided. On the other hand, high values of the E_0 factor ($3-5$ mW^{-1}) typical of organic liquids are achieved.[396, 537] As an example, Fig. 14 shows the ranges of detectable concentrations of the same compound in aqueous, organic and aqueous-organic media.[271]

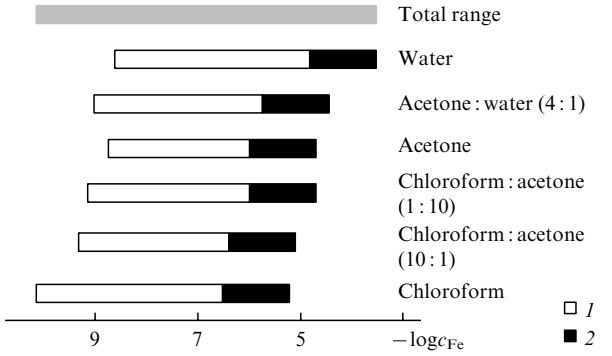


Figure 14. Ranges of quantifiable concentrations of iron(II) tris(1,10-phenanthrolinate) by thermal lens spectrometry in various solvents; the power of laser radiation inducing a thermal lens is 400 (*1*) and 40 mW (*2*).[271]

Due to the fact that the sensitivity of thermooptical measurements depends on the characteristics of the medium, thermooptical spectroscopy can be used for determining characteristics of the medium, such as the thermal conductivity, viscosity, density and the temperature dependence of the refractive index.[285–288] The results of determination of these characteristics for benzene, toluene, carbon disulfide, acetone, methanol and white Burgundy wine from the time evolution of the thermal lens signal correspond to the reference data.[286] Dual-beam thermal lens spectrometry was used to measure the thermal conductivity coefficients of krypton, carbon dioxide, methane, ethane, propane and butane.[288]

It was demonstrated that trace amounts of colourless organic compounds in water can be determined with the use of the thermal lens signal as a function of thermooptical characteristics of a medium (the thermal conductivity, viscosity, density, the temperature dependence of the refractive index, *etc.*) rather than as an analogue of the absorbance. For example, the determination limits of ethanol and DMSO thus determined are 0.05 and 0.04 mass %, respectively.[513]

b. Photochemical thermooptical spectroscopy

The high power and intensity of laser radiation in thermooptical spectroscopy are responsible for initiation of photochemical processes involving reaction products and reagents (Refs 281–284, 411, 430, 440, 538–545). These effects were observed often.[440, 538–540, 542, 543] However, they have attracted considerable attention only in recent years. One of the pioneering series of studies was devoted to photoreduction of complex heteropoly acids of phosphorus and silicon in ethanolic solutions giving rise to bright coloured reduced forms of heteropoly acids (the determination limits $y \times 10^{-9} - y \times 10^{-8}$ g ml^{-1}, see Refs 298 and 546).

Thermal lens spectrometry can be used to study the kinetics of photodecomposition and the formation of radicals in various solvents. For example, the photochemical reaction involving the 2-naphthylmethyl radical was discovered,[430] and the behaviour of benzophenone in acetonitrile and propan-2-ol was investigated.[545]

Photochemical thermooptical spectroscopy is used to determine the thermodynamic characteristics (the enthalpy, entropy and free energy) of chemical processes and to control the parameters of chemical reactions by varying the intensity of excitation laser radiation.[455, 538, 541, 547] Procedures in which the thermooptical detection is coupled with a method for concentrating an analyte component photoinduced by the laser beam,[548] photocatalysis and photocoagulation [398, 399, 549] are similar to the above-described thermooptical measurements.

c. Thermooptical cytometry

Two studies [550, 551] have laid the groundwork for thermooptical cytometry. The method is based on measurements of the response of living cells to short-time heating induced by a laser pulse. Elements of the theory of thermooptical microscopy in a pulsed mode of operation of an excitation laser were developed. The method was used for non-destructive control of living cells,[552–554] control of selective photothermolysis, investigations of DNA and studies of defects and impurities in ultrapure optics and semiconductors. This method can be performed in modes of thermal lens spectrometry, photothermal deflection spectroscopy and photothermal radiometry.

