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## Improvement in thallium hydride generation using iodide and Rhodamine B



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### ABSTRACT

A continuous flow hydride generation atomic absorption spectrometry (CF-HG-AAS) system was used to study the enhancement effect of different substances for conventional chemical HG of thallium. At room temperature, the acidified sample solution containing the respective enhancement reagent merged with the aqueous NaBH<sub>4</sub> solution. The generated thallium hydride was stripped from the eluent solution by the addition of a nitrogen flow and thereafter the bulk phases were separated in a gas–liquid separator. The main factors under study were concentration and type of enhancement reagent (Te, iodide added as KI, Rhodamine B, malachite green and crystal violet) and acid (HCl, H<sub>2</sub>SO<sub>4</sub> or HNO<sub>3</sub>). Other parameters affecting the thallium hydride generation, such as: NaBH<sub>4</sub> concentration, carrier gas flow rate, length of reaction–mixing coil and reagents flow rates, were studied and optimized. Among the enhancement reagents tested, the combination of Rhodamine B and iodide produced the best results. A linear response was obtained between the detection limit (LOD (3σ)) of 1.5 μg L<sup>-1</sup> and 1000 μg L<sup>-1</sup>. The RSD% (n=10) for a solution containing 15 μg L<sup>-1</sup> of Tl was 2.9%. The recoveries of thallium in environmental water samples by spiking the samples with 10 and 20 μg L<sup>-1</sup> of Tl were in the 97.0–102.5% range. The accuracy for Tl determination was further confirmed by the analysis of a water standard reference material (1643e form NIST, USA). Finally, it was demonstrated that malachite green and crystal violet showed similar enhancement effect like Rhodamine B for thallium HG.

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### 1. Introduction

Thallium (Tl) is a highly toxic element and it is well known as one of 13 priority metal pollutants listed by the United States Environmental Protection Agency (US EPA) [1]. It can be found in two oxidation states, Tl<sup>+</sup> and Tl<sup>3+</sup>, each of which manifests different bioavailability and toxicity [2]. In fact, it has been shown that Tl<sup>3+</sup> is approximately 50,000-fold more toxic than the lower valence and, in comparison with other elements Tl<sup>3+</sup> is 43,000-fold more toxic than cadmium (Cd) on a free-ion basis [3]. Therefore, determination of Tl species in biological and environmental samples is of great interest due to its clinical and environmental roles.

Hydride generation (HG) techniques in atomic spectrometry (AS) are very popular because of the enhanced detection limits compared to conventional nebulization of sample into a given atom reservoir. The number of elements forming volatile hydrides is limited to As, Sb, Bi, Ge, Sn, Pb, Se, Te, In, Tl and some transition

metals from groups 3–12 of the Periodic Table, including noble metals. However, only a few can be conveniently transformed into volatile species at room temperature [4]. In 1984, Yan et al. [5] reported for the first time the determination of Tl by atomic absorption spectrometry (AAS) prior to its vapor generation, using an electrically heated quartz tube atomizer. These workers used a batch method, which resulted less sensitive than conventional flame AAS with a characteristic concentration of 6 μg mL<sup>-1</sup>, whilst being subject to large positive interferences from the presence of other covalent, hydride-forming elements. For example, the addition of 2 pg of Te resulted in an 11-fold increase in the absorbance of Tl. Thereafter, Ebdon et al. [6] reported the use of continuous flow vapor generation to improve the determination of Tl by AS. Attempts to generate volatile organothallium compounds were unsuccessful but using sodium tetrahydroborate (THB) a volatile thallium species was produced. The authors suggested that the vapor phase species was thallium(I) hydride, TIH. At room temperature noisy signals were obtained, but when the reaction manifold was chilled to 0 °C the signals were far more stable. Cooling did not significantly change the sensitivity. A characteristic concentration of 4 ng mL<sup>-1</sup> was obtained; this is a 1500-fold improvement on the sensitivity reported in the previous work [5].

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As far as our review shows, there are only four additional reports on Tl chemical vapor generation (CVG), presumably as hydride [7–10]. Liao et al. [7], extended the former research on the generation of TIH [5] in order to enhance the sensitivity for Tl determination using the *in situ* concentration of TIH in a graphite furnace coated with palladium. Their experiments were performed using Tl aqueous standard solution with added Te as an enhancing reagent for hydride generation; it was found that the generation efficiency of the volatile TIH greatly depended on the concentration of hydrochloric acid injected, the acidity of the sample and the reaction temperature. The results also showed that Se, Te, Cu, Co and Ni increased the sensitivity for Tl. Among them the effect of tellurium and copper is more significant, but the latter is effective only in a limited concentration. E.g.: the addition of 0.5–2.0 mg of tellurium led to a 7-fold increase in the absorbance of Tl. It was predicted that the effect of Te on Tl is due to a co-hydride formed between tellurium and Tl.

The first application of HG for the determination of Tl in real samples by AS was reported by Wei et al. [8]. A simple and inexpensive flow injection (FI) laboratory-built vapor generator was used with isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS) for the determination of Tl in sea-water samples. In this study, several metal ions were tested as catalysts for Tl hydride formation (e.g., As, Se, Te, Ni and Cu). A greater Tl signal was obtained when 1.0 mg mL<sup>-1</sup> of Te was used as catalyst. Additionally, a series of organic reagents, mainly nitrogen- and sulfur-containing compounds, which are able to form water soluble complexes with Tl, did not improve the TIH generation efficiency.

