

# A Sequential Injection On-Line Column Preconcentration System for Electrothermal AAS Determination of Thallium in Geochemical Samples

Zhang-Run Xu, Shu-Kun Xu, and Zhao-Lun Fang\*  
Research Center for Analytical Sciences, Northeastern University  
Chemistry Building, Box 332, Shenyang, 110006, P.R. China

## INTRODUCTION

Environmental pollution from thallium compounds, released from fuel combustion and semiconductor production, is of increasing concern due to their high toxicity and biological accumulative nature. Since the natural concentration level of thallium in environmental samples is rather low, highly sensitive methods are required for its determination.

Despite the high sensitivity of electrothermal atomic absorption spectroscopy (ETAAS), thallium concentrations in environmental samples are usually below the quantitative limits. The direct determination of thallium usually suffers from interference from matrix constituents such as hydrochloric acid, perchloric acid, and sodium chloride (1). Therefore, before ETAAS analysis of environmental samples, separation and preconcentration of the analyte is usually required to enhance the sensitivity and selectivity. Though batch methods for separation and preconcentration are effective, the operations are usually tedious, time-consuming, and liable to contamination from the laboratory environment.

The flow injection (FI) on-line separation and preconcentration system combined with ETAAS has proved to be an effective and efficient means for enhancing the performance for the determination of trace constituents without using matrix modifiers (2,3). Ivanova et al. (4) reported a system for the

## ABSTRACT

A sequential injection system for on-line sorbent extraction preconcentration in electrothermal atomic absorption spectroscopy was developed for the determination of trace thallium in geochemical samples. The  $\text{TlBr}_4^{-1}$  complex was adsorbed on a 20- $\mu\text{L}$  micro-column (located at the tip of the furnace sampling probe) packed with XAD-8 resin. After sequentially aspirating separate zones of acetone, rinsing acid, and sample (pretreated with bromine) into a 2.5-m long, 1-mm i.d. holding coil, the flow was reversed and directed to the column. Sample loading, analyte adsorption, column rinsing and analyte elution were achieved within a single reversed syringe stroke. The adsorbed analyte was eluted into the furnace with 50  $\mu\text{L}$  acetone. Mutual mixing between sample, rinsing acid, and eluent were prevented by separating the zones with small air segments during metering. Tightening of column packing was avoided by a slight back-suction through the column after each operational cycle. With 1-mL sample loading, an enrichment factor of 15 was obtained with a detection limit of 18 ng/L thallium ( $3\sigma$ ). A precision of 2.4% RSD ( $n=11$ , 4  $\mu\text{g/L}$ ) and a sampling frequency of 11/hour were achieved. The method was applied to the analysis of geochemical samples. The results were in good agreement with the certified values of standard reference geochemical materials.

determination of thallium in sediments by ETAAS combined with a FI on-line sorbent extraction system in which thallium-APDC complex was adsorbed on the inner tube walls of a knotted reactor from a mineral acid medium. The adsorbed analyte was subsequently eluted with ethanol into the graphite furnace for detection. However, the manifold is rather complicated and may lack the robustness to operate optimally under routine conditions.

The sequential injection (SI) approach proposed by Ruzicka and Marshall (5), particularly when operated with syringe pumps, was shown to have significant advantages over FI systems in simplicity of manifold design, reliability and robustness. Recently, we developed an SI on-line column preconcentration system (6) for the ETAAS determination of cadmium in water samples. A SI system was used for the preconcentration of ultratrace cadmium with a micro-column packed with  $\text{C}_{18}$ . Considerable simplification of the manifold was achieved with significant improvement in robustness compared to its FI counterpart.

In this work, a simple and robust SI on-line preconcentration system has been developed for the ETAAS determination of trace amounts of thallium in geochemical samples in which thallium is preconcentrated in the form of  $\text{TlBr}_4^{-1}$  complex using a column packed with XAD-8 sorbent.