8. Colloidal systems

a. Coarsely dispersed colloidal systems †

Coarsely dispersed systems, *viz*., coarse slurries, suspensions and emulsions, are most often used in thermooptical measurements.[4, 18, 37, 38] Several studies [54, 295, 529, 555, 556] were concerned with measurements of thermooptical deflection of the probe laser beam from the reflecting surface formed by large suspension particles. In the case of spontaneous formation of coarsely dispersed systems, the efficient power of the excitation beam decreases proportionally to the number of reflecting particles and, consequently, the detection sensitivity decreases, which limits the use of these systems in analytical practice.[398, 399]

b. Finely dispersed colloidal systems

Finely dispersed systems with particle sizes $y \times 10^{-7} - y \times 10^{-9}$ m also affect the sensitivity of thermooptical detection. In this respect, surfactants are of considerable interest (Refs 4, 18, 47, 397, 410, 536, 537, 557). A micellar mechanism of modifications of thermooptical properties of a medium involves an increase in the temperature gradient of the refractive index and a decrease in the thermal conductivity coefficient due to disruption of the rigid water structure.[558]

In the study,[557] the concentrations of the hydrophilic salt TbCl were determined using surfactants, which form micelles with the analyte in non-polar solvents. The thermal lens signal corresponding to the absorbance of 1×10^{-7} was recorded. The simultaneous determination by fluorescence spectroscopy and the thermal lens techniques demonstrated that the determination limits of tetracycline in the presence of Triton X-100 are three times lower than those in the absence of the surfactant.[410] The micellar effect in aqueous solutions was examined in the study of 9-nitroanthracene.[536] Being highly soluble both in polar and non-polar solvents at concentrations lower than $y \times 10^{-7}$ mol litre^{-1}, this compound was chosen for testing the validity of the assumption that the change in the thermal lens signal depends only on the thermooptical characteristics of the medium. The mechanism of interaction of this signal with surfactants of different nature was elucidated and it was noted that the thermal lens signal strength is proportional to the degree of hydrophobicity of the environment of the molecule.[536] This fact was confirmed by the data obtained in the study of 9-nitroanthracene derivatives. The presence of long hydrocarbon chains is favourable for higher solubilisation, which leads to a substantial increase in the signal strength.[536]

It was demonstrated [47] that microemulsions can be studied by thermal lens spectrometry. Microemulsions of differently charged particles were studied above and below their percolation threshold. Microemulsions of negatively charged particles are subjected to percolation at rather high concentrations of surfactants (30%), and the thermal lens signal is independent of the water content. Apparently, microemulsions consist of small reverse micelles, and this structure exists both above and below the percolation threshold. In contrast, percolation of microemulsions of positively charged particles occurs at relatively lower concentrations of surfactants (10%), and the thermal lens signal depends on the concentration of water in the system.[47] Consequently, the structure of these microemulsions changes upon percolation, and these microemulsions above the percolation threshold consist of large bound aggregates or two-dimensional structures.[47]

It was proved [557] that an increase in the thermal lens signal upon the addition of surfactants occurs primarily due to an increase in dn/dT of the solution. The influence of surfactants and various dissolved compounds on the water structure can be characterised by the following two parameters: the temperature at which $dn/dT = 0$, and the temperature dependence d^2n/dT^2. These parameters decrease upon the addition of substances disrupting the water structure (for example, of urea), whereas the addition of, for example, *tert*-butyl alcohol leads to an increase in these parameters.[47, 557] The molecular structure of the surfactant plays an important role in the observed effect. A reduction of water structurisation is more pronounced when a surfactant exists in the micellar rather than monomeric form.[557] The disruption of the water structure in the presence of surfactants, such as polyoxyethylene lauric ester (**1**), hexadecyltrimethylammonium bromide (**2**), 3-(*N*-dodecyl-*N*,*N*-dimethylammonium)propane-1-sulfonic acid (**3**) or sodium dodecylsulfate (**4**), was examined. At concentrations of a surfactant lower than the critical micelle concentration, this effect decreases in the series **1** > **2** > **3** > **4**. For micellar solutions, **1** > **2** = **3** = **4**.

