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Laser-enhanced ionization and laser-induced atomic fluorescence as element-specific detection methods for gas chromatography Application to organotin analysis

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Abstract

We have demonstrated that flame laser-enhanced ionization (LEI) and flame laser-induced atomic fluorescence (LIAF) techniques can be used as, alternative sensitive detectors for gas chromatographic (GC) analysis of organotin compounds. These two element-specific detection methods are free from interferences from the organic solvent. Two types of LEI schemes for Sn detection are employed. For the two-step LEI scheme (TLEI), the tin atoms in the flame were stepwise excited and then ionized collisionally. In contrast, in detection with the single-step LEI scheme (SLEI), only one dye laser is used. For the analysis of tetramethyltin and tetraethyltin, the GC–TLEI, GC–SLEI, and GC–LIAF systems yield linear dynamic ranges of 0.015–400, 0.39–600 and 0.5–600 ng, respectively. The corresponding detection limits reach 0.15, 3.9 and 5.0 mg/l, with absolute quantities corresponding to 15, 390 and 500 pg, respectively, for an injection volume of 0.1 μl. These detection methods prove to be more sensitive and selective than the conventional flame ionization detection, which achieves absolute detection limits of 800 and 1667 pg for tetraethyltin and tetramethyltin, respectively, under identical GC conditions.

Keywords: Laser-enhanced ionization detection; Laser-induced atomic fluorescence detection; Detection, GC; Tetramethyltin; Tetraethyltin; Organotin compounds

1. Introduction

Organotin compounds have been widely used as catalysts and additives in industry as well as biocides in agriculture [1–3]. Due to their persistence and toxicity, a sensitive, efficient analytical method is strongly desired.

Over the past decade, there have been several techniques, which couple gas chromatography (GC) to element-specific detection methods successfully applied to organotin analysis, such as atomic absorption spectrometry (AAS) [4–6], microwave-induced plasma atomic emission spectrometry (MIP-AES) [6–9], direct current plasma emission spectrometry [6,10], and inductively-coupled plasma mass spectrometry (ICP-MS) [11–14]. In this work, we demonstrate two new detection methods, flame laser-enhanced ionization (LEI) and flame laser-induced atomic fluorescence (LIAF), which can be alter-

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natively used as element-specific detection methods coupled to GC.

With the LEI technique, the analyte atoms in the flame are selectively excited by laser irradiation to a higher energy level, from which they are much easier to be ionized by collision with the components in the flame [15–18]. The rate of collisional ionization is thus greatly enhanced. In this sense, the LEI detection method should be more sensitive than conventional flame ionization detection (FID). Because of its capability for the trace detection at the sub-pg/ml level [15–24], LEI has been successfully coupled to high-performance liquid chromatography (HPLC) [25,26].

LIAF spectroscopy is another technique popularly applied to a flame analyzing the contained trace species. The advantage of LIAF detection lies in its freedom from the flame background and the analyte emission interferences, as well as simplicity of using non-resonance fluorescence to eliminate noise caused by scattered radiation from particles within the flame gases [27,28]. This technique has also been coupled to HPLC to analyze the organotin compounds and achieved a detection limit of 500 pg [29].

In this work, we have demonstrated that the LEI and LIAF techniques can be successfully coupled to GC. The resulting GC–LEI and GC–LIAF devices appear to have higher selectivities and better detection limits than the GC–FID system in analyzing the organotin compounds. Tetramethyltin and tetraethyltin are used for analysis. The limits of detection for Sn can reach the pg range. The related dynamic ranges of concentration and detection precision are also characterized. Although these reagents are less important to environmental analysis, we focus on the novelty of the combined detection methods.

2. Experimental

2.1. Apparatus

2.1.1. GC set-up

For the separation of organotin compounds, a Shimadzu GC-14B GC system was used with a 30 m×0.25 mm I.D. capillary column packed with 100% crossbonded dimethylpolysiloxane. The N_2 carrier gas was employed at a flow pressure 175 kPa. The temperature of the injection port was 180°C. The chromatography was temperature programmed at a rate of 40°C/min. The FID system housing was maintained at 220°C. The air and H_2 pressures used in the FID system were controlled at 60 and 90 kPa, respectively. The signal output was stored in a personal computer through a communication bus (Shimachi, CBM-101). When either LEI or LIAF was implemented as the detection method, the capillary column was alternatively connected to a pneumatic nebulizer (Perkin-Elmer). This portion of the 20-cm long column, exposed outside the housing of the GC device, was surrounded with a heating tape (Glas-col, cc-3) to maintain the temperature at 250°C. The outlet of the capillary column could be easily coupled to the flame nebulizer without involving complicated interface assembly.

