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Tellurium speciation analysis using hydride generation *in situ* trapping electrothermal atomic absorption spectrometry and ruthenium or palladium modified graphite tubes

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ABSTRACT

Speciation of tellurium can be achieved by making use of different kinetic behaviors of Te(IV) and Te(VI) upon their reaction with sodium borohydride using hydride generation. While Te(IV) can form H_2Te, Te(VI) will not form any volatile species during the course of hydride formation and measurement by atomic absorption spectrometry. Quantitative reduction of Te(VI) was achieved through application of a microwave assisted prereduction of Te(VI) in 6.0 mol/L HCl solution. Enhanced sensitivity was achieved by *in situ* trapping of the generated H_2Te species in a previously heated graphite furnace whose surface was modified using Pd or Ru. Overall efficiency for *in situ* trapping in pyrolytically coated graphite tube surface was found to be 15% when volatile analyte species are trapped for 60 s at 300 °C. LOD and LOQ values were calculated as 0.086 ng/mL and 0.29 ng/mL, respectively. Efficiency was increased to 46% and 36% when Pd and Ru surface modifiers were used, respectively. With Ru modified graphite tube 173-fold enhancement was obtained over 180 s trapping period with respect to ETAAS; the tubes could be used for 250 cycles. LOD values were 0.0064 and 0.0022 ng/mL for Pd and Ru treated ETAAS systems, respectively, for 180 s collection of 9.6 mL sample solution.

1. Introduction

Humans are frequently exposed to tellurium as a result of its extensive usage. Tellurium species are known to have toxic effects on living organisms. Target organs of tellurium poisoning are kidneys, nervous system, lungs and gastrointestinal tract [1].

Since tellurium is present at trace levels in the environmental and biological samples, usually a preconcentration step is required for its determination. One of the preconcentration techniques is the coprecipitation of Te species with metals and metal hydroxides. Coprecipitation procedures with $La(OH)_3$ [2], $Fe(OH)_3$ [3,4], $Mg(OH)_2$, arsenic [5] and Hg collector [6] have been successfully applied.

Another preconcentration technique is use of solid phase extraction cartridge. Pedro et al. developed two methods for the preconcentration of Te [2]. In the first method, Dowex 1X8 resin was used and in the second method coprecipitation with $La(OH)_3$ followed by preconcentration with XAD resin was employed. After the preconcentration step, Dowex 1X8 and XAD columns were eluted with acetic acid and nitric acid, respectively. Eluted solutions were used for analytical determination by electrothermal atomic absorption spectrometry (ETAAS) employing Ir pretreated graphite tubes. LOD values of the two methods were 7 ng/L and 66 ng/L, respectively, for Dowex 1X8 and XAD.

An alternative preconcentration technique is the use of online *in situ* trapping of gaseous H_2Te in a preheated graphite furnace; where the volatile analyte species is generated by reaction with sodium borohydride. This technique offers high sensitivity, reproducibility, low atomization interferences and easy operation [7]. This approach is a combination of hydride generation (HG) and ETAAS and will be called as *in situ* trapping HG-ETAAS [8–10]. Extensive reviews on this subject has been presented by Tsalev [11,12].

Sensitivity of the method can further be increased by the application of high boiling point metals into the graphite tube prior to trapping. Introduction of permanent or temporary modifiers also prolongs the lifetime of the tube by allowing the application of lower trapping and/or atomization temperatures. Liao and Haug trapped H_2Te in graphite tubes that were pretreated with Zr, Nb, Ta, W, Ir, Ir/Mg and Pd/Ir permanent modifiers [13]. Among the modifiers, Ir and Ir/Mg provided the best analytical performance; it was possible to reach absolute

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detection limits of 0.011 ng (Ir coated) and 0.014 ng (Ir/Mg coated) for Se and 0.007 ng for Te with both coatings, according to peak height measurements. They also investigated the long term stability of the Ir/Mg coating and found out that coating was stable over 400 cycles.

In addition to the total tellurium determination, characterization and quantification of the element with different oxidation states is very important due to the unique behavior of these species in the surrounding environment. It is well known that Te(IV) is 10 times more toxic than Te(VI) species [14].