\*Corresponding author.  
e-mail: fangzl@pub.sy.ln.cn

## EXPERIMENTAL

### Instrumentation

A PerkinElmer Model 2100 AAS instrument (PerkinElmer Instruments, Norwalk, CT USA) was used, equipped with deuterium arc background correction, Model HGA®-700 graphite furnace, and an autosampler. A thallium hollow cathode lamp was operated at 6 mA and a wavelength of 276.8 nm and 0.7-nm bandpass. Pyrolytically coated graphite tubes were used for the measurements. Integrated absorbance was used for evaluation. Atomization peaks were recorded by high-resolution graphics with a measurement time of 5 seconds and printed out on an Epson® EX-800 printer. The graphite furnace program is shown in Table I.

The SI sample processing system used for thallium preconcentration was constructed from a Model ASD-10 sample diluter syringe pump (Bodenseewerk PerkinElmer Instruments, Überlingen, Germany) with double syringes and a Model E10-220 10-position stepper motor-operated selector valve (Valco, Houston, TX). Each pump syringe was equipped with a two-way valve at its outlet, and the plunger position programmable in 3000 steps, but only a single 5-mL syringe was used in this work. The operation of the syringe pump and valves were

synchronously controlled from a computer program written in Visual Basic.

The experimental setup is shown in Figure 1. The syringe pump and the central port of the selector valve were connected by a holding coil produced from a 250-cm long, 1.0-mm i.d., PTFE tubing (1960 µL dead volume). Four of the surrounding ports of the selector valve were connected by the shortest possible length of transport conduits made of 0.75-mm PTFE tubing to vessels containing the sample, 0.3 mol/L H<sub>2</sub>SO<sub>4</sub> rinsing acid, acetone eluent, and waste, respectively. A further port was connected to the micro-column fixed on the tip of the graphite furnace's sampling probe via a PTFE tubing of 80 cm length and 0.7 mm i.d.. The conical micro-column (1.5 cm long) was produced using the lower section of an Eppendorpf pipet tip, packed with 50-100 mesh Amberlite XAD-8 resin sorbent. The packing material was held in place with glass wool, and the packed volume was 20 µL.

### Reagents and Standard Solutions

All chemicals were of analytical reagent grade and demineralized water was used throughout.

Thallium standard solutions in the 1.0-4.0 µg/L range were

prepared daily by stepwise dilution of a stock solution of 1000 mg/L thallium using 2 mol/L nitric acid.

Saturated bromine solution was prepared by dissolving the appropriate amount of bromine in water and stored with excess bromine.

Amberlite XAD-8 resin (20–50 mesh) (Serva Feinbiochemica, Heidelberg, Germany): mesh size reduced to 50–100 by grinding and sieving.

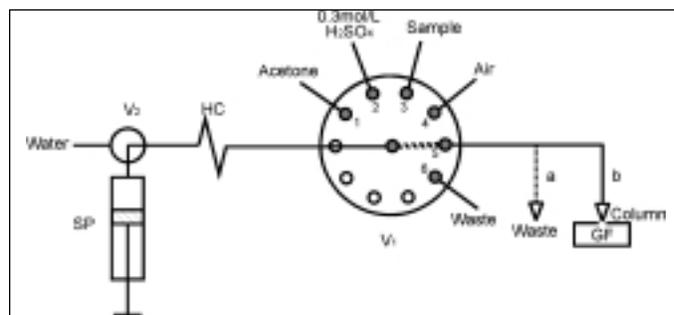
### Procedures

Before begin of the pretreatment steps, the syringe was filled with water with the two-way valve in left position. The water was expelled to waste through the selector valve with the two-way valve in right position. With this operation, the holding coil was filled with water. The sequence of operation for the column preconcentration is shown in Table II together with the function of each step of the operation. The complete procedure is composed of 18 steps, of which steps 1–9 involved the sequential metering of two acetone eluent zones, followed by zones of rinsing acid and sample solution with an air segment between each zone to avoid dispersion. The resulting sequence of the metered zones in the holding coil before sample loading is shown schematically in Figure 2. In steps 10 to 13,

**TABLE I**  
**Graphite Furnace Program**  
**for the Determination of Thallium**

Step No.	Furnace Temp. (°C)	Time (s) Ramp	Time (s) Hold	Argon (mL/min)
1	80	5	20	300
2	150	10	0	300
3	700	10	20	300
4	1200	0	3	0*
5	2200	1	3	300

\*Initiation of 5-second read cycle.



