



Compact integration of gas chromatographer and atomic fluorescence spectrometer for speciation analysis of trace alkyl metals/semimetals



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ARTICLE INFO

Article history:

Received 21 November 2013

Accepted 25 November 2013

Available online 4 December 2013

Keywords:

Atomic fluorescence spectrometry

Gas chromatography

Dimethyl selenide

Dimethyl diselenide

Tetramethyl tin

Tetraethyl lead

ABSTRACT

Gas chromatographic separation was coupled with atomic fluorescence spectrometry (GC–AFS) directly via argon–hydrogen flame for integrated GC–AFS instrumentation, i.e., the outlet end of the GC column was directly put into the bottom of the Ar–H₂ flame atomizer without any transportation interface. This laboratory-constructed GC–AFS instrument was preliminarily characterized by its application for the speciation analysis of dimethyl selenide ((Met)₂Se) and dimethyl diselenide ((Met)₂Se₂) as well as the two-channel simultaneous determination of tetramethyl tin (Sn(Met)₄) and tetraethyl lead (Pb(Et)₄). Under the optimized experimental conditions, the absolute limits of detection of 9.4 pg for (Met)₂Se, 3.8 pg for (Met)₂Se₂, 0.23 ng for Sn(Met)₄ and 0.39 ng for Pb(Et)₄ were obtained. The coupling is simple, and the whole instrument is compact.

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1. Introduction

Atomic fluorescence spectrometry (AFS) has many advantages such as high sensitivity, high selectivity, wide linear range, simple instrumentation, low instrumental and running cost; and it can also be used as an excellent element-specific spectrometric detector especially when coupled with various chemical vapor generation (CVG) technologies. However, the CVG-based speciation analysis was strictly affected by the CVG conditions; furthermore, the detectable elemental range can be quite limited. Chromatography is a widely used speciation analysis method, since AFS was first employed as a liquid chromatographic detector by Van Loon et al. in 1977 [1], and so far Chromatography-based AFS has been successfully applied to speciation analysis of Hg, Pb, Sn, As, Se, Sb compounds, and so on. Sánchez-Rodas et al. [2] summarized AFS as an ideal detection technique for speciation studies concerning hydride forming elements (mainly As, Se and Sb) and Hg when coupled with chromatographic (HPLC and GC) and non-chromatographic separations (CE), with 148 papers published from 2000 to 2010 included. Analytical features show that AFS is a suitable elemental detector in speciation studies for single element species, and in many aspects it is superior to AAS and equal to ICP–MS or ICP–AES for some elements.

GC–AFS retains the merit of atomic fluorescence spectrometry while owns capacity of separation and therefore turns into a superior speciation analysis means for organic metal compounds especially for volatile ones and those can be derivatized into volatile ones. In early studies [3–5] on GC–AFS, Radziuk et al. [3] used an atomic fluorescence spectrometric system as a gas chromatographic detector, in which electrothermally heated graphite tube and quartz tube atomization systems were compared by detecting alkyl lead compounds. In 1986, D'Ulivo and Papoff [5] described the simultaneous detection of alkyl selenides, alkyl leads and alkyl tins by a multi-channel non-dispersive atomic fluorescence spectrometer with an argon–hydrogen flame (Ar–H₂ flame) atomizer coupled with a gas chromatographer. Later home-made GC–AFS instruments are mostly applied to speciation analysis of Hg compounds, with common analytical procedures [6–18] contained derivatization followed by GC separation, and an additional pyrolysis device (with temperature as high as 700–900 °C) for decomposing them to degradation products such as gaseous mercury atoms for AFS detection before the derivatives entering the subsequent atomizer. GC–AFS has also been applied to speciation analysis of other organic metal compounds in water samples, biological samples and food for organic leads [3,5], organic tins [5,19,20], organic selenides [3,21] and organic arsenics [22].