One of the approaches for Te speciation is chromatographic separation followed by an element specific detection technique. Kuo and Jiang used ion chromatography coupled to dynamic reaction cell-ICPMS for the separation and subsequent quantification of tellurium and selenium species [15]. They applied the developed method to urine, milk powder and rice flour samples and achieved LOD values of 0.01 and 0.08 ng/mL for Te(VI) and Te(IV), respectively.

In addition to chromatographic techniques, some nonchromatographic methodologies have been applied [16,17]. Körez et al. used a mercapto-modifed silica microcolumn for selective separation and preconcentration of Te(IV) from water samples [18]. Te(IV) was determined by direct preconcentration and elution of sample solution from a mercapto column followed by HGAAS analysis; total Te was determined by a similar procedure after the prereduction of Te(VI) species to Te(IV) in 6.0 mol/L HCl solution. Te(VI) concentration was determined as the difference between total Te and Te(IV). Cava-Montesinos et al. developed a method for the speciation of Te in milk samples by hydride generation atomic fluorescence spectrometry [19]. They used a simple procedure for the quantitative extraction of Te and Se species. Procedure involves sonication of 1.0 g of milk samples in 2.0 mL of aqua regia solution for about 10 min. Tetravalent forms of Te and Se were determined without application of a pre-reduction step and total Te and Se were determined after reduction by KBr.

Aim of the current study is to develop a sensitive and practical online preconcentration and speciation procedure for the determination of ultratrace amounts of Te. Speciation parameters were optimized by HGAAS system. Preconcentration was achieved by hydride generation and *in situ* preconcentration in a graphite tube atomizer, HG-ETAAS. Pd and Ru modifiers were studied for improving sensitivity. Analyses using HGAAS and ETAAS study were carried out for comparison.

2. Experimental

2.1. Chemicals and reagents

All reagents used throughout this study were of analytical grade or higher purity. A 1000 mg/L Te(IV) stock solution was prepared by dissolving appropriate amount of TeO_2 (Fisher Laboratory Chemical, USA) in 10% (v/v) HCl solution by the help of an Elma S40 H ultrasonic water bath (Germany). A 1000 mg/L CertiPUR Te (VI) solution prepared from H_6TeO_6 in 0.5 mol/L HNO_3 was obtained from Merck (Darmstadt, Germany). Working solutions of Te(IV) and Te(VI) were prepared daily by successive dilutions. Dilutions were made using 18 MΩ cm deionized water obtained from a Millipore (Molsheim, France) Milli-Q water purification system which was fed using the water produced by Millipore Elix 5 electro deionization system. Working standard solutions were acidified with proanalysis grade HCl (Merck, Darmstadt, Germany). Purity of the acid used was controlled routinely by comparing the blank values of stock and distilled acid obtained using a PTFE subboiled acid distillation system (Eningen, Germany). Since no blank reading was observed, acids were used directly without further purification. High purity Ar (99.999%) obtained from HABAŞ, Ankara was used throughout the study.

Working solutions were prepared in 4.0 mol/L HCl solution. Prepared solutions were transported and stored in polypropylene bottles. All glassware and plastics used throughout the study were immersed in 10% (v/v) HNO_3 for at least 24 h and rinsed with deionized water before use.

Reductant solution was prepared daily or more frequently by dissolving appropriate amount of powdered proanalysis grade $NaBH_4$ (Merck, Darmstadt, Germany) in 0.5% (m/v) NaOH (Riedel, Germany). Solution was used directly without filtration.

A 1000 mg/L Pd stock solution was prepared by dissolving solid $K_2(PdCl_6)$ in 1.0 mol/L HNO_3. 100 mg/L Ru solution was prepared by dissolving appropriate amount of solid $RuCl_3 \cdot 3H_2O$ (Aldrich) in 5.0 mL aqua regia followed by dilution to final volume.

2.2. Instrumentation and apparatus

For the optimization of hydride generation parameters, a continuous flow hydride generation system was used. All measurements were performed by the use of a Varian AA140 (Victoria, Australia) atomic absorption spectrometer equipped with a deuterium arc background correction system. Instrument was controlled and data were processed by the help of SpectrAA software, version 5.1. A Photron (Australia) uncoded Te hollow cathode lamp was used as the radiation source; 10 mA current was used. Analytical wavelength and spectral bandwidth used were 214.3 nm and 0.2 nm, respectively. For ETAAS and HG-ETAAS systems Varian PSD 120, programmable sample dispenser, was used.

