1
2
3
4
5
6
7 **Selective determination of Sm (III) in Lanthanide Mixtures by**
8
9 **Thermal Lens Microscopy**
10
11
12
13
14

15 Nader Shokoufi ^a, Javad Yoosefian ^{b,*}
16
17
18
19

20 ^a*Analytical Instrumentation & Spectroscopy Laboratory, Faculty of Clean Technologies, Chemistry &*
21

22 *Chemical Engineering Research Center of Iran (CCERCI), Tehran, Iran*
23

24 ^b *Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-175,*
25

26 *Tehran, Iran*
27

28 *Corresponding author: Javad Yoosefian*
29

30 *Tel.: +98 21 82883409; fax: +98 21 82883455.*
31

32 *E-mail address: javad.yoosefian@modares.ac.ir*
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

Abstract

Since lanthanides are inner transitional elements with their $4f$ and $5d$ 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 $0.5\text{-}500\text{ }\mu\text{g mL}^{-1}$ range and a limit of detection (LOD) of $0.08\text{ }\mu\text{g mL}^{-1}$. The relative standard deviation (RSD) is smaller than 5%. This method can be potentially applicable to environmental studies.

Keywords: Sm; Thermal Lens Microscopy; Closed $4f$ and $5d$ energy levels; Lanthanide Species.

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 ultratrace 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 4f and 5d 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 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).

“Here Figure 1”

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 λ 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, λ the laser wavelength, k the thermal conductivity, E the enhancement of this effect relative to Beer 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 $2000 \mu g mL^{-1}$. Working standard solutions were prepared by appropriate dilution of the stock solution. A $200 \mu g mL^{-1}$ 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 $\mu\text{g mL}^{-1}$, 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 $^{\circ}\text{C}$ in 3-5 minutes. 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 $\text{TLM}_{\text{signals}}$ 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.

“Here Figure 2”

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 the 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 the Fig. 4, a steady-state thermal lens signal is observable.

“Here Figure 3 &4”

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 non-polar organic solvent are higher than those of polar organic solvents and water. Therefore, it must be advantageous to use organic solvents to improve the sensitivity of TLS for analysis of elemental and molecular analytes in ultra-trace level (especially for lanthanides which have low absorption coefficient). The effect of organic solvents such as carbon tetrachloride, carbon disulfide, chloroform and ethanol was investigated on the thermal lens signal (Fig. 5).

“Here Figure 5”

As it is shown in Table 1, organic solvents have better thermo-optical properties than the water medium at thermal lens spectrometry. Suitable solvents must dissolve Sm and other ions and they should have good thermo-optical properties. Although, carbon tetrachloride, carbon disulfide and chloroform represent improved E factor but because of their inability to dissolve some of the mentioned ions, ethanol is a profitable solvent.

“Here Table 1”

Figures of merit

The calibration curve was plotted for different concentrations of Sm (Fig. 6).

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

“Here Figure 6”

Under the optimum conditions, the calibration curve was linear from 0.5 to 500 $\mu\text{g mL}^{-1}$ with a correlation coefficient of 0.9976 (R^2). The intercept and slope of the linear calibration curve at the mentioned concentration range were 0.0021 and 0.1024, respectively. The limit of detection was calculated as the ratio of three times of the standard deviation of the blank signals over the slope of the calibration curve. The value of 0.08 $\mu\text{g mL}^{-1}$ was obtained for LOD. To study the method precision, relative standard deviations (RSD) were measured. The relative standard deviations were lower than 5% for five samples subjected to the complete procedure.