The characteristic features of thermooptical non-linearity in cast films of polymer-encapsulated nematic liquid crystals were studied experimentally. The dynamics of changes in the light transmission of the film on heating of liquid crystal drops by a laser radiation pulse was examined.[559]

IV. Study of interfaces in condensed systems

Photothermal methods have wide application in studies of interfaces in condensed heterogeneous systems.[176] They are virtually the only methods suitable for non-contact studies of the thermal and optical properties of condensed phases. The use of photothermal methods in studies of interfaces is dictated primarily by the necessity of solving a number of important problems [158, 173, 560–563] associated with experiment planning. The characteristic features of photothermal methods were efficiently

† This section deals with colloidal systems, in which liquids serve as a dispersion medium. In the case of colloidal systems, thermooptical spectroscopy examines changes in the macroproperties of solutions caused by changes in the number and size of colloidal particles.[4]

used in specific investigations concerned with the dynamics of absorption processes [119, 183, 564–577] and the extraction equilibrium in microspace.[219, 223, 531] Non-transparent solid samples with smooth and rough surfaces [158, 172, 173, 212, 563, 578–586] and transparent substances, including transparent films (Refs 174, 562, 587–594), were also studied by these methods. Modern apparatus allows one to perform two- and even three-dimensional surface imaging.[174, 579, 583, 593]

1. Physical models

Simulation of experiments with consideration for all characteristic features of the system under examination and apparatus employed gives the best results. The main results in this field are concerned with the solid–gas (air) interfaces. The influence of the form of the energy profile in a pulse on the thermal response was examined by the mirage effect method,[158] and the theoretical data were compared with the experimental results with and without considering this form. Investigation of a gold (1.5 μm)/tetrahedral amorphous carbon (80 nm) coating on a silicon substrate demonstrated that the thermal properties of carbon are virtually independent of the pulse form, whereas the correct characterisation of the thermal properties of gold requires that the pulse form of the incident laser radiation be taken into account. This approach simplifies the mathematical apparatus for the description of multilayer structures of semiconducting products.[560, 561]

A model for simulation of the photothermal beam deflection (for a perpendicular crossed-beam configuration of an instrument) in samples, including weakly absorbing thin films on substrates with high light absorption, was considered in the study.[562] The model was employed to determine the thermal conductivity of thin films on substrates. The influence of the intersection angle of the excitation and probe beams at the sample, the modulation frequency of the excitation beam, the thickness and absorption of the thin film and the thermal properties of the substrate on the thermal conductivity of thin films was discussed. This method proved to be suitable for thermal conductivity measurements of thin films with high thermal conductivity, for example, of diamond and diamond-like carbon films deposited on substrates with relatively low thermal conductivity at low modulation frequencies.

The crossed-beam configuration of the optical scheme of photothermal deflection was investigated.[173] Equations describing the probe beam deflection were deduced. In particular, the role of the incident angle of the probe beam [see Eqn (16)] was demonstrated to be analogous to the role of the height at which this beam passes above the surface in photothermal deflection measurements employing the parallel configuration of the probe beam [see Eqn (15)]. An analogy between these two configurations was found by comparing the dependences of the signals on the incident angle and the height at which the probe beam passes. To confirm the results of theoretical calculations, photothermal deflection measurements on invar samples were performed (since this compound has a small thermal expansion coefficient, a thermally induced surface displacement in a limited range of the incident angles can be ignored).

A new model of the laser-induced thermal lens on the surface of semiconducting materials was devised.[563] The model is based on the Fresnel diffraction theory and other photothermal effects, such as photothermal deflection, the thermal lens effect and photoreflection. According to this model, the photothermal reflection makes the major contribution to the detectable signal and the diffraction pattern, but the air-thermal lens effect at low modulation frequencies and the photothermal reflection at high frequencies are also significant. It was demonstrated that the sensitivity can be enhanced by choosing an optimum position of the sample, which depends on the modulation frequency.

2. Adsorption

The surface of a gold film electrode (a polycrystalline gold film of thickness 1 μm on a polymer substrate) was studied [564] by the transient reflecting grating method. The thermal response to both the formation of a double layer and oxidation at anode potentials above +1 V and the acoustic response only to the formation of an oxide film were detected using a cyclic potential scan in 0.05–0.1 M solutions of acids (HCl, HClO). The thickness of the oxide film varied from one to several monolayers. Thermal grating spectroscopy proved to be more sensitive than other photothermal and photoacoustic methods. However, attempts to describe the observed phenomena in terms of a simple model based on enhancement of oxygen adsorption at anode potentials failed.

