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# Selective determination of Sm (III) in lanthanide mixtures by thermal lens microscopy

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ABSTRACT

Since lanthanides are inner transitional elements with their 4*f* and 5*d* energy levels closed, they possess narrow electronic absorption peaks, which are little affected by their chemical environment. In this research, a thermal lens microscope (TLM) that utilizing diode lasers as pump and probe beams was constructed for selective determination of Sm (III) without any pre-concentration and separation procedure. The calibration plot has a linear behavior over the 0.5–500 μg $mL^{-1}$ range and a limit of detection (LOD) of 0.08 μg $mL^{-1}$. The relative standard deviation (RSD) is smaller than 5%. This method can be potentially applicable to environmental studies.



## Introduction

Thermal lens spectrometry (TLS) is a member of photothermal techniques family applicable to physical and chemical analysis [1–3]. The benefits of TLS include the high sensitivity and small volume requirements, which make it ideal for ultra-trace measurements in chemical analysis [4–9]. Generally, the thermal lens effect (TLE) is generated from non-radiative relaxation of excited species within a sample exposed to a laser beam with a Gaussian intensity profile [10]. The generated heat at the center of beam profile is more than the wings, and hence there is a refractive index gradient. As the beam passes through the solution, depending upon conditions, it gives a variable degree of divergence proportional to the power of the laser beam, and the absorption coefficient of the sample [11]. Thermal lens microscopy is a well-developed method among the other photothermal techniques. The signal-generation mechanism in TLM is based on the TLE, which can be used for sensitive determination of analyte in micro volume of liquid samples. In TLM, exciting beam generates TLE which causes a divergence in the center of a probe beam. Since, achromatic microscopes are unable to detect the TLE, chromatic aberration objective lens is used to solve this problem in TLM [12,13].

Among the transitional elements, separation and determination of lanthanides is crucial due to their close similarity in chemical and physical properties [14–18], since they are inner transitional elements with close 4*f* and 5*d* energy levels [19]. Therefore, the demand for the separation and analysis of highly pure lanthanides is rapidly growing due to their wide applications [20,21].

Currently, few methods exist for reliable determination of individual rare earth elements (REE) at trace and ultra-trace levels. They include Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [22–24], Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [25,26], and Neutron Activation Analysis (NAA).

Lanthanide and actinide ions have narrow absorption bands for transitions to empty *f* orbitals, since the electrons responsible for absorption by these elements are shielded from external influences by electrons that occupy orbitals with larger principal quantum numbers. As a result, their absorption bands tend to be narrow and relatively unaffected by their matrix and ions present.

Herein, we present construction of a thermal lens microscope, which utilizes a 400 nm diode laser, for the determination of Sm in mixtures of lanthanides. This method eliminates pre-treatment and separation steps from the analysis procedure.

## Experimental

### *Apparatus*

A thermal lens microscope was constructed in our laboratory (Fig. 1). In order to obtain the thermal lens signal, semiconductor lasers were used as pump/probe sources. The utilized heating beam was a modulated diode laser (400 nm, 50 mW), and the

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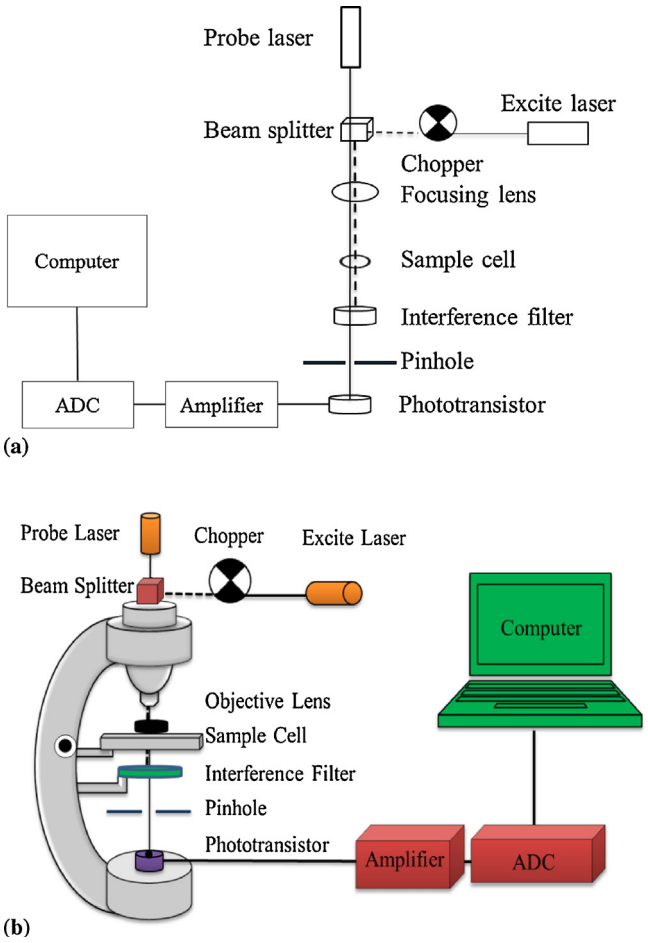