Interferences

As shown in Fig. 7a, absorption spectrum of lanthanides, Sm shows an absorbance peak at 400 nm, where the other lanthanides do not. This peak was chosen for measurement of Sm to eliminate separation steps, and simplify the procedure. Excitation diode laser, which has a unique narrow emission band at 400 nm, is suitable for selective excitation of Sm in the presence of the other lanthanides (Fig. 7b). Since lanthanides are not affected by their matrix, the presence of other species has no effect on the Sm absorption spectrum. $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ and MgSO_4 have no absorption in the 400 nm region [29, 30], and samples containing them is not expected to interfere with the Sm measurement at this wavelength, however, for the sample containing Eu_2O_3 , $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$, MgSO_4 , $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$ there was no observable thermal lens signal. The presence of these species showed less than ~5% error compared to their absence in the matrix. Among the ions tested, none of them showed interference at concentration >20 times higher than the Sm concentration.

“Here Figure 7” [31]

Analysis of real sample

To investigate the applicability and reliability of TLM response to Sm concentrations in the presence of the other lanthanide species, and in real water samples, the thermal lens signal of the analyte was studied in various environments. For this purpose, tap water, CCERCI, “Surprise” mineral water, and a synthetic sample containing Eu_2O_3 , $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$, MgSO_4 , $\text{LaN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$ and $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$ were analyzed. The results are shown in Table 2.

“Here Table 2”

Comparison of TLM with other spectroscopic techniques for the analysis of Sm

Recently, several studies were carried out to determine the trace amounts of lanthanide elements in various samples (Table 3).

“Here Table 3”

In ICP-AES, there are several spectral interferences. In addition, separation of REE from the mixture of elements is necessary for a precise analysis [26]. Besides, classical spectrophotometric techniques are only suitable for determination of the total amount of REEs [38, 39] due to their low absorption coefficient. According to Table 3, provided LODs are mostly in the range of $\mu\text{g mL}^{-1}$ which are comparable with our obtained LOD. Moreover, determination of lanthanides in graphite furnace atomic absorption spectrometry (GFAAS) results in low sensitivity and memory effects, one reason can be the formation of REE carbides and a carbon film on the surface of REE oxides [40]. As shown in Table 3, most of these methods require lanthanides standard solutions and complicated separation procedures.

Conclusions

A TLM was constructed and applied to the determination of trace amounts of Sm (III) in the presence of other lanthanide ions. The advantages of this technique over other spectroscopic methods include elimination of chemical pre-treatment and separation steps, wide linear range ($0.5\text{-}500\text{ }\mu\text{g mL}^{-1}$), comparability in LOD with the other conventional methods despite its simplicity, time and cost saver, and applicability to small samples, in addition to being non-destructive. Low absorption coefficient of lanthanides has made their measurements hard by conventional spectrophotometric methods. In addition, due to the fact that lanthanides have narrow absorption peaks, a single wavelength diode laser could be used as the excitation source for selective excitation. The inner behavior of lanthanides when presented in mixture solutions, have made the TLM an outstandingly selective method.

Acknowledgement

Support of this investigation by the Research Council of Chemistry & Chemical Engineering Research Center of Iran is gratefully acknowledged.

References

- [1] N. J. Dovichi, S. E. Bialkowski, *Critical Reviews in Analytical Chemistry*, 17 (1987) 357-423.
- [2] J. Georges, J. M. Mermet, *Analysis* 16 (1988) 203.
- [3] R.C.C. Leite, R.S. Moore, J. R. Whinnery, *Applied Physics Letters* 5 (1964) 141-148.
- [4] N. Shokoufi, S. Madarshahian, *Thermal Lens Spectrometry*, Lap Lambert, Germany (2012).
- [5] J. Harris, *Analytical Applications of Lasers* vol 87, ed EH Piepmeier, Wiley, New York (1986).
- [6] N. J. Dovichi, J. Harris, *Analytical Chemistry*, 51 (1979) 728-731.
- [7] N. Shokoufi, F. Shemirani, *Talanta*, 73 (2007) 662-667.
- [8] N. Dovichi, J. Harris, *Analytical Chemistry*, 53 (1981) 106-109.
- [9] K. Nakanishi, T. Imasaka, N. Ishibashi, *Analytical Chemistry*, 57 (1985) 1219-1223.
- [10] M. Franko, C. D. Tran, *Encyclopedia of Analytical Chemistry*, John Wiley & Sons Ltd, New York (2010).
- [11] R. D. Snook, R. D. Lowe, *Analyst*, 120 (1995) 2051-2068.
- [12] T. Kitamori, M. Tokeshi, A. Hibara, K. Sato, *Analytical Chemistry*, 76 (2004) 52 A-60 A.
- [13] K. Uchiyama, A. Hibara, H. Kimura, T. Sawada, T. Kitamori, *Japanese Journal of Applied Physics*, 39 (2000) 5316-5322.
- [14] T. Wannachod, N. Leepipatpiboon, U. Pancharoen, K. Nootong, *Journal of Industrial and Engineering Chemistry* 20 (2014) 4152-4162.
- [15] T. Wannachod, N. Leepipatpiboon, U. Pancharoen, S. Phatanasri, *Journal of*