*Fig. 1. Schematic of SI-ETAAS system. SP = syringe pump; GF = graphite furnace; V1 = selector valve; V2 = syringe valve; HC = holding coil.*

the moving direction of the syringe piston was reversed. The selector valve connects the holding coil and micro-column and sequentially executes sample loading and column rinsing. In the loading and rinsing phases, the column effluent was directed to waste. The pump then aspirated additional water into the syringe with its valve in left position in preparation for transporting the eluate to the furnace, while the column tip was moved into the furnace port as shown in Figure 1 (b). The latter was done by manually swinging the sampling probe arm of the autosampler sampling probe arm, on which the column was fixed, into inject position. In step 14, the syringe valve was returned to right position and the pump

delivered the 50- $\mu$ L of the eluate zone into the furnace, which was transported by the freshly aspirated water. Water aspiration was repeated in step 15, while the column was withdrawn from the furnace. In step 16, the residual adsorbed content on the column was eluted to waste and the column rinsed. In step 17, a back suction with residual water and air flowing through the column was implemented. The last step was for rinsing of the holding coil.

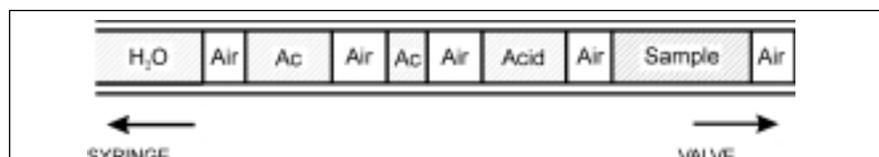
The furnace program shown in Table I for the electrothermal atomization was initiated, while another SI pretreatment cycle was initiated in parallel for the next sample.

### Method Development

Optimization of the experimental parameters was performed on the basic experimental setup described in the Instrumentation section. The length of the holding coil chosen was sufficient for accommodating the various zones introduced prior to sample loading. The pump speeds chosen in each step were the highest applicable without forming air bubbles during aspiration with non-degassed liquids. A univariate approach was adopted for the optimization of sample, eluent and rinsing solution volumes with enrichment factors (sensitivity) as the main figure of merit, but simultaneously considering sample throughput and precision.

**TABLE II**  
**Operational Sequence of SI-ETAAS System**

Sequence No.	Valve 1 position	Valve 2 position	Syringe steps moved	Volume processed ( $\mu$ L)	Time (s)	Function
1	4	right	9	15	1	Air aspiration
2	1	right	150	250	5	Acetone aspiration
3	4	right	60	100	2	Air aspiration
4	1	right	30	50	2	Acetone aspiration
5	4	right	60	100	2	Air aspiration
6	2	right	60	100	2	Washing solution aspiration
7	4	right	9	15	1	Air aspiration
8	3	right	600	1000	20	Sample aspiration
9	4	right	9	15	1	Air aspiration
10	5	right	-180	-300	18	expel water and air from transfer line to waste
11	5	right	-630	-1050	126	Sample loading,
12	5	right	-90	-150	9	Column washing
13	5	left	300	500	10	Water aspiration, insert column to GF tube
14	5	right	-69	-115	7	Elution of column and injection of 50 ml eluate into furnace
15	5	left	270	450	8	Water aspiration, take out column
16	5	right	-261	-435	26	Column 2nd elution and washing
17	5	right	120	200	4	Air back-suction
18	6	right	-447	-745	12	Holding coil washing



*Fig. 2. Schematic of sequence of zones in the holding coil before sample loading. Acid, 0.3 mol/L H<sub>2</sub>SO<sub>4</sub>; Ac, acetone eluent.*

### Sample Pretreatment

Geochemical samples of 0.1000 g were treated with 5 mL nitric acid-hydrofluoric acid mixture (7+3 v/v) in PTFE beakers. The vessels were heated on a hot plate at 140°C and gently boiled to near dryness. A further 2 mL of the acid mixture was added and the solution brought to near dryness. After cooling, the digests were diluted to 50 and 100 mL for GSS-1 and GSR-1, respectively, with 2 mol/L nitric acid.

