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Review

Matrix effects in thermal lens spectrometry: Influence of salts, surfactants, polymers and solvent mixtures

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Abstract

In this paper, we present an overall view of the matrix effects that can change or alter the signal in thermal lens spectrometry and we report the main works published in this field. The addition of salts, surfactants and polymers in aqueous solutions or the use of solvent mixtures is often needed in a variety of applications either to enhance the sensitivity of the thermal lens method or more generally because such media are required in the separation process prior to thermal lens detection. In most cases, matrix effects result in small changes in the thermo-optical properties of the solution and small signal variations. However, most important signal alterations can arise from the Soret effect. In binary mixtures as well as in solutions with macromolecular species which are initially homogeneous, the temperature gradient will induce the migration of molecules and the formation of a concentration gradient. This results in the formation of a concentration-dependent refractive index gradient which adds to the temperature-dependent refractive index gradient and contributes to the formation of a new signal. This effect can seriously alter the analytical signal and lead to erroneous interpretation of the experimental data. In contrast, time-resolved measurements can help in separating both signal components and have allowed to derive mass-diffusion times and mass-diffusion coefficients for a variety of micelles and polymers.

Keywords: Thermal lens; Matrix effects; Micelles and polymers; Soret effect; Mass-diffusion coefficients

Contents

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1. Introduction

Thermal lens spectrometry is, of all the photothermal methods, the best known and most used for analytical applications [1–8]. The method is based on the optical measurement of the thermal energy released by a sample subsequently to light absorption and nonradiative relaxation of the excited species. The magnitude of the thermal lens effect depends not only on the amount of energy absorbed, i.e. on the excitation power and sample absorbance, but also on the thermo-optical properties of the medium in which the thermal lens is formed. These properties are the temperature-dependent refractive index, d*n*/d*T*, and the thermal conductivity, *k*, or heat capacity, C_p, of the medium. It is therefore important to know and control the properties of the medium because they can affect the thermal lens response when specific solvents or media are used. This can arise when thermal lens spectrometry is used as a detection method in separation techniques such as liquid chromatography or electrophoresis, due to the addition of salts, electrolytes, surfactants and gels, or to the use of solvent mixtures. Matrix effects have been observed in the determination of phosphate in saline solutions [9], of iron in calf serum [10] and of heavy metals using ion chromatography [11,12]. Surfactants have been used in micellar liquid chromatography for the determination of catecholamines [13], of clenbuterol in urine [14] or of etoposide and etoposide phosphate in human plasma [15]. Solvent mixtures have been used for the determination of pesticides using gradient elution chromatography [16] and mixed organic solvent/aqueous buffer systems have been used for capillary zone electrophoresis [17–19]. Polymer gels are widely used as analytical medium, especially in gel electrophoresis [20,21] such as for the determination of hemoglobin and cytochrom c [22]. In addition to d*n*/d*T* inducing the thermal lens effect, the refractive index of the irradiated area can be influenced by others factors than the temperature. Especially, in solutions with more than one constituent, the temperature gradient induces thermal diffusion and migration of molecules in the thermal gradient. This tendency of species to diffuse under the influence of a temperature gradient, known as the Soret effect [23,24], may result in the formation of a concentration gradient leading to local changes in the thermo-optical properties of the solution. This effect has been observed for thermal lens experiments in binary liquid mixtures near a consolute critical point [25–27] or at room temperature in binary mixtures [28,29], in micellar systems [30–32] and in solutions of polymers and gels [33,34] or of ferrofluids [35,36].

The aim of this review was to investigate all the matrix effects that can change or alter the thermal lens signal and lead to erroneous results in analytical applications or when the photothermal method is applied to the determination of the thermo-optical properties of a solution. An overview of the works reported in this field is presented including an application of the thermal lens method to the measurement of mass-diffusion coefficients.

Table 1
Effect of electrolytes on the thermo-optical properties of the solvent and on the relative thermal lens signal; from [30,37]

Solvent	Electrolyte (1 M)	$(dn/dT)/(dn/dT)_s$	$(k/k_s)^{-1}$	*R*
Water		1	1	1
	$LiNO_3$	1.34	1.08	1.45
	NaCl	1.34	1.02	1.37
	NaI	1.30	–	1.35
	$NaNO_3$	1.57	1.02	1.59
	KNO_3	1.48	1.06	1.57
	$RbNO_3$	1.51	1.01	1.53
Ethanol		1	1	1
	NaI	0.87	–	0.91

2. Modification of the thermo-optical properties of the neat solvent

The response of the thermal lens method is evaluated using Eq. (1):

$$S \approx -2.3AP\frac{dn/dT}{k\lambda} \tag{1}$$

where *P* is the laser power, λ the probe laser wavelength and *A*, d*n*/d*T* and *k* are the absorbance, the temperature coefficient of the refractive index and the thermal conductivity of the sample, respectively. It is therefore possible to enhance the signal by altering the thermo-optical properties of water or by selecting a solvent with better thermo-optical properties.

2.1. Influence of salts

The effect of salts on the thermal lens signal has first been reported by Phillips et al. [9] and then investigated in aqueous solutions [30] as well as in ethanol [37] (Table 1). In water, the addition of electrolytes results in an enhancement of the thermal lens signal. The observed enhancement has been interpreted as due to changes in d*n*/d*T* and, to a smaller extent, in the thermal conductivity of the solution. A theoretical investigation of the thermal lens signal with respect to the structure of water has revealed that the origin of these changes was dependent upon the expansion coefficient of water molecules, which dominates the change in d*n*/d*T* [38]. The effect depends on the nature of the electrolyte and the influence of the anion is more important than that of the cation. On the contrary, the addition of sodium or potassium iodide in ethanol produces a reverse effect. As corroborated by the measurements of the refractive index gradient as a function of the temperature, d*n*/d*T* increases by 27% in water and decreases by about 13% in ethanol upon the addition of 1 M sodium iodide [37]. It is important to know these effects when the photothermal method is applied to the analysis of seawater, body fluids or other complex media. Experiments made for the determination of iron in calf serum have shown that the signal obtained in the test solution composed of acids and salts at 1 M and 2 M, respectively, was twice greater than that in pure water [10]. The matrix effect is also important when the method is used in fluorescence quenching experiments [39]. The variation of the photothermal signal observed upon the addition of an electrolyte to quench the fluorescence of a species will account for both an increase in the amount of heat released by the sample and a change in the thermo-optical properties of the medium.