Industrial and Engineering Chemistry 21 (2015) 535–541.

[16] S. J. Yoon, J. G. Lee, H. Tajima, A. Yamasaki, F. Kiyono, T. Nakazato, H. Tao, Journal of Industrial and Engineering Chemistry 16 (2010) 350–354.

[17] S. U. Yesiller, A. E. Eroglu, T. Shahwan, Journal of Industrial and Engineering Chemistry 19 (2013) 898–907.

[18] P. Samaddar, K. Sen, Journal of Industrial and Engineering Chemistry 20 (2014) 1209–1219.

[19] R. S. Dybczyński, E. Czarska, B. Danko, K. Kulisa, Z. Samczyński, Applied Radiation and Isotopes, 68 (2010) 23–27.

[20] P. D. Blair, TrAC Trends in Analytical Chemistry, 5 (1986) 220–223.

[21] J.I. G. Alonso, D. Thoby-Schultendorff, B. Giovanonne, L. Koch, H. Wiesmann, Journal of Analytical Atomic Spectrometry, 8 (1993) 673–679.

[22] L. Weltje, H. Heidenreich, W. Zhu, H.T. Wolterbeek, S. Korhammer, J.J.M.d. Goeij, B. Markert, Science of The Total Environment, 286 (2002) 191–214.

[23] M. Krachler, C. Mohl, H. Emons, W. Shotyk, Journal of Analytical Atomic Spectrometry, 17 (2002) 844–851.

[24] M. S. Navarro, S. Andrade, H. Ulbrich, C.B. Gomes, V.A. Girardi, Geostandards and Geoanalytical Research, 32 (2008) 167–180.

[25] B. Markert, Z. D. Li, Science of the total environment, 103 (1991) 27–35.

[26] M. S. Navarro, H. Ulbrich, S. Andrade, V. A. Janasi, Journal of Alloys and Compounds, 344 (2002) 40–45.

[27] F. Shemirani, N. Shokoufi, Analytica Chimica Acta, 557 (2006) 238–243.

[28] N. Shokoufi, A. Hamdamali, Analytica Chimica Acta, 681 (2010) 56–62.

[29] Y. Ding , H. Zhao , Y. Sun , G. Zhang, H. Wu, Y. Qian, International Journal of Inorganic Materials 3 (2001) 151–156.