## RESULTS AND DISCUSSION

### Considerations in System Design

Various approaches have been proposed for the preconcentration of thallium on adsorption columns, based on the adsorption of  $\text{TlBr}_4^{-1}$ -rhodamine B ion pair on polyethylene powder (7,8),  $\text{TlBr}_4^{-1}$  on polyurethane foam (9),  $\text{Tl(III)}$ -halogen complexes after ion pairing with cationic surfactants on silica gel  $\text{C}_{18}$  (10). Based on our experiences with Amberlite XAD-8 adsorbent for on-line adsorption of  $\text{AuCl}_4^{-1}$  in rock extracts (11), this adsorbent was successfully employed for the direct adsorption of  $\text{TlBr}_4^{-1}$  without ion pairing to produce a simple and efficient preconcentration system.

The SI approach was employed to improve the ruggedness of the preconcentration system. In the system described, the sample and bromine reagent were mixed to achieve complexation of the analyte with bromine before sample introduction. Mixing of the metered solution zones were avoided by introducing small air segments between the zones to prevent dispersion during metering and for transport to the column.

The column capacity of 20  $\mu\text{L}$  is too large to allow the complete elution of the adsorbed components in an eluate volume small enough to be introduced into the graphite fur-

nace using single injection. Therefore, two eluant zones were aspirated during the metering stage, separated by air segments, to achieve two elution phases. The main fraction of the adsorbed analyte (about 90%) was eluted from the column within the first elution phase in a volume readily applicable to the furnace (50  $\mu\text{L}$ ), while the analyte eluted in the second phase, after moving the column out of the furnace, was discarded.

As reported in the literature (6), in order to avoid the gradual tightening of the column packing, which gradually increases the back-pressure, a brief back-suction sequence was included after each preconcentration cycle, with residual water and air sucked through the column. We applied a similar approach in this study.

### Optimization of Ashing and Atomization Temperatures

Thallium is a volatile element that can be lost at high ashing temperatures (12). Sulphuric acid was employed as the matrix modifier to increase the pretreatment temperature to 700°C without loss in sensitivity (12). In this work, a small amount of sulphuric acid was

entrained into the sample during elution after rinsing the column with the acid. This amount proved to be sufficient to avoid analyte loss during ashing. The effects of the ashing and atomization temperatures on peak area at 700 and 1200°C, respectively, are shown in Figure 3.

### Elution Conditions

Ethanol was often used as an eluent in FI adsorbent extraction systems for the elution of metallo-organic complex (11). In this work, for the elution of the thallium-bromo complex from the XAD adsorbent, the elution efficiencies of acetone and ethanol were compared, and acetone was found to perform much better than ethanol (Figure 4 a and b). A 50- $\mu\text{L}$  amount of ethanol eluted about 60% of the analyte, while the same volume of acetone eluted 90%.

### Effects on Sensitivity

The effects on sensitivity using nitric acid, sulphuric acid and hydrochloric acid were compared. It was found that the first two acids show similar effects on sensitivity, while hydrochloric acid significantly reduces the sensitivity.

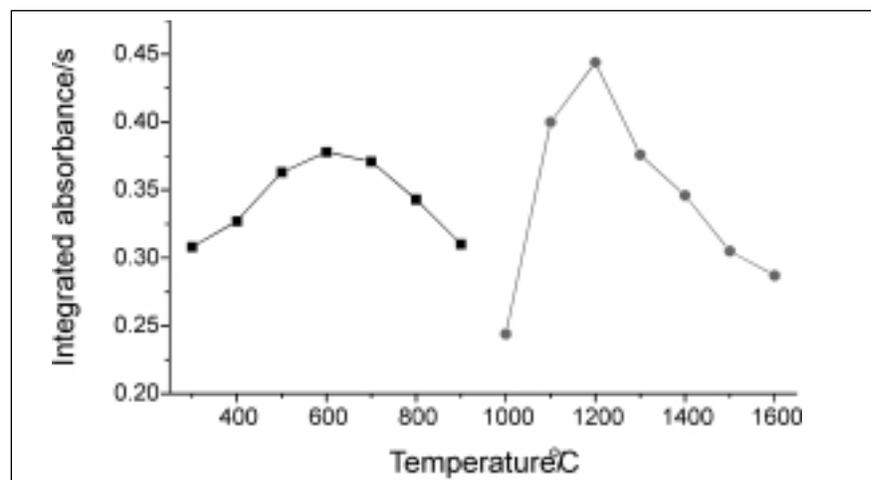


Fig. 3. Effects of graphite furnace ashing and atomization temperatures on peak area with the SI preconcentration system shown in Figure 1 and the operating conditions in Table II. Thallium, 4  $\mu\text{g/L}$ , 50- $\mu\text{L}$  eluate.