**Fig. 1.** (a) Schematic diagram of TLM, (b) TLM instrument.

probe beam was unmodulated diode laser, which emits at 650 nm (10 mW). Probe and pump beams waist were exactly concentric by a beam splitter, and introduced into an optical microscope. The coaxial beam of the excitation, and the probe beam were focused into the liquid sample in the microcell by an aberration objective lens. The excitation beam formed a thermal lens in the confocal region, and the probe beam was focused just below the center of the thermal lens. Pump beam was filtered by an interference filter, and probe beam was passed from the pinhole. Intensity changes in the probe beam center were detected by a phototransistor, and fed into the amplifier. Generated analog signal was converted to digital data by an analog-digital convertor (ADC).

*Data treatment*

Under CW laser excitation, the intensity measured at the beam center, $I(t)$, will initially ($t = 0$) reflect only the Beer's law response of the sample. After sufficient time when a steady-state temperature difference is reached, the intensity at the detector, $I(\infty)$, will depend on the optical arrangement of the system. In this configuration, using a $TEM_{00}$ laser beam to probe a sample whose length, $L$, is sufficiently small ($L \gg 2\pi w_0^2 n/\lambda$, where $w_0$ is the beam waist radius, $n$ the refractive index, and $\lambda$ is the laser wavelength), the following expressions govern the initial and final intensities [27,28]:

$$TLM_{signal} = \frac{I_0 - I_\infty}{I_\infty} = -\frac{2.303(dn/dT)}{\lambda k} PA \quad (1)$$

$$E = -\frac{dn/dt}{\lambda k} P \quad (2)$$

where $P$ is the power of laser, $dn/dT$ the change in solvent refractive index with temperature, the laser wavelength, $k$ the thermal conductivity, $E$ the enhancement of this effect relative to Beer's law behavior and $A$ is the absorbance of the sample. For each sample, the signal was derived from the averaging of five records of the thermal lens.

*Reagents and solutions*

All solutions were prepared in pure ethanol (Merck) because of thermal lens signal enhancement. Stock standard solution of $SmCl_3{\cdot}6H_2O$ (Fluka) was prepared at a concentration of 2000 μg $mL^{-1}$. Working standard solutions were prepared by appropriate dilution of the stock solution. A 200 μg $mL^{-1}$ solution of $Eu_2O_3$ (Fluka), $CdCl_2{\cdot}2H_2O$ (Merck), $MgSO_4$ (Merck), and $La(NO_3)_3{\cdot}6H_2O$ (Fluka) was prepared as a synthetic sample. The tap, CCERCI, and mineral water (Surprise) as the real samples were analyzed for the method development.

*Analytical procedure*

After preparing standard solutions at the range of 0.5–500 μg $mL^{-1}$, the real water samples were prepared. 300 μL of standard solutions was added to 500 μL of real water samples and then, the mixture of solvents was evaporated at 60 °C in 3–5 min. 300 μL of pure ethanol was added to the residue of precipitate and thermal lens signals were recorded after dissolving the sample content under the ultrasonic irradiation. Following procedure was repeated for synthetic sample and $TLM_{signals}$ for all samples were calculated.

## Results and discussion

*Spectral features and selection of wavelength*

In the thermal lens investigations, laser is the excitation source, since like other lanthanide ions, Sm has a narrow and weak absorption at 400 nm, which matches well with the emission line of the diode laser at 400 nm. Fig. 2 exhibits the absorption spectrum of Sm.

*Chopper frequency and time of steady-state thermal lens optimization*

Steady-state thermal lens effect corresponds to the formation of the temperature-dependent refractive index gradient. For this purpose, various chopper frequencies were examined. It should be noted that at frequencies lower than the 20 Hz, the thermal lens signal is not well formed. As indicated in Fig. 3, chopper frequency has a reverse effect on the intensity of the obtained signals, while upon increasing the frequency, the signal intensity decreases slowly. Therefore, the chopper frequency was fixed on 20 Hz for all investigations. In Fig. 4, a steady-state thermal lens signal is observable.

*Solvent selection*

Based on Eq. (1), enhancement of the thermal lens signal is obtained for a solvent with small thermal conductivity ($k$), and large absolute temperature dependent refractive index ($dn/dT$) [27,28]. The order of magnitude of $E$ predicts that organic solvents produce higher enhancement for TLS relative to Beer's law. We have calculated $E$ parameter for organic solvents and water at 400 nm and 50 mW. The results show that the $E$ parameters for