2.1.2. Laser-enhanced ionization detection

Fig. 1a shows the schematic of the laser-enhanced ionization set-up. Two tunable dye lasers (Spectra-Physics, PDL-2A and PDL-3), each pumped by an individual frequency-doubled Nd–YAG laser (Spectra-Physics, DCR-2A and GCR-3) at 10 Hz repetition rate, were used as radiation sources. One dye laser with rhodamine 590 emitted at 568 nm, while the other laser with rhodamine 640, dissolved in a 0.1% methanolic NaOH solution, emitted at 603.8 nm. The output frequency of the former laser was then doubled through a KH_2PO_4 (KDP) crystal emitting at 284 nm for excitation of the Sn atom in the $5p^2\,^3P_2 \rightarrow 5p6s\,^3P_2$ transition. The second dye laser at 603.8 nm was simultaneously used to further excite Sn from the $5p6s\,^3P_2$ to $5p7p\,^3P_2$ state. Two beams unfocused were propagated in opposite directions along the flame axis, each through a pinhole of 3.0–4.5 mm^2 cross section, and overlapped spatially and temporally inside the flame, 10 mm above the burner head. In this work, two types of LEI schemes were adopted: two-step LEI (TLEI) and single-step LEI (SLEI). With the former scheme, the tin atoms in the flame were stepwise excited to a higher energy state via a process of absorption of two different photons, and then ionized collisionally. The initial $5p^2\,^3P_2$ state (Fig. 2a) can be populated by thermal excitation. In contrast, with the SLEI scheme, only one dye laser at 284 nm was used. The output energies for 284 nm and 603.8 nm were 300 μJ and

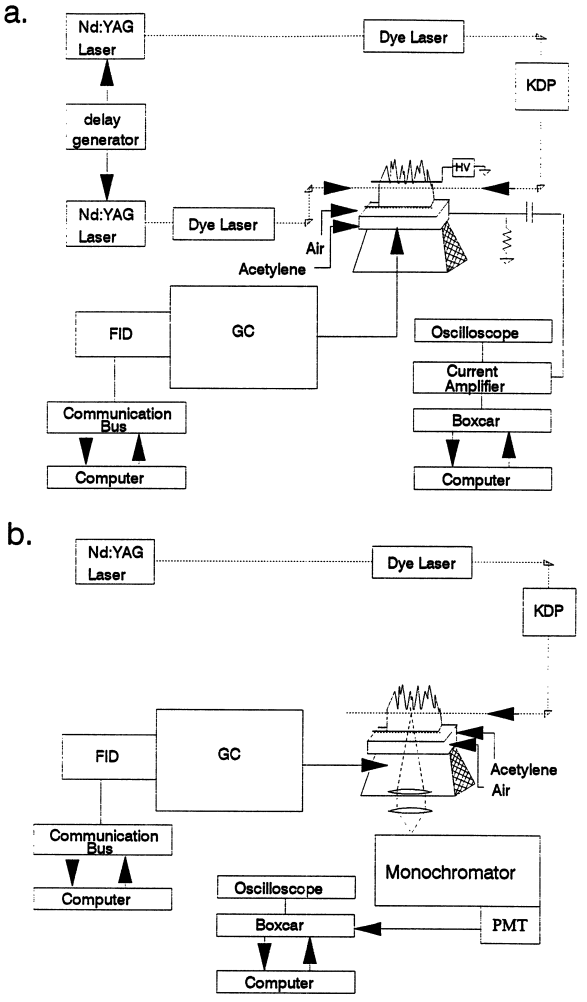

Fig. 1. Schematics of (a) GC–TLEI apparatus and (b) GC–LIAF apparatus.

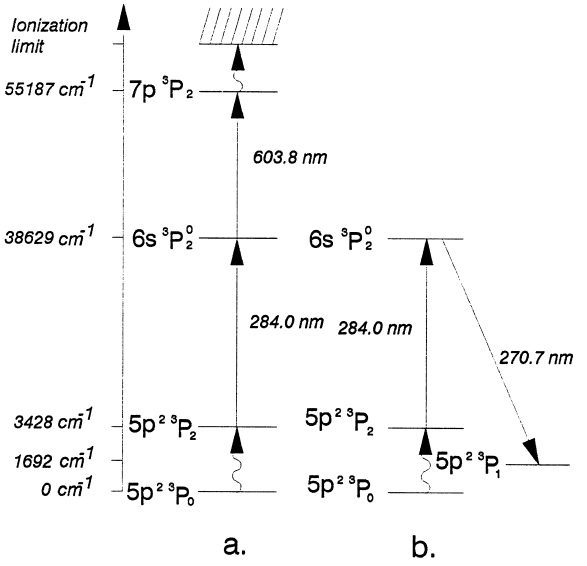

Fig. 2. Energy diagrams for (a) LEI scheme and (b) LIAF scheme. The $5p^{23}P_2$ state is populated by thermal excitation.