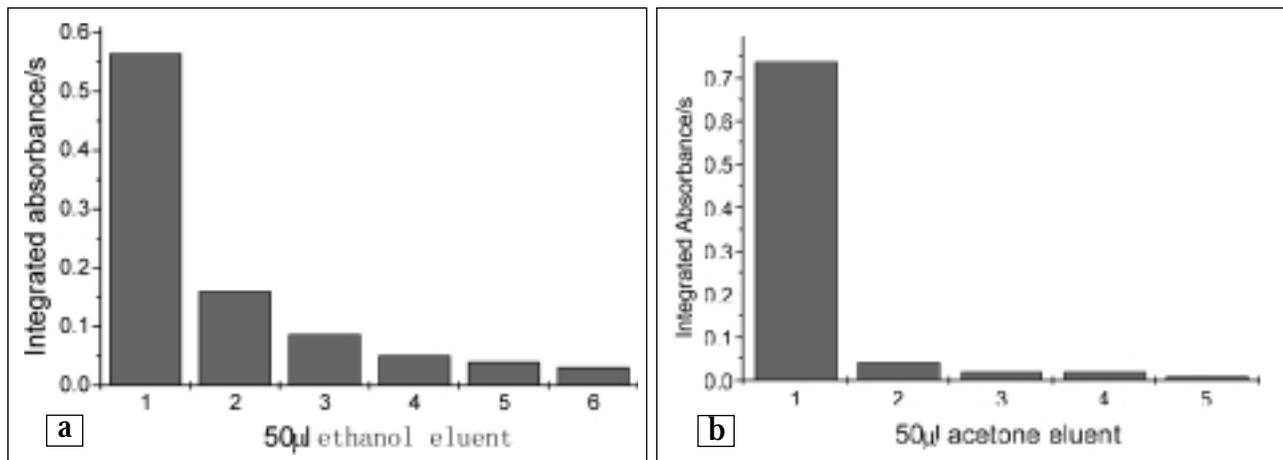


Fig. 4. Elution efficiencies of acetone and ethanol. Thallium, 10 µg/L, other conditions as shown in Figure 1, Tables I and II.

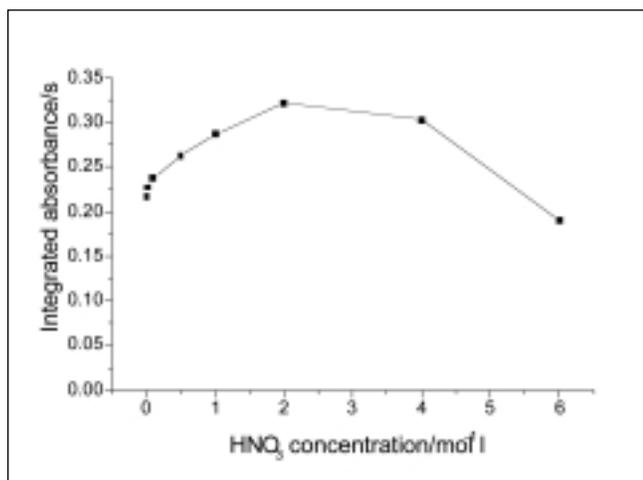


Fig. 5. Effects of nitric acid concentration in sample solutions on the peak area of 4 µg/L thallium. Other conditions as shown in Figure 1, Tables I and II.