A highly sensitive method for the detection of antigens on the blood cell surface by thermal lens microscopy was considered in the study.[565] Colloidal gold coated with antibodies was used for staining leukocyte membrane antigens. Human leukocyte antigens on lymphocytes and mononuclear leukocytes were observed by thermal lens microscopy. Antigens of particular chromosomes on lymphocytes were detected and determined for a single cell. Antigen mapping studies were carried out on mononuclear leukocytes. Thermal lens microscopy allows one to perform non-degrading biochemical studies directly on living cell membranes.

Studies of sorption of various classes of model compounds on a series of sorbents showed that thermal lens spectrometry is suitable for investigations of adsorption of nanogram amounts of these compounds by measuring their residual concentrations in solution. The sorption kinetics were studied, adsorption isotherms were constructed and characterised, and the maximum adsorption and the conditional adsorption coefficient were determined.[566]

It was demonstrated that thermal lens spectrometry can be used to study adsorption on low-capacity sorbents (chemical glass and quartz). Thermal lens spectrometry was applied for the direct determination of the concentration of iron(II) tris(1,10-phenanthrolinate) on the quartz surface upon adsorption from aqueous solutions. It is possible to determine quantitatively the concentrations to about pmol litre^{-1} [$\sim$0.01 monolayer for adsorption of iron(II) tris(1,10-phenanthrolinate) on quartz glass] and the absolute amounts of about tens of attomoles.[566, 570] The limiting sensitivity of thermal lens determination is $\sim$100 times higher than that of diffuse reflection measurements under the same conditions. The adsorption characteristics of iron(II) tris(1,10-phenanthrolinate) and nickel(II) dimethylglyoximate from aqueous and aqueous-ethanolic solutions on laboratory glass were evaluated at nanogram levels of the sorbate in solution, and the surface concentrations of irreversible and reversible sorption centres were estimated.[407, 570] The process is most adequately described by the Freundlich equation for monomolecular adsorption.[568]

It was shown that thermal lens spectrometry is suitable for investigating of the continuity and surface concentrations of molecular layers grafted onto the quartz glass surface [567, 569, 595, 596] and for the direct detection of the dye Reactivrot B5A on the glass substrate.[567] The method allows one to perform quantitative determinations up to a monolayer of the grafted dye. Rapid ($\sim$5 min) laser-induced photodestruction of the grafted dye was observed for the first time.[567]

Investigation of adsorption of the dye acridine orange at the quartz glass–water interface by total internal reflection thermal lens spectrometry demonstrated [119] that the thermal lens effect is induced only by the penetrating wave. The adsorption depth profile can be obtained. The determination limit of the dye Sudan II in acetone is 3.0×10^{-5} absorbance units (the 2s criterion, the concentration of the dye was 3.8×10^{-5} mol litre^{-1}), which is hundreds of times lower than that achieved by the attenuated total reflection method. Under these experimental conditions, adsorption of the dye acridine orange on silanol groups of glass was observed. The adsorption isotherm is consistent with the Langmuir model.

Adsorption of diphilic surfactants at the water–hexane interface was studied [571] by surface thermal lens spectrometry. A thin thermal lens was observed for the diphilic molecules of 10-(1-pyrene)decanoic and 4-(1-pyrene)butanoic acids present at the

hexane – phosphate buffer solution interface. This method gives a linear response to the number of molecules; the detection limit is ~ 0.01 monolayer.

A procedure was proposed [572] for studying liquid – liquid interfaces. This method is called total internal reflection optical beam deflection (OBD). A comparison with total internal reflection thermal lens spectrometry [571] demonstrated that the background noise in the OBD method is substantially lower. The fact is that the probe beam in thermal lens measurements should be precisely focused onto the centre of the excitation region at the interface. In this case, even small variations in the conditions affect the background signal. In OBD measurements, the probe beam passes at a particular distance from the interface in an isotropic medium, due to which it is less dependent on the accuracy of tuning and external conditions. The maximum sensitivity is reached when the probe beam passes in dodecane in the vicinity of the interface (due to the higher sensitivity enhancement factor for dodecane compared to that for water). The method was used to examine the complex formation of iron(II) with 4,7-diphenyl-1,10-phenanthroline upon the contact of an aqueous solution of iron with a dodecane solution of the ligand. The detection limit (the 3*s* criterion), which is 750 molecules per 1 μm^2 or 2.8×10^{-6} absorbance units, is ~ 3 orders of magnitude lower than the detection limit provided by total internal reflection thermal lens spectrometry.

