

Atomic Absorption**Authors:**

Sara Wei

PerkinElmer, Inc.
Shanghai, China

Direct Determination of Thallium in Water by Pre-concentration with the PinAAcle 900H GFAAS

Introduction

Thallium (Tl) has been identified to be an environmentally significant element because of its toxicity. It is considered one of the most toxic heavy metals. The minimum

lethal dose of soluble thallium salts is estimated to be 0.7 g to 1.1 g for adults with a body mass of 70 kg or 10 mg/kg to 15 mg/kg of body mass.¹ Thallium is considered a cumulative poison that can cause adverse health effects and degenerative changes in many organs.² The main threat to humans is through occupational exposure and environmental contamination.

The World Health Organization (WHO) has been discouraging the use of thallium as a rodenticide and an insecticide since 1973, however it was widely used in the last century and is still in use in some underdeveloped countries.³ Plus, industry use of thallium is widespread, mostly in specialized electronic equipment and as an additive in glass to increase its refractive index and density, a catalyst or intermediate in the synthesis of organic compounds, and a component in high-density liquids for sink-float separation of minerals. Leaching from ore processing operations is the major source of elevated thallium concentrations in water.³

Because of thallium's potential to cause adverse health effects in exposed people, a number of regulations and guidelines have been established by agencies around the world. According to U.S. EPA, the maximum contaminant level (MCL) for thallium in drinking water is at 0.002 mg/L.⁴ Canadian Council of Ministers of the Environment (CCME) regulated the guideline value for thallium in freshwater at 0.8 µg/L.⁵ The Office of Environmental Health Hazard Assessment (OEHHA) developed a Public Health Goal (PHG) of 0.1 µg/L for thallium in drinking water.⁶ In China, the thallium limit for drinking water and surface water is regulated at less than 0.1 µg/L.^{7,8} This level in drinking water indicates estimated concentration that would pose no significant health risk to individuals consuming water on a daily basis over a lifetime.⁶

Inductively coupled plasma mass spectrometry (ICP-MS) can successfully measure Tl at these levels, but it requires a high initial investment, is complex to use, and is not always widely available. Graphite furnace atomic absorption spectrometry (GFAAS) is a lower initial investment, widely used, and has proven to be a well-established technique over the years, but it is challenged with meeting the low detection limit requirements of the regulations by direct analysis. So the pre-concentration procedure is often needed. For example, an enrichment method using pre-concentration by co-precipitation with iron in ammonia medium is recommended by China EPA.⁹ However, the pretreatment process is very cumbersome, requiring large sample volumes (500 mL/sample), very slow (about 24 h/sample), and apt to have a significant amount of deviation. The need for a highly sensitive and reliable method for the determination of ultra-trace levels of thallium in water samples continues to be a challenging problem.

In order to meet the acceptance performance criteria, referring to U.S. EPA Method 200.9, samples were pre-concentrated prior to analysis by depositing multiple aliquots on the graphite tube platform.¹⁰ A method for direct analysis of ultra-trace level thallium in various water samples using GFAAS was developed without sample pretreatment. With excellent reproducibility, the method detection limit is much lower than with the traditional pre-concentration and is nearly the same as ICP-MS. The pre-concentration procedure and method validation are discussed in this paper.

Experimental

Standard Preparation and Sample Information

For the preparation of all solutions, ultrapure deionized (DI) water from a MiliQ-Element system (Millipore®, Milford, Massachusetts, USA) was used throughout. Calibration standards were prepared by serial dilutions of a 1000 ppm stock solution to yield the final concentrations shown in Table 1.

When choosing a matrix modifier for GFAAS, many factors must be considered, including potential interferences and chemical effects with the analyte of interest. Studies have shown that chloride, which is typically present in various types of water samples like waste water, surface water, drinking water, etc., can suppress the Tl signal by as much as 90% without a matrix

modifier, while thallium forms the volatile chloride and is lost before atomization. In this work, Pd/Mg was chosen as the matrix modifier which reduces the chloride suppression to less than 10%, since thallium decomposes to the more stable compound during the ash stage.¹⁰

Three types of water samples were used including drinking, surface, and waste water. Drinking water was collected from the local tap water, surface water was collected from an urban area river (connected to SuZhou Grand Canal in Jiangsu Province, China), and waste water was collected from a glass factory sewage prior to discharge to a waste water pretreatment plant. These samples represent a range of different matrices and dissolved solids and were chosen to test the effectiveness of the methodology. All samples were provided by the SuZhou city environmental monitoring station in JiangSu province, China.