A FI-HG-AAS method [9] was developed for Tl determination at the µg L<sup>-1</sup> levels. The main aim of that work was to select an appropriate enhancement reagent for the generation of TIH and to establish a method for its analysis. These authors reported that Au, Pt, and Pd in the sample solution at a certain concentration could enhance the signal of Tl at the µg L<sup>-1</sup> level. Of the three metal ions, Pd provided the best performance and since it is the most economical, it was chosen as the enhancement reagent. The experiments also showed that 0.0005% of Rhodamine B, an alkaline dye extensively used in the spectrophotometric determination of Tl, enhances the peak height of Tl in the presence of Pd by 40%.

The latest report on thallium CVG describes a hydride generation-integrated atom trap (HG-IAT) atomizer coupled to flame AAS for the determination of In and Tl in a reference material [10]. The design of HG-IAT-FAAS hyphenated technique achieved dramatic improvement in the detection limit compared with that obtained using other atom trapping techniques. The achieved limit of detection (LOD) of 0.40 µg L<sup>-1</sup> for Tl was at least ten times better than that obtained using *in situ* trapping technique in a commercial graphite furnace [7]. In this study, only Rhodamine B was used as the catalyst for Tl hydride formation.

The aim of this work was to study the enhancement effect of different substances for conventional chemical HG of Tl. Thus, a series of experiments were carried out in order to corroborate the improving effect reported for some substances, as well as testing some new reagents. The attention was focused on studying the co-enhancement effect of Rhodamine B and iodide ions on the hydride generation of Tl.

## 2. Materials and methods

### 2.1. Reagents

All chemicals were of analytical reagent grade, unless otherwise stated. Ultra-pure deionized water, (> 18 MΩ cm), from a Milli-Q system (Millipore, Bedford, M.A, USA), was used

throughout the experiments. The following reagents were used: thallium nitrate (TlNO<sub>3</sub>, 99.5%, Merck), Rhodamine B (C<sub>28</sub>H<sub>31</sub>ClN<sub>2</sub>O<sub>3</sub>, 99%, Merck), Malachite green oxalate (C<sub>23</sub>H<sub>25</sub>N<sub>2</sub>·C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>·0.5C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>, dye content ≥ 90%, SIGMA), Crystal violet (C<sub>25</sub>H<sub>30</sub>N<sub>3</sub>Cl, Dye content ≥ 90%, SIGMA), potassium iodide (KI, 98%, BDH Chemicals), sodium hydroxide (NaOH, 99%, Merck), sodium borohydride (NaBH<sub>4</sub>, 98%, Sigma), nitric acid (HNO<sub>3</sub>, 69%, Riedel de Haën) and hydrochloric acid (HCl, 37%, Riedel de Haën). The stock standard solution of Tl (1000 mg L<sup>-1</sup>) was prepared by dissolving the appropriate mass of TlNO<sub>3</sub> in 0.005 mol L<sup>-1</sup> HNO<sub>3</sub>. Working solutions of Tl were prepared daily by appropriate dilution of 1000 mg L<sup>-1</sup> solution. Sodium borohydride 1.0% and 1.2% w/v in sodium hydroxide solutions were prepared just prior to use by dissolving an appropriate amount of NaBH<sub>4</sub> in 500 mL of NaOH 0.075 mol L<sup>-1</sup> solution. Hydrochloric and nitric acid solutions were prepared by diluting appropriate volumes of concentrated acids in deionized water. Finally, a water standard reference material (1643e from NIST, USA) was used to further test the accuracy of the analytical procedure.

### 2.2. Instrumentation

The detection unit used was a Perkin-Elmer, model 3100 atomic absorption spectrometer. The instrument was interfaced with a DTK 286 personal computer, and programmed/controlled with Perkin-Elmer Gem (version 3.10) and 3100 EDS/3300 (version 7.10) software's. The atomizer was a quartz 'T' shaped tube heated with an air-acetylene flame. A Perkin-Elmer Lumina hollow cathode lamp was used as radiation source with detection at a wavelength of 276.8 nm, operated at 8 mA. An Orion pH meter calibrated daily with pH 4 and with 7 buffers solutions was used to measure the pH of the reaction mixture.

The manifold shown in Fig. 1 was assembled from 0.8 mm i.d PTF tubing. One Gilson Mini Plus 3 peristaltic pump and Tygon tubing of 1.52 mm i.d was used to carry the solutions. The gas-liquid separator (GLS) consisted of a glass device with glass beads (Perkin-Elmer, part No B019-3772). Reaction coil length was fixed at 8 cm.

### 2.3. Procedure

Experiments were carried out using the manifold shown in Fig. 1. TIH was generated on-line by mixing the acidified analyte solution with NaBH<sub>4</sub> solution. The volatile species was stripped from the eluent solution by the addition of a nitrogen flow and the bulk phases were separated in the gas-liquid separator and transported to the atomization cell. The one-factor-at-a-time method was employed to study the enhancements effects of the different species tested and the other reagents had on TIH generation efficiency. The optimization process was carried out in order to achieve the maximum sensitivity (absorbance) and reproducibility of the system. The main factors under study were the concentration of: enhancements reagents (Te, iodide, Rhodamine B, malachite green and crystal violet) and the concentration and type of acid (HCl and HNO<sub>3</sub>). These reagents

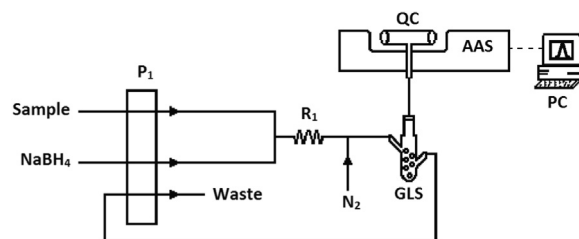


Fig. 1. Schematic diagram of the continuous flow system set up for thallium determination. P<sub>1</sub>, peristaltic pump; R<sub>1</sub>, reaction coil; QC, quartz cell; GLS, gas-liquid separator; PC, computer; AAS, 3100 atomic absorption spectrometer.

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