Adsorption of asphaltenes on glass substrates was studied by photothermal deflection and displacement spectroscopy.[573, 574] Adsorption isotherms for asphaltenes were measured at room temperature in toluene on a glass substrate.[573, 574] Multilayer adsorption was detected in three experiments, where the time of the contact was longer than 3 days. The isotherms measured during short periods of time show a linear dependence of adsorption on the concentration.[573] In the case of an appropriate ratio of the radii of the excitation and probe beams at the sample surface, an analytical signal can be measured by a single photodiode.[574]

A series of studies by Japanese researchers were concerned with the dynamics of diffusion and isomerisation of coloured compounds. They examined *N*-(4-methoxybenzylidene)-4-*p*-butylaniline (MBBA) in ethanol [575, 576] and other organic solvents,[576] in experiments with total internal reflection of the probe beam and the vertical direction of the excitation beam and studied spiropyran at the water – air [577] and solid – liquid [576] interfaces by the transient reflecting grating method. Surfaces of pure and polystyrene-coated sapphire [575, 576] and porous glass [576] were investigated. In the presence of a molecular layer of spiropyran, diffusion of molecules and their aggregates was demonstrated to occur at the water – air interface (fast and slow components of a biexponential decrease in the signals).[577] Studies with MBBA showed that the surface strongly catalyses isomerisation. This fact was confirmed by measurements in porous glass.[575, 576]

The possibilities of photothermal deflection spectroscopy and photothermal radiometry were examined as applied to characterisation of plates, which are used in thin-layer chromatography to determine the surface and depth distributions of various compounds on a sorbent.[183] Photothermal radiometry proved to be of little use for characterisation of thin-layer chromatograms. The observed low reproducibility of measurements is presumably associated with poor reproducibility of the separation conditions and inhomogeneity of different chromatographic plates.

3. Semiconductors

Semiconducting materials are most often studied by photothermal deflection methods (mirage effect) [578 – 580] and photothermal radiometry.[212, 581, 582] The photothermal reflection technique [583] and surface thermal lens spectrometry are also used for these purposes.[563]

The nature of surface defects in insulator films and defects between a-Si : H and insulator layers were examined [578] by ESR and photothermal deflection spectroscopy. The surface defect densities for a-Si : H, a-$SiN_{1.7}$: H and a-SiO were estimated from the dependence of the ESR signal intensity on the thickness. The surface state density in a-$SiN_{1.7}$: H/a-Si:H and a-SiO_2/a-Si : H was evaluated by analysis of the layered structure of thin layers. For an a-Si : H film, the results obtained by ESR agree well with the results of photothermal deflection spectroscopy. However, defects in a-$SiN_{1.7}$: H and a-SiO_2 films were not observed by the photothermal deflection technique in spite of the fact that their concentrations were virtually equal to that in a-Si : H films. The reason is that the spectral range of excitation of a photothermal spectrometer does not coincide with the absorption range of defects in a-$SiN_{1.7}$: H and a-SiO films. Defects in these structures were demonstrated to appear in the course of the plasma surface reaction and are located on the a-Si:H side of the interface. A combination of these methods holds promise. Thus, the energy distribution of defects can be studied by photothermal deflection spectroscopy, and their chemical environment can be revealed by ESR. Therefore, these methods supplement each other.

Non-contact imaging of the buried structures in air was performed by the photothermal deflection technique.[579] The method was employed to analyse layered CdTe (50 nm)/glass (0.15 mm)/carbon black (10 μm) samples. Photothermal amplitude and phase images of optically nontransparent buried structures were obtained. The phase images were more smooth and regular. The thermal diffusivity and the absorptivity of the material were calculated from the amplitude and phase parameters of the photothermal image. The thermal diffusivity of buried structures can be determined (non-destructively) from the data on photothermal deflections at two modulation frequencies.