Method Validation

According to the most stringent regulations, the maximum Tl content in water is 0.1 µg/L.^{6,8} In order to better simulate actual content of water samples, the GSB07-1978-2005 Environmental Reference Materials Thallium 206705 (Thallium in Water, Institute For Environmental Reference Material Ministry of Environmental Protection, Beijing, China) was diluted 320 times to give a Tl concentration less than 0.1 µg/L for method validation. For QC samples, a 1000 ppm thallium standard (General Research Institute for Nonferrous Metals, Beijing, China) was diluted.

Instrument Conditions

The measurements were performed using a PerkinElmer PinAAcle™ 900H atomic absorption spectrometer (Shelton, Connecticut, USA). The spectrometer was equipped with an AS900 autosampler, which can easily achieve the enrichment function through multiple injections into the graphite tube. A PerkinElmer System 2 Electrodeless Discharge Lamp (EDL) was used as the light source, and a standard HGA tube was used throughout for all measurements. The instrument settings and furnace temperature program are shown in Tables 1 and 2.

As seen in Table 2, two drying steps are included in the GFAAS program. These steps were used to evaporate the samples to dryness between injections, allowing for sample pre-concentration in the graphite tube. Once all five injections were complete, the last three steps of the GFAAS program were run. This sequence of events is controlled by Syngistix™ for AA software, with no need for user intervention once the Analyze button is clicked.

Table 1. Instrument Settings for the PinAAcle 900H AA spectrometer.

Parameter	Value
Wavelength (nm)	276.79
Slit (nm)	0.7
Lamp Type	EDL
Integration Time (s)	5
Signal Measurement	Peak area
Calibration Standards (µg/L)	0.1, 0.2, 0.3, 0.4, 0.5
Sample Volume (µL)	40
Number of Injections per Sample	5

Table 2. Optimized furnace program for measuring Tl in water samples using the PinAAcle 900H spectrometer.

Step		Temp (°C)	Ramp Time (sec)	Hold Time (sec)	Internal Flow (mL/min)	Gas Type
1	Drying	120	5	30	250	Normal
2	Drying	140	15	50	250	Normal
3	Pyrolysis	600	10	20	250	Normal
4	Atomization	1300	0	4	0	Normal
5	Clean out	2600	1	5	250	Normal

Results and Discussion

According to the co-precipitation enrichment method specified in HJ 748-2015, each sample requires a minimum of 24 hours of manual pre-treatment time. With the developed method of multiple injections, each sample takes only 15 minutes and is completely automated.

The calibration curve was constructed using online auto-dilution and multiple injections of a working stock thallium standard solution of 0.5 µg/L by the AS900 autosampler. As shown in Figure 1, the calibration curve has excellent linearity, with a correlation coefficient greater than 0.9999. With the optimized graphite furnace program, the peaks for standards and samples are symmetrical, and the peak time is consistent as shown in the overlay graph (Figure 2), indicating good peak productivity and no matrix interference.

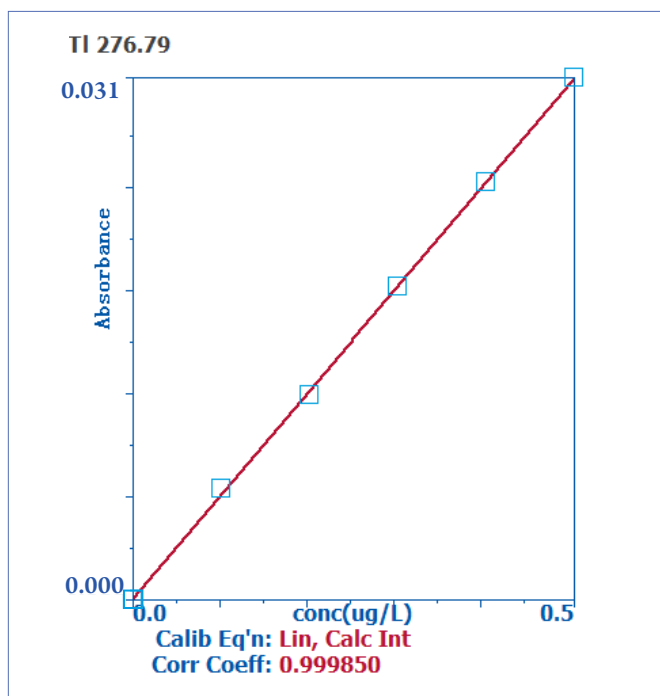


Figure 1. Calibration curve for thallium.