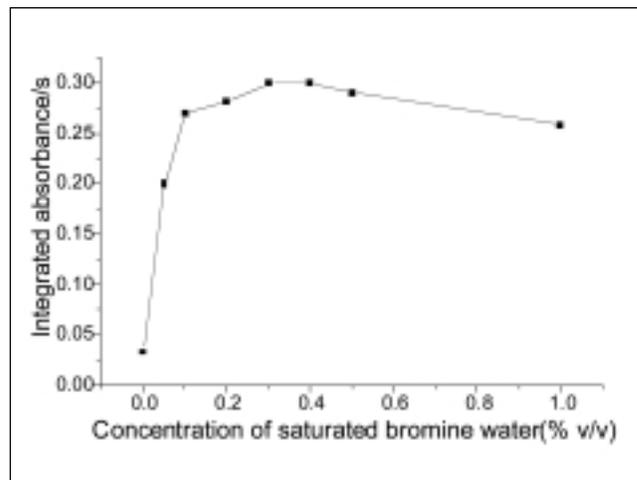


Fig. 6. Effects of saturated bromine water concentration in sample solutions on the peak area of 4 µg/L thallium. Other conditions as shown in Figure 1, Tables I and II.

The effects of nitric acid concentration on the determination is shown in Figure 5. The peak area increased at acidities below 2.0 mol/L and remained almost constant between 2.0 and 4.0 mol/L. Thus, 2.0 mol/L was chosen for further studies.

#### Optimization of Bromine Concentration in Sample Solution

Bromine oxidizes Tl(I) to Tl(III) in the sample solution, producing bromide ions to react with Tl(III) and to form the  $TlBr_4^{-1}$  complex.

The effects of the concentration of saturated bromine water solution on the peak area is shown in Figure 6. The highest sensitivity was obtained in the 0.3–0.4% range for (v/v) saturated bromine water and 0.4% was selected for further studies.

#### Rinsing Solution

The effects of water, hydrochloric acid, nitric acid, and sulphuric acid as rinsing agents for removing residual sample from the column were compared. Sulphuric acid pro-

duced the best sensitivity within a wide concentration range of 0.25–1.0 mol/L, apparently because in addition to column rinsing, sulphuric acid also acts as a matrix modifier (12) (see Optimization section). We selected 0.3 mol/L sulphuric acid for column rinsing.

#### Interference Studies

Potential interferents in geological samples were studied using a 2-µg/L thallium standard solution. The results in Table III show that a

**TABLE III**  
Investigation of Tolerance  
of Potentially Co-existing Elements

Element	Concentration (M)/(Tl) (mg/L)		Recovery (%)
Al(III)	50	25000	96
Fe(III)	50	25000	95
Mn(II)	5	2500	95
Pb(II)	2	1000	109
Cu(II)	1	500	103
Zn(II)	1	500	109
Cr(VI)	0.5	250	99
Ni(II)	0.5	250	106
Cd(II)	0.05	25	102

25000-fold Fe(III) and Al(III), 500-fold Cu(II), Pb(II), Mn(II), and Zn(II), 250-fold Cr(VI) and Ni(II), and 25-fold Cd(II) did not interfere.

#### Performance of SI Adsorption Column Preconcentration ETAAS System

A detection limit of 0.018 µg/L (3σ) thallium was obtained with 1-mL sample loading, achieving a sampling frequency of 11/hr. The precision was 2.4% RSD (n=11) at the 4-µg/L thallium level. Compared with conventional ETAAS determination of thallium without preconcentration, using a 50-µL direct injection, the sensitivity was enhanced by a factor of 15.

A regression equation  $A=0.093C+0.001$  (n=3, r=0.9998) was obtained ranging from 0–4 µg/L, where A stands for integrated absorbance (peak area) and C for concentration (µg/L).

#### CONCLUSION

The method was validated using geochemical standard reference samples, with the results shown in Table IV. The thallium concentration in these samples was not sufficiently low to take full advantage of the high sensitivity of the method described. However, good agreement between the found values and the certified values does show the general validity of the procedure.

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**TABLE IV**  
Results of Thallium Determination  
in Geochemical Samples

Samples	Certified value (µg/g)	Found value (µg/g)	Number of determinations
GSR-1	1.93	1.95 ± 0.13	10
GSS-1	1.0	0.89 ± 0.03	6

± signs = 95% confidence ranges.

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