The thermal conductivity, adhesion and mechanical stress in diamond films, which were synthesised on a ceramic aluminium nitride substrate, were studied.[580] The thermal conductivity of this composite was examined by photothermal deflection spectroscopy. It was found that this parameter is 73% larger than the thermal conductivity of pure aluminium nitride. Scanning electron microscopy and Raman spectroscopy revealed the influence of a diamond film on the thermal conductivity of samples. Unusual stability and very high adhesion of a diamond film to an aluminium nitride substrate are associated with the formation of an aluminium carbide underlayer in the synthesis of a diamond film. It was noted that diamond-coated aluminium nitride substrates are promising materials for heat removal from semiconducting electronic devices.

Photothermal radiometry was demostrated to be suitable for non-contact temperature measurements of semiconductors.[212] This method can be used to measure the temperature of high-alloy silicon samples, but it is necessary to find experimental conditions to minimise the effect of formation of electron – hole pairs (for example, to use a low modulation frequency of the excitation laser). The latter effect can be eliminated by using a laser, whose wavelength is smaller than the energy gap width of the semiconductor. For semiconductors characterised by a very short lifetime of electron – hole pairs, this effect is insignificant and has virtually no influence on the measurements.

In the study,[581] the non-contact diagnostics of the SiO_2/Si interface was carried out by photothermal radiometry. Two silicon plates containing aluminium and silicon gate metal-oxide-semiconductor structures were analysed by this method. Diffusion of charge carriers, their lifetime and the surface recombination rate were examined. The activation energies measured by two photothermal methods have close values, which are 0.15 – 0.17 and 0.21 eV lower than the lower limit of the conduction band for plates with aluminium and silicon gate devices, respectively.

Three-dimensional photothermal radiometric microscopy was employed in non-contact non-destructive studies of electron transfer in integrated schemes of lithographed silicon plates.[582] The surface resolution was 20 μm. It was demonstrated that scribeline photothermal probing can be efficiently used for non-contact monitoring of local changes in the lifetime of charge

carriers, which provides a way of determining contaminations and plate damage during the manufacture of integrated devices.

The structure of a metal-oxide-semiconductor insulated-gate field-effect transistor (MOSFET) was studied by reflection microscopy.[583] In the optical range for probing of the gate surface, the resolution was ~ 1 μm, and the constituent electro- and thermal reflections were found in the signal. Depending on the configuration of the gate valve, six different types of images with different sharpness can be obtained. In the cited study, it was also demonstrated that this method is suitable for the detection of subsurface effects.

4. Non-transparent films

Electron transitions in C_{60} under the influence of oxygen were investigated.[584] Absorption of atmospheric oxygen was demonstrated to impair dark conductivity and photoconductivity of C_{60} films. Light absorption was measured at 300 and 77 K by the photothermal deflection method. A new method, *viz*., photothermal bending, was described in the literature.[584] Absorption of excitation laser radiation which is incident perpendicular to the film surface leads to expansion of the external absorbing layer of the sample fixed at one end, resulting in bending of the sample, which is accompanied by a change in the reflection angle of the probe laser beam. This method can be used *in vacuo* (this is of considerable importance in studies of materials sensitive to an environmental medium). The method is also sensitive to temperature changes; however, it is applicable only to thin samples.

Two schemes of photothermal deflections were used to study a non-transparent film deposited on Corning 7059 glass substrates.[585] At low modulation frequencies, both schemes give similar results and it is preferable to detect the phase shift, because it is less affected by the thermal thickness of the sample.

The photothermal deflection method was employed for the non-destructive non-contact study of artificial and natural copper patina.[172] This approach is used in non-destructive analysis of ancient copper production.

Photothermal radiometry was used to characterise nickel-pigmented aluminium oxide solar cells.[586] After heating of a sample with a modulated laser beam, thermal radiation emission was measured as a dependence on the modulation frequency in a range from 10 Hz to 10 kHz. The experimental results were described by a simple one-dimensional model, which made it possible to estimate the thermal parameters of light-absorbing coatings. The radiation ability measured by conventional methods was compared with that determined by photothermal radiometry.