Although liquid chromatographer coupled with atomic fluorescence spectrometer (LC–AFS) has been commercialized for many years, there have been no commercial GC–AFS instruments available yet. One important reason is that LC–AFS usually relatively easily uses hydride generation [23,24] or other chemical vapor generation techniques [25] to convert analytes into measurable volatile forms for AFS. As to GC–AFS, the oven temperature is one of the most important GC

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instrumental conditions, and it is critical to ensure the effluent constituents not to be cooled down and to be kept similar behavior until they enter the AFS atomizer; therefore an extra heated transportation interface is usually needed to achieve the coupling of GC and AFS. It should be pointed out that the potential problems may be caused by the transportation interface, such as increased dead volume, peak broadening and even measurement error due to its inaccurate and inconsistent temperature control.

In this work, therefore, we reported a fully integrative GC–AFS instrument without any transportation interface. The AFS was directly coupled with the GC and integrated into a single instrumental unit, i.e., the outlet end of the GC column was directly put into the bottom of the Ar–H₂ flame atomizer. The coupling is very simple, and the integrative GC–AFS is compact. Furthermore, volatile alkyl metal/semimetal compounds including dimethyl selenide ((Met)₂Se), dimethyl diselenide ((Met)₂Se₂), tetramethyl tin (Sn(Met)₄) and tetraethyl lead (Pb(Et)₄) were selected as the model analytes to characterize the GC–AFS instrument for the fact that the determinations of organic selenides [21,26–31], organ tins [19,32–35] and organ leads [36,37] are frequently concerned, and simultaneous detection of alkyl leads and alkyl tins is needed [38–42] in many cases.

2. Experimental

2.1. Instrumentation

The integrative GC–AFS instrument mainly consisted of a dual-channel atomic fluorescence spectrometer (SK-2003A, Beijing Jinsuokun Technology Developing Co., LTD, Beijing, China), a home-made argon-hydrogen flame atomizer and a home-made GC unit, as shown in Fig. 1. The pump, the gas/liquid separator and the hydride generation system equipped in the commercial AFS instrument were removed, and its original flame atomizer was replaced by the home-made atomizer to realize the direct coupling of GC and AFS without any transportation interface. The current for hollow cathode lamps (HCLs; HCLs of Se, Sn and Pb were obtained from General Research Institute of Non-Ferrous Metals, Beijing, China) was set at 80 mA and the voltage for the photomultiplier tube was –280 V. The external dimension of the home-made GC oven was 300 mm × 350 mm × 300 mm and its thickness was 50 mm, with two independent temperature control units for sample oven and GC oven, respectively. The GC column (TM-5, 0.53 mm i.d. × 1.0 μm × 15 m, Shanghai Techcomp Instrument LTD, Shanghai, China) was rolled up to a coil (60 mm dia.) and set into the

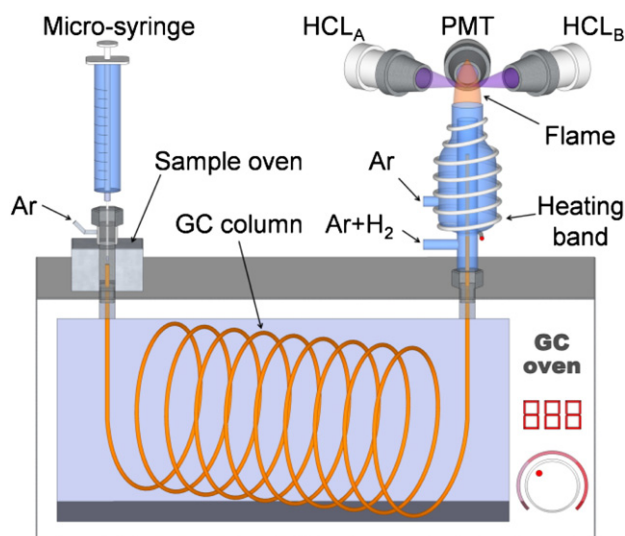


Fig. 1. Schematic of the integrative GC–AFS instrument.