1.4 mJ. The energy of the first dye laser was kept small to minimize ionization interference of background species from the burned organic solvent.

In the work, we utilized a burner assembly (Perkin-Elmer) with a 100 mm×0.5 mm slot burner head coupled with an interlocked gas control system [30–33]. The fuel C_2H_2 and air were regulated at flow-rates of 0.8 and 13 l/min, respectively, and were premixed prior to reaching the burner head. The corresponding flame temperature was measured as about 2500 K [30,32].

A water-cooled cylinder electrode was biased at −1000 V and suspended 1.5–2.0 cm above the burner head [21,24,33]. The electrode was made of 1/4 in. O.D. stainless steel tubing, through which the water was immersed (1 in.=2.54 cm). The burner served as the other electrode, from which the ion current was collected and amplified with a current-to-voltage converter (Model 428, Keithley), and then fed into a boxcar integrator (EG&G, PAR 4402, 4420, and 4422) for an improved signal-to-noise ratio. Each data point was averaged over 10 laser shots. The LEI signal was displayed on an oscilloscope or stored in a personal computer for data treatment.

2.1.3. Laser-induced atomic fluorescence detection

The schematic of the LIAF detection system is displayed in Fig. 1b. When the Sn atoms released in the flame were excited from the $5p^{23}P_2$ to the $5p6s^3P_2$ state by the dye laser at 284 nm, the non-resonance fluorescence at 270.7 nm in the $5p6s^3P_2 \rightarrow 5p^{23}P_1$ transition was monitored. The excitation and emission schemes were shown in Fig. 2b. The signal was collected perpendicularly relative to the laser beam axis onto a monochromator (McPherson 270) via a pair of lenses of 5 inches and 10 inches. The entrance and the exit slits of the monochromator were open to 750 μm and the grating was

set at 270.7 nm. The transmitted fluorescence was detected by a photomultiplier tube (PMT, Hamamatsu, R955) and fed into a boxcar integrator (EG&G, PAR 4402, 4420, and 4422) for the signal-to-noise ratio improvement. Each data point was averaged over 10 laser shots and then stored in a personal computer for further treatment.

2.2. Reagents

Two compounds, tetramethyltin (Merck, reagent grade, >99%) and tetraethyltin (Janssen, reagent grade, 97%) were selected as analytes. They are thermally stable, having low temperature of volatilization. Each compound was dissolved in *n*-octane and prepared to contain equal concentrations of tin. A 0.1-μl volume of a mixture (1:1) of these two compounds was loaded each time into the GC system for analysis; the amount of Sn in the injection volume was in the range 5–1000 ng.

3. Results and discussion

3.1. FID

Fig. 3 shows the chromatogram containing both tetramethyltin and tetraethyltin detected by GC–FID. The N_2 flow pressure is optimized at 175 kPa, which can make both compounds separate within 3 min, free from solvent interference.

The tetramethyltin with a lower boiling point of 106°C [1] appears at a retention time earlier than the tetraethyltin. Its peak is found to be weaker, since the corresponding concentration of tetramethyltin is smaller. The fact that the first peak is also broader than the second peak may be attributed to a temperature effect. Given that the column temperature rises 40°C/min, the tetraethyltin is vaporized at higher temperature, leading to a faster diffusion rate and the subsequent narrower bandwidth. The dynamic range of calibration curve and detection limit, defined as a ratio of three times the standard deviation of blank measurements to the slope of the calibration curve [34], are characterized and listed in Table 1.