5. Weakly absorbing films

The optical and thermal properties of defect polycrystalline boron-doped diamond films were investigated.[587, 588] The absorptivities of thin (< 10 μm) diamond films cannot be determined by conventional methods because of a small film thickness and large scattering due to surface roughness. Both problems can be overcome by determining the absorptivity from the results of measurements of heat adsorbed by the surface using photothermal deflection spectroscopy. The method was used to study defects and impurities in polycrystalline diamond. Absorption, which is caused by local structures that appear upon implantation of polycrystalline diamond films, and reduction after annealing were observed for the first time.

An application of surface thermal lens spectrometry to investigations of weakly absorbing films was proposed in the study.[579] The results were compared with the data from photothermal deflection spectroscopy. Laser-induced deformation is considered as a bent mirror, which either focuses or defocuses the probe beam depending on the geometry used. Surface thermal lens spectrometry does not require the precise tuning of the probe beam and has the same high sensitivity as photothermal deflection spectroscopy. The exact size and shape of the region deformed upon excitation can be observed with a CCD camera. This fact is of considerable importance in studies of thermal expansion and absorbance. The reproducibility of measurements increases by a factor of ~ 5. The spatial resolution depends only on the size of the excitation beam, which can be focused to a submicrometre size by near-field photothermal microscopy. The above advantages were exemplified by studies of adsorption and characterisation of defects of weakly absorbing films of titanium(IV), tantalum(V), zirconium(IV) and silicon(IV) oxides on the surface of BK7 glass. The accuracy of the detection of absorbance is retained down to 2.6×10^{-6}.

Photothermal displacement spectroscopy was used to examine defects and attendant damages of coatings of optical elements under high-power pulsed laser irradiation, for example, in photolithographic devices.[590] Multilayer Al_2O_3/SiO_2 coatings on quartz glass, which reflect strongly at 248 nm, were investigated.

Photothermal deflection spectroscopy was used to study transparent amorphous diamond-like graphite films deposited on the quartz surface.[591] These films are resistant to damages and are transparent in the visible region.

A series of studies [174, 592, 593] were concerned with the properties of polymer materials for waveguides. The photothermal deflection spectra of non-oxidised polyalkylthiophenes containing alkyl side chains of different lengths were measured in the near-field IR region.[592] This field is used in non-linear optical waveguides. Fluorination of polyalkylthiophenes does not lead to a noticeable improvement of the waveguide properties (for example, in a range of 1700–1800 nm). Besides, purification from iron trichloride is required; otherwise, such materials are unsuitable for the construction of non-linear optical devices. The best wavelength range for waveguide materials is about 1300 nm.

Photothermal beam deflection imaging of the refractive index structure was described in the publications.[174, 593] Poly(methyl methacrylate) (PMMA) and polythiophene containing the dissolved dye Disperse Red 1 were studied. A mixture of PMMA with the dye was analysed by the laser photodecomposition technique.[593] The refractive index distribution in the polymer was determined. The method, in essence, is to examine the absorption spectrum changes caused by decomposition and subsequent image contrast reversal due to the corresponding change in the excitation beam wavelength. Images of integrated waveguide devices constructed from PMMA and polythiophene were obtained by photodecomposition and photothermal deflection on a photolithographic instrument. Structures of dimensions > 50 μm were resolved. Attempts to image structures of dimensions < 30 μm by the photothermal deflection technique failed. Photothermal displacement spectroscopy would be expected to overcome this limitation.

Scanning photothermal deflection was compared with scanning photothermal displacement.[174] A 20% solution of the dye Disperse Red 1 in PMMA was examined. Two methods show similar depth resolution. Data on photothermal deflection are rather easy to interpret due to a simple relation between the signal and excitation source power. Due to enhancement of the signal by an auxiliary liquid, images with an acceptable signal/noise ratio can be obtained even at low excitation power. However, immersion of a sample into an auxiliary liquid may be a drawback if the latter cannot be removed after the experiment. Besides, signal accumulation time is large due to a rather low chopping frequency.