- [30] X. Chen, X. Y. Shen, E. Guan, Y. Liu, A. Qin, J. Z. Sun and B. Z. Tang, Chemical Communications, 49 (2013) 1503-1505.
- [31] <http://digitalcommons.calpoly.edu/star/85>.
- [32] I. Berregi, J. S. Durand, J. A. Casado, Talanta 48 (1999) 719 – 728.
- [33] Z. Varga, R. Katona, Z. Satefanka, M. Wallenius, Talanta, 80 (2010) 1744-1749.
- [34] M. Soylak, O. Turkoglu, Talanta 53 (2000) 125 – 129.
- [35] E. H. Borai, M. A. Eid and H. F. Aly, Analytical and Bioanalytical Chemistry 372 (2002) 537.
- [36] F. Faridbod, M. R. Ganjali, R. Dinarvand, P. Norouzi and S. Riahi, Sensors, 8 (2008) 1645.
- [37] A. Arrebola, M. G. Bagur, M. Sanchez, D. Gazquez, R. Romero and M. Camino, Journal of Analytical Atomic Spectrometry, 13 (1998) 765–768.
- [38] S. Bhattacharya, S. J. Lyle, R. Maghzian, Talanta, 27 (1980) 59-60.
- [39] S. J. Lyle, N. A. Za'tar, Analytica Chimica Acta, 135 (1982) 327-332.
- [40] G. Yungeng, D. Bo, Spectrochimica Acta Part B: Atomic Spectroscopy, 51 (1996) 1147-1153.

Figure Caption

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

Fig. 2 Absorption spectrum of Sm.

Fig. 3 Optimization of chopper frequency

Fig. 4 Steady-state of thermal lens signal.

Fig. 5 The effect of organic solvents on the thermal lens signal

Fig. 6 Calibration curve

Fig. 7 (a) Absorption spectrum of Lanthanides, (b) Selective excitation of Sm in the presence of the other lanthanides using diode laser which has a unique narrow emission band at 400 nm

FIGURES

Fig. 1 (a)

Fig. 1 (b)

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7 (a)

Fig. 7 (b)

Table caption

Table 1. Obtained enhancement factors using various solvents (for Sm)

Table 2. Determination of Sm in spiked and synthetic samples

Table 3. Comparing various methods for Sm determination

Table 1

Solvent	dn/dT (k ⁻¹)	K (Wm ⁻¹ k ⁻¹)	E ^a
Carbon tetrachloride	-6.12 × 10 ⁻⁴	0.103	742.718
Carbon disulfide	-8.09 × 10 ⁻⁴	0.150	674.166
Chloroform	-6.03 × 10 ⁻⁴	0.117	644.230
Ethanol	-3.87 × 10 ⁻⁴	0.167	289.670
Water	-0.91 × 10 ⁻⁴	0.598	190.217

^a Calculated at 400 nm and 50 mW of laser.

Table 2

Sample	Added (µg mL ⁻¹)	Found ^a (µg mL ⁻¹)	Recovery (%)
Tap Water	-	N.D	-
	10.00	9.82 ± 0.18	98.2
	125.00	126.65 ± 0.18	101.3
CCERCI Water	-	ND	-
	10.00	10.22 ± 0.15	102.2
	125.00	123.70 ± 0.21	99.0
Mineral Water	-	N.D	-
	10.00	9.82 ± 0.20	98.2
	125.00	124.48 ± 0.22	99.6
Synthetic sample	10.00	10.30 ± 0.24	103.0

^a Mean ± S.D. (n=10)

Table 3

Determined REE	Matrix	Detection method	Preconcentration method or speciation	Obtained LOD for Sm ($\mu\text{g mL}^{-1}$)	Ref.
Lanthanides	Lanthanides	Spectrofluorimetric	Using reagents	0.03	[32]
Lanthanides	Uranium ore concentrates	ICP-SF-MS ^a	Separation using selective extraction Chromatography	0.20	[33]
Sm ³⁺	Na ⁺ , K ⁺ , Mg ²⁺ , Ca ²⁺	UV-Vis	With Chromeazurol S	0.03	[34]
Lanthanides	Lanthanides	ICP-OES	Preconcentration by Ion Chromatography	0.10	[35]
Lanthanides	Lanthanides	Potentiometry	-	0.50	[36]
Lanthanides	La, Y, Pr, Nd, Sm	Flame Atomic Absorption	Extraction	0.01	[37]
Sm ³⁺	Sm ³⁺ , Eu ³⁺ , La ³⁺ , Cd ²⁺ , Mg ²⁺ , Ho ³⁺	TLM	-	0.08	Present work

^a Inductively coupled plasma sector-field mass spectrometry