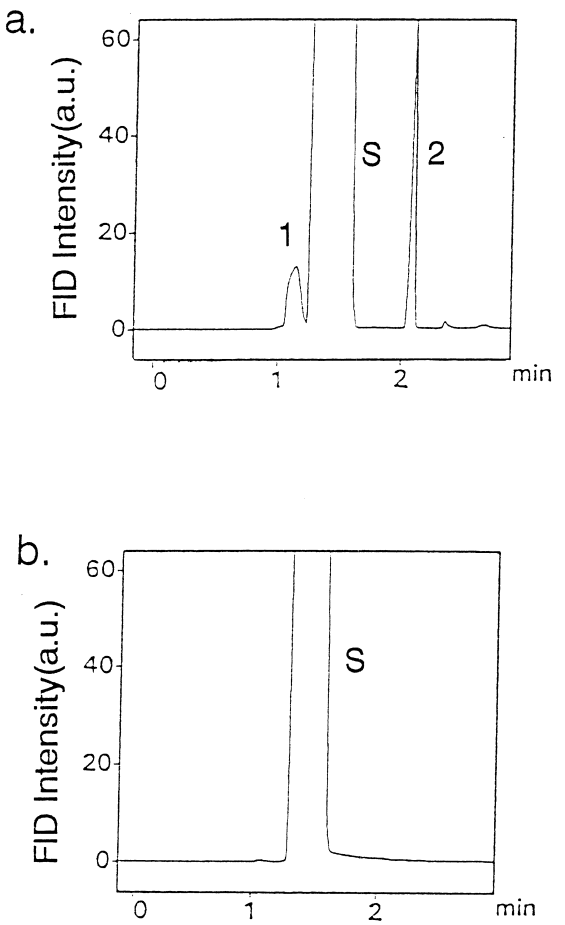

Fig. 3. Chromatograms obtained by GC–FID for (a) mixed solution containing tetramethyltin and tetraethyltin in *n*-octane, and (b) *n*-octane solvent alone. Compound 1 is tetramethyltin, compound 2 is tetraethyltin, and S is the solvent. a.u.=Arbitrary units.

3.2. LEI and LIAF detection

Fig. 4 shows the chromatograms obtained by TLEI, SLEI, and LIAF detectors, as individual 0.1-μl volumes of organotin mixture is loaded. Intensities of the two TLEI, SLEI, or LIAF peaks are comparable, since each compound contains an equal concentration of Sn corresponding to 10 ng. As compared to GC–FID, measurements by element-specific detectors are free from interferences from solvent and impurities existing in the sample.

The chromatographic peak intensities for both organotin compounds increase as the laser energies

Table 1
Comparison of chromatographic data obtained by FID, SLEI, TLEI, and LIAF

Method of detection	Sample[a]	Limit of detection, Sn (pg)[b]	Linear dynamic range, Sn (ng)	Precision[c] (%)
FID	Et_4Sn	800	$8\cdot10^{-1}$–$5.0\cdot10^{2}$	
	Me_4Sn	1667	1.7–$5.0\cdot10^{2}$	
SLEI	Et_4Sn (or Me_4Sn)	390	$3.9\cdot10^{-1}$–$6.0\cdot10^{2}$	4
TLEI	Et_4Sn (or Me_4Sn)	15	$1.5\cdot10^{-2}$–$4.0\cdot10^{2}$	2
LIAF	Et_4Sn (or Me_4Sn)	500	$5.0\cdot10^{-1}$–$6.0\cdot10^{2}$	5

[a] Tetraethyltin and tetramethyltin contain 10 ng of tin for each in a 0.1 μl injection volume.
[b] Absolute detection limit of Sn per 0.1 μl injection volume of mixed solution.
[c] Standard deviation of signals in five measurements.

in either LEI or LIAF increase. For the energy dependence measurement of the GC–TLEI detection of the organotin compounds, the peak intensity exhibits a linear proportion with the energies in the range 25–300 μJ for the rhodamine 590 dye laser and 0.23–1.4 mJ for the rhodamine 640 dye laser. Similarly, the linear relationship for the energy dependence measurement in the LIAF detection is found from 50 to 250 μJ.

The calibration curves of Sn concentrations for LEI and LIAF detection have also been characterized. The linear dynamic ranges for TLEI, SLEI, and LIF are found to be 0.015–400, 0.39–600 and 0.5–600 ng, respectively. Their corresponding detection limits are 0.15, 3.9, and 5.0 mg/l, with absolute quantities corresponding to 15, 390, and 500 pg, respectively, for each injection volume. Of these detection methods, TLEI leads to the lowest detection limit. This is mainly attributed to a two-step LEI configuration, under which an atom can be further excited to a higher energy level than that with one laser beam alone and its ionization rate becomes faster [16,24,33]. As reported, the ion enhancement of TLEI over SLEI is strongly affected by the second-step excitation. To optimize the ion enhancement induced by the TLEI scheme, several related