To interpret the results of photothermal displacement spectroscopy, numerous factors should be taken into account. The convexity theory is complex and is additionally complicated in the case of focused-beam excitation. For thin samples, a convexity is formed primarily in the substrate. Hence, it is necessary to know the distribution of the thermal and optical properties of the substrate. The advantages are a high rate of signal accumulation (due to a high chopping frequency) and the possibility of performing analysis in air. Hence, it was concluded that the photothermal deflection method is more convenient for studying polymer films (due to higher reproducibility of the results) compared to the photothermal displacement technique.[174]

Amorphous graphite films, which were prepared on polystyrene under its irradiation with He^+ and H^+ ions, were analysed in the study.[594] These films are used in particular types of protective coatings. The photothermal deflection method was employed to record an absorption spectrum in a wavelength range from 1.2 to 2.0 μm. The mechanical, electrical and optical properties of such films depend on the ratio between the contents of the sp^2- and sp^3-hybridised carbon atoms. The changes occurring in the film can readily be observed from evolution of particular overtones in the absorption spectrum in the above-mentioned range.

V. Conclusion

When considering the development of analytical thermooptical spectroscopy, it is necessary to mention a considerable contribution of the research team headed by Professors V I Grishko and I G Yudelevich (A V Nikolaev Institute of Inorganic Chemistry of the Siberian Branch of the Russian Academy of Sciences, Novosibirsk), who laid the groundwork for analytical investigations in the field of thermal lens spectrometry. Initial studies using thermooptical spectroscopy methods have been concerned with chemical interactions at low concentrations of reacting compounds. The metrological characteristics of the method have been comprehensively evaluated, and its possibilities in the determination of traces of organic and inorganic compounds have been examined.[82, 86, 87, 106, 298, 353, 541, 546] In addition, this research team published the only Russian monograph [2] (and the first monograph in the world), which was completely devoted not only to the physics of the thermooptical phenomena but also to instrumental possibilities of thermal lens spectrometry and (which is of most importance) to its analytical applications. The results of the studies performed by this research group in the field of thermooptical spectroscopy were so voluminous that they are still being published (even ten years after the completion of their research).[359]

Nowadays, thermooptical methods for analysis are being developed and used in leading research centres in Russia and Former Soviet Republics, such as M V Lomonosov Moscow State University,[313, 401, 402, 548, 595–600] St Petersburg State University,[218, 229, 232, 443–445, 510, 531] Institute of Physics of Microstructures of the Russian Academy of Sciences (Nizhnii Novgorod),[239, 240, 248–251, 313] A V Lykov Institute of Heat and Mass Transfer (Minsk, Republic of Belarus),[552–554] N E Bauman Moscow State Technical University,[5, 552, 554] L V Kirensky Institute of Physics of the Siberian Branch of the Russian Academy of Sciences (Krasnoyarsk) [559] and Dnepropetrovsk State University (Ukraine).[601] Considerable experience has been gained in the field of thermooptical spectroscopy. Numerous studies were published, many of which made a considerable contribution to the theory and practice of thermooptical investigations.

The section 'Thermooptical Methods' was included in the Handbook 'Analytical Chemistry' (Ed. Yu A Zolotov, Nauka, Moscow, 1998, 2d edition). This is the only example of the inclusion of information a review format on thermooptical methods in a handbook for university students. Nowadays, the fundamentals of thermooptical spectroscopy are included in training courses of the Departments of Physics [602] and Chemistry (the Chair of Analytical Chemistry, the training course 'Analytical Chemistry',[603] and the Chair of Laser Chemistry, the training course 'Introduction to Laser Chemistry' [604]) of Moscow State University, St Petersburg State University (the training course 'Physical Fundamentals of Optical Methods of Analysis of Substances and Materials') [605] and Krasnoyarsk State University (the Chair of Physical Chemistry, the training courses 'Materials Science and Technology of New Materials' and 'Modern Methods of Analysis').[606]

In conclusion, it should be noted that, in addition to high sensitivity, methods of thermooptical spectroscopy provide much more information than spectrophotometric methods. This makes it possible to increase substantially the range of the problems, which can be solved. Apparently, the main advantages of thermooptical methods (the possibility of the simultaneous detection of several analytical signals and the use of specific effects not as a passive way of detecting but as an active component of new analytical methods) will assist the development of analytical thermooptical spectroscopy.

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