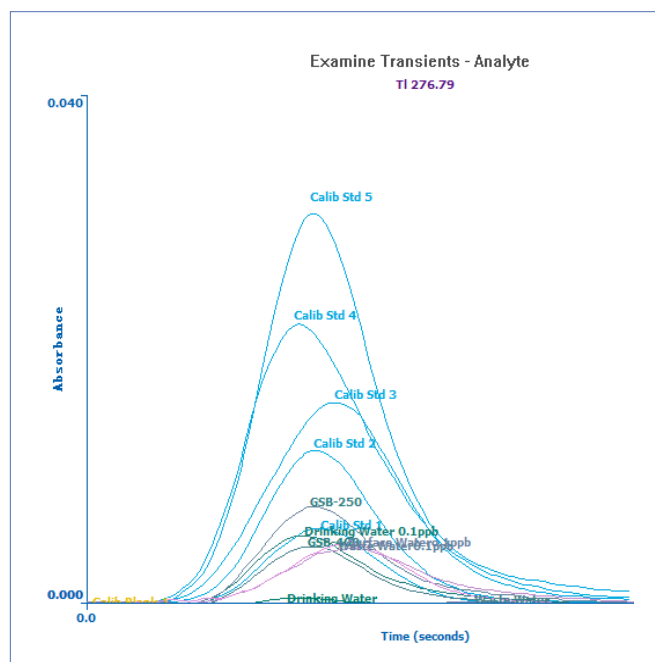


Figure 2. Overlay peaks for Tl in the calibration standards and samples.

To assess the stability of the method, four measurements were made for each standard. Table 3 displays the absorbance for each measurement, which shows excellent reproducibility, indicating that the multiple-injection on-line enrichment method is reproducible.

Table 3. The absorbance for each replicate of calibration standards.

Replicates (µg/L)	1 (Abs)	2 (Abs)	3 (Abs)	4 (Abs)	SD	RSD %
0.1	0.0067	0.0065	0.0058	0.0062	0.00039	6.2
0.2	0.0122	0.0122	0.0118	0.0121	0.00019	1.6
0.3	0.0184	0.0188	0.0187	0.0188	0.00019	1.0
0.4	0.0247	0.0250	0.0241	0.0246	0.00037	1.5
0.5	0.0309	0.0312	0.0307	0.0309	0.00021	0.7

The validity of the developed method has been ensured by incorporating quality control (QC) checks, which were analyzed directly after the calibration standards, and analysis of an environmental reference material (ERM). The QC standards gave good recovery with a variation of less than 10%, as usually prescribed by the regulatory bodies. The agreement between the certified values and the measured values were excellent, which demonstrates the accuracy of the method (Table 4).

Table 4. Results of ERM and QCs recovery studies.

QC/ERM	Certified Value (µg/L)	Measured Value (µg/L)	Recovery %
QC #1 (µg/L)	0.1	0.104	104
QC #2 (µg/L)	0.5	0.500	100
GSB07-1978-2005	25.7±1.6	25.14	98
Thallium 206705	0.080±0.005 (diluted 320 times)	0.079 (diluted 320 times)	-

Method detection limits (MDLs) were calculated based on the standard deviation of eleven replicates of 0.2% HNO₃ (Table 5). Compared with direct analysis and pre-concentration by co-precipitation analysis with GFAAS, the developed method has lower detection limits, which is nearly the same level as that of ICP-MS. The detection limits obtained show the capability of the PinAAcle 900H AA spectrometer to measure ultra-trace levels of thallium in water samples.

With the accuracy of the methodology established, the three different water samples were analyzed. The results (Table 6) show that the thallium content of all the samples is less than the method detection limit. When spiked with 0.1 µg/L TI, the recovery range for each sample is 90-98%, indicating that the enrichment process did not cause any sample loss and showed good accuracy of the method.