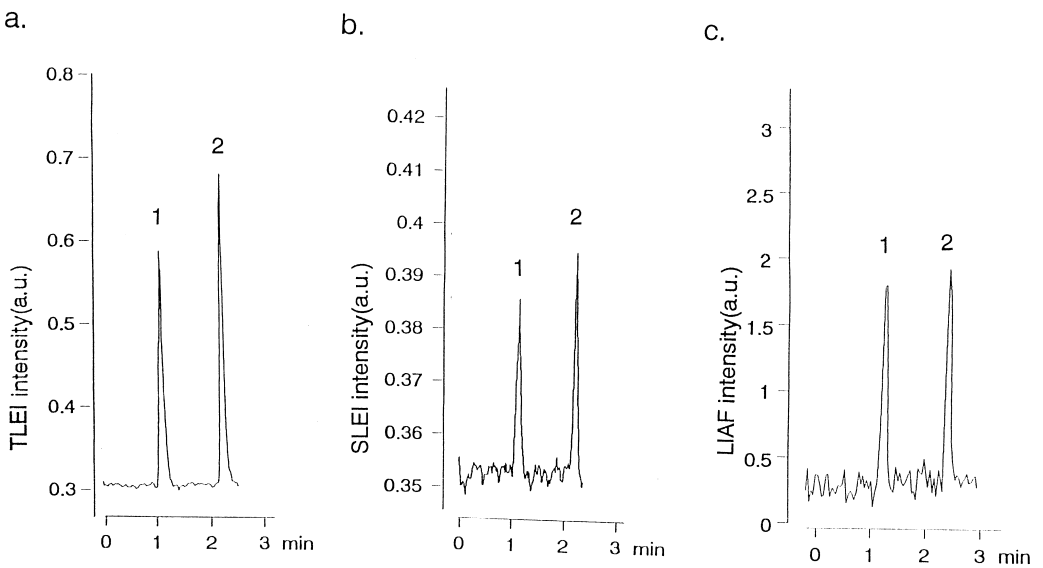

Fig. 4. Chromatograms obtained by (a) GC–TLEI, (b) GC–SLEI, and (c) GC–LIAF systems, respectively, as 0.1 μl of mixture of tetramethyltin and tetraethyltin in *n*-octane is loaded in the GC system. Compound 1 is tetramethyltin and compound 2 is tetraethyltin. The amount for each compound corresponds to 10 ng.

factors should be considered including second-step transition probability, laser intensity, collisional ionization rate coefficients, and the effective lifetimes of the states involved in the transition [35]. In our work, TLEI can achieve an Sn detection limit better by a factor of 25 than SLEI, comparable with the enhancement factor of 27 reported by Turk et al. [36]. Still, the detection limit obtained by SLEI is slightly better than that by LIAF, since the latter is restricted by a small signal collection angle and a small quantum efficiency of the PMT. Comparison of chromatographic data obtained by the aforementioned detectors is listed in Table 1.

In comparison, the LEI and LIAF detection methods coupled to GC in this work result in detection limits comparable with or lower than those obtained in HPLC for organotin analysis [25,26,29]. For easy comparison with other detection methods used, Table 2 surveys some of detection limits obtained by various detectors coupled to either GC or LC for organotin analysis [4,11,13,14,25,29,37–47].

4. Conclusion

This work has shown that LEI and LIAF can be used alternatively as sensitive detection methods for GC, with better detection limits and higher selectivities for specific element identification than conventional GC–FID. Using tetramethyltin and tetraethyltin for the test, we have demonstrated the effectiveness of these new techniques. These detection methods should also be extendable to other partly alkylated organotin compounds, which seem more important to environmental analysis.

Table 2
Comparison of detection limits achieved by various detection methods

Method	Detection limit		Ref.
	Concentration, Sn (ng/ml)	Absolute, Sn (pg)	
GC–flame photometric detection		3[a]	[37]
GC–FID		2000[b]	[38]
GC–flame ionization-quenching		0.5[b]	[39]
GC–laser ionization time-of-flight (TOF) MS	0.0013[c]	0.00075[c]	[40]
GC–AAS		25[d]	[4]
GC–low-pressure inductively coupled plasma (ICP) MS		11[e]	[41]
GC–ICP-MS		0.0035[f]	[11]
GC–ICP-MS		0.3–0.8[a]	[13]
GC–ICP-MS		0.05[a]	[14]
GC–MIP-AES		0.4[a]	[42]
GC–MIP-AES		0.15[a]	[43]
GC–ICP-TOF-MS		0.012[e]	[44]
LC–TLEI	3[a]	60[a]	[25]
LC–ICP-MS		400[g]	[45]
LC–ICP-MS		8[g]	[46]
LC–ICP-MS		20–40[a]	[47]
LC–LIAF		500[a]	[29]
GC–TLEI	150	15	This work
GC–LIAF	5000	500	This work

[a] For butyltin species.
[b] For tetraethyltin in 1 μl.
[c] For tetraethyltin in 0.6 μl.
[d] For tetrabutyltin.
[e] For tetraethyltin.
[f] For tetrabutyltin in 100 μl.
[g] For trimethyltin chloride.

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