

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.

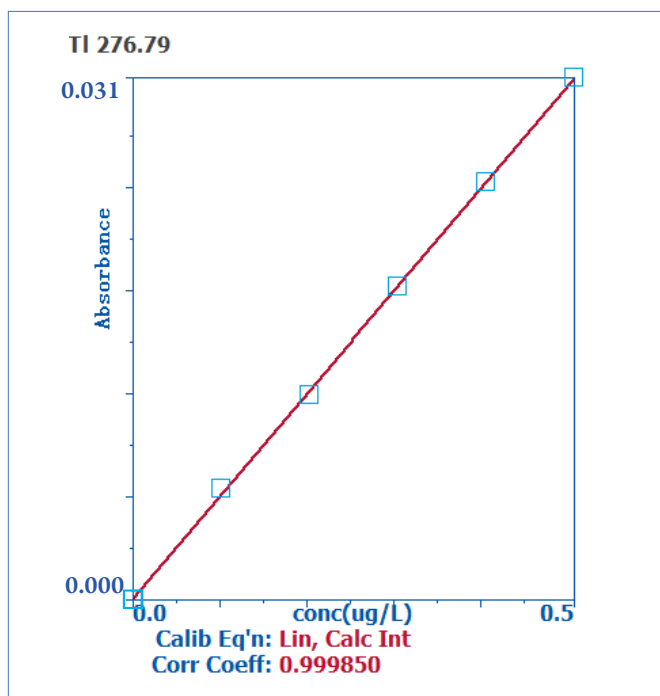


Figure 1. Calibration curve for thallium.

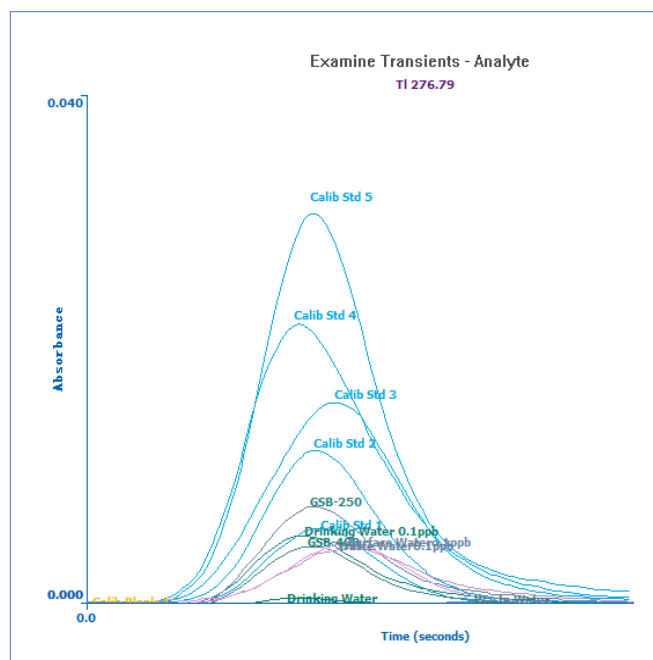


Figure 2. Overlay peaks for Tl in the calibration standards and samples.

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

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- Canadian Council of Ministers of the Environment (CCME). Canadian Water Quality Guidelines for the Protection of Aquatic Life: Thallium.
- Office of Environmental Health Hazard Assessment (OEHHA). Thallium Public Health Goal.
- Ministry of Health of PRC. GB 5749-2006 Standards for Drinking Water Quality.
- State Environmental Protection Administration of China (SEPA). GB 3838-2002 Environmental Quality Standards for Surface Water.
- State Environmental Protection Administration of China (SEPA). HJ 748-2015 Water quality-Determination of Thallium-GFAA.
- US Environmental Protection Agency (US EPA). Method 200.9 Determination of Trace Elements by Stabilized Temperature Graphite Furnace Atomic Absorption.
- 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

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