GC oven, with the outlet end directly inserted into the bottom of the flame atomizer.

The home-made pear-shaped quartz atomizer was 110 mm long, and consisted of an inner tube (6 mm o.d.) and an outer tube (8 mm i.d. at top), the distance between the tops of inner and outer tubes was 10 mm. A flow of makeup carrier gas consisted of Ar and H₂ passed through the inner tube to the top of the quartz atomizer and formed an argon-hydrogen flame for atomization of the analytes. A flow of Ar served as the shield gas and passed through the gap between the outer and inner tubes to prevent extraneous air from entering the inner tube thus resulting in the oxidation of the analyte species and affecting the stability of the flame. Furthermore, a heating band was tightly wrapped around the quartz atomizer to keep the effluent constituents from cooling, which was connected to a transformer (TPGC2]-1, Shanghai Pafe Electronic Equipment Ltd. Co., Shanghai, China) for power supply and convenient adjustment of its heating temperature.

2.2. Reagents and materials

All chemicals used in this work were of at least analytical grade. (Met)₂Se (98%), (Met)₂Se₂ (98%), Pb(Et)₄ (0.20 mg mL⁻¹) and methanol (HPLC grade) standards were obtained from J&K Scientific (China), and Sn(Met)₄ (98%) was bought from Alfa Aesar (Karlsruhe, Germany). Stock solutions of (Met)₂Se (0.98 mg mL⁻¹), (Met)₂Se₂ (0.98 mg mL⁻¹), Sn(Met)₄ (1.0 mg mL⁻¹) and Pb(Et)₄ (0.1 mg mL⁻¹) were prepared by appropriate dilution with methanol and stored at 4 °C in the dark. Working solutions were prepared daily by serial dilution of the stock solutions. High purity (99.99%) Ar was obtained from Qiaoyuan Gas Co. (Chengdu, China). Hydrogen was generated using a hydrogen generator (SPGH-300, Zhongya Gas & Instrument Research Institute, Beijing, China).

2.3. Analytical procedure

Mixed solutions (0.2 μL (Met)₂Se and (Met)₂Se₂ or 0.5 μL Sn(Met)₄ and Pb(Et)₄) were injected into the gasification chamber in the sample oven through the inlet port by a micro-injector; gasified analytes were carried into the GC column by carrier gas argon and were separated under suitable GC conditions; and then the effluent species were atomized in the argon-hydrogen flame on top of the quartz atomizer, where gaseous Se, Sn and Pb atoms were excited by their respective HCLs, and the corresponding fluorescence signals were detected by the solar blind photomultiplier (PMT). The peak area (integral atomic fluorescence) signal was recorded for quantification in this work. Speciation analysis of (Met)₂Se and (Met)₂Se₂ was achieved by single channel detection, while simultaneous determination of Sn(Met)₄ and Pb(Et)₄ was performed by dual-channel detection. The main instrumental parameters of the integrative GC–AFS were summarized in Table 1.

3. Results and discussion

3.1. Chromatographic characteristics

In this work, the chromatographic separation characteristics were firstly investigated. Experimentally, the baseline separation of (Met)₂Se and (Met)₂Se₂ was achieved within 40 s, and simultaneous detection of Sn(Met)₄ and Pb(Et)₄ could be accomplished within 100 s. Fig. 2a is a typical chromatogram obtained with a mixed solution of 2 μg mL⁻¹ (Met)₂Se and 2 μg mL⁻¹ (Met)₂Se₂, and Fig. 2b shows a typical chromatogram obtained with a mixed solution of 4 μg mL⁻¹ Sn(Met)₄ and 4 μg mL⁻¹ Pb(Et)₄. Symmetrical and narrow peaks without any tailing were obtained by this system; besides, for the high selectivity of AFS and the interface-free integration, the chromatogram is also quite clean.

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