Table 5. Method detection limits (MDLs) comparison between different methods.

Method	MDL (3σ, µg/L)
This Work	0.014
Enrichment by Co-precipitation Analysis with GFAAS ⁹	0.03
Direct Analysis with GFAAS ⁹	0.83
ICP-MS ¹¹	0.01

Table 6. Thallium analysis of water samples by pre-concentration using GFAAS.

Unknown Samples	Result (µg/L)	Spike (µg/L)	Spike Recovery %
Drinking Water	< MDL	0.1	98
Surface Water	< MDL	0.1	90
Waste Water	< MDL	0.1	96

Conclusions

Using a PinAAcle 900H AA spectrometer combined with Syngistix for AA software, an accurate and reliable sample enrichment method for the determination of ultra-trace level thallium in water samples is described. As the standard method described in U.S. EPA Method 200.9 for sample pre-concentration in the graphite tube from multiple injections, compared with the precipitation enrichment method in HJ 748-2015[9], the developed method shortens the pretreatment time from 24 hours to 15 minutes, thereby simplifying the analysis and increasing sample throughput. This method has a low detection limit, good reproducibility, and does not result in any analyte loss after multiple injections of the sample. The result is well proven by determined values of the analytes in ERM and QC samples. It meets many global regulations for water quality control on ultra-trace level thallium detected in drinking, surface, and waste water.

References

1. Moeschlin S. Thallium poisoning. Clin Toxicol 1980; 17:133-146.
2. Cvjetko P, et al. Thallium Toxicity in Humans. Arh Hig Rada Toksikol 2010; 61:111-119.
3. Galvan-Arzate S, Santamaria A. Thallium toxicity. Toxicol Lett 1998; 99:1-13.
4. US Environmental Protection Agency (US EPA). National Primary Drinking Water Regulations.
5. Canadian Council of Ministers of the Environment (CCME). Canadian Water Quality Guidelines for the Protection of Aquatic Life: Thallium.
6. Office of Environmental Health Hazard Assessment (OEHA). Thallium Public Health Goal.
7. Ministry of Health of PRC. GB 5749-2006 Standards for Drinking Water Quality.
8. State Environmental Protection Administration of China (SEPA). GB 3838-2002 Environmental Quality Standards for Surface Water.
9. State Environmental Protection Administration of China (SEPA). HJ 748-2015 Water quality-Determination of Thallium-GFAA.
10. US Environmental Protection Agency (US EPA). Method 200.9 Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption.
11. State Environmental Protection Administration of China (SEPA). HJ 700-2014 Water quality-Determination of 65 elements-Inductively coupled plasma-mass spectrometry.

Instrument Options

Model	Part Number
PinAAcle 900H Combined Flame/Furnace AA Spectrometer	N3200073 (with TubeView™ furnace camera)
	N3200075 (without TubeView furnace camera)
Syngistix for AA Software Assembly (Standard Version)	N1010302

Consumables Used

Component	Part Number
1% Pd(NO ₃) ₂ Matrix Modifier Solution	B0190635
1% Mg(NO ₃) ₂ Matrix Modifier Solution	B0190634
Autosampler Cups, 1.5 mL, Polypropylene	B3001262 (5-pack)
	B3001264 (20-pack)
	N9300651 (40-pack)
Autosampler Cups, 1.5 mL, Polypropylene	B0087056 (1000-pack)
Autosampler Cups, 7 mL, Polypropylene	B3001567 (100-pack)
1000 ppm Thallium Standard in 2% HNO ₃	N9300170 (125 mL)
	N9300158 (500 mL)
Tl Electrodeless Discharge Lamp	N3050183
EDL Driver Assemblies	03030997

PerkinElmer, Inc.
940 Winter Street
Waltham, MA 02451 USA
P: (800) 762-4000 or
(+1) 203-925-4602
www.perkinelmer.com



For a complete listing of our global offices, visit www.perkinelmer.com/ContactUs

Copyright ©2018, PerkinElmer, Inc. All rights reserved. PerkinElmer® is a registered trademark of PerkinElmer, Inc. All other trademarks are the property of their respective owners.