Gilson Minipuls 3 (Villers Le Bell, France) 4-channel peristaltic pumps with yellow-blue color coded 1.27 mm id Tygon® peristaltic pump tubings were used for hydride generation system.

Three way T-shaped PTFE connectors (Cole Palmer, Illinois, USA) were used in junction points of solutions and gasses. PTFE connection tubings (Cole Palmer) with 0.56 mm id were used throughout the construction of system. A laboratory made cylindrical type borosilicate gas–liquid separator (GLS) with 5.0 cm long and inner diameter of 1.5 cm was placed after stripping coil. Schematic representation of HGAAS system is given in Fig. 1.

For continuous flow HGAAS system, a laboratory made quartz T-tube atomizer was used. Optical length of the T tube is 13.5 cm with an inner diameter of 1.2 cm. Formed hydrides were sent from the midpoint of the tube by the help of 8.8 cm inner diameter quartz tube inlet arm. Quartz atomizer was heated by an air–acetylene flame using a 10.0 cm burner head.

Graphite furnace studies were performed by replacing the flame assembly with Varian GTA 120 graphite tube atomizer apparatus. Measurements were performed by the help of Varian PSD 120 programmable sample dispenser. Longitudinally heated pyrolytic coated graphite tubes (VARIAN Part No 63-100012-00) were used throughout the study.

3. Procedures

3.1. ETAAS study

As recommended by the producer, the automix mode of the instrument was used. 20.0 μL of sample solution was injected and whenever necessary, it was coinjected with 5.0 μL of 1000 mg/L Pd. Temperature program given in Table 1 was followed and a transient signal was obtained.

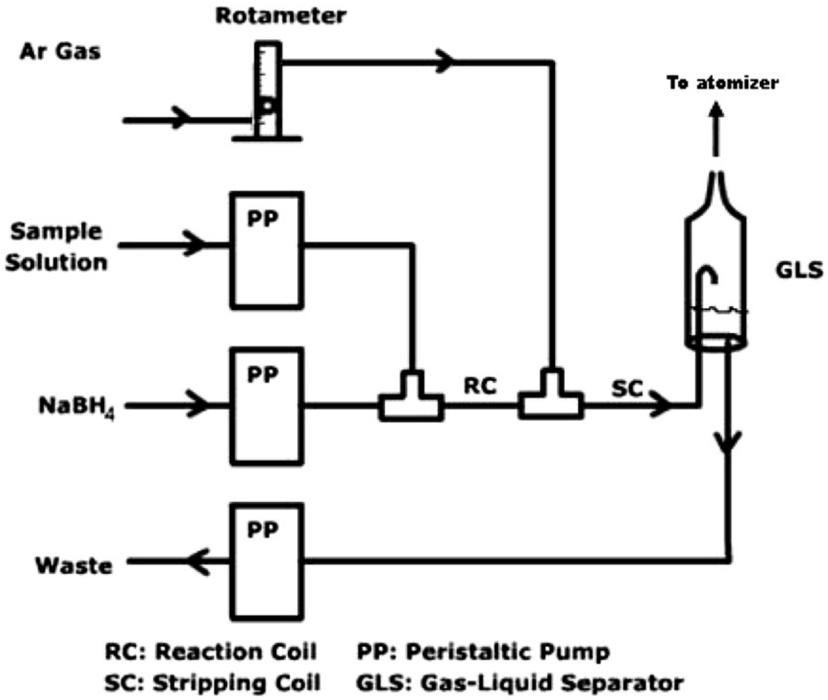

Fig. 1. Schematic representation of HGAAS system.

Table 1
Temperature program used for ETAAS studies.

Step	Function	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow (L/min)
1	Preheating	85	5.0	0	0.3
2	Drying	95	40.0	0	0.3
3	Drying	120	10.0	0	0.3
4	Ashing	Variable	5.0	3.0	0.3
5[a]	Atomization	Variable	0.7	0.8	0
6	Cleaning	2500	0.5	2.0	0.3

[a] Readings were taken at this step.

Table 2
Temperature program applied for the permanent coating of graphite tube with Ru.

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow (L/min)
1	95	5	60	0.30
2	150	5	60	0.30
3	300	5	30	0.30
4	1800	1.1	2.0	0
5	2000	0.1	2.0	0.30

3.2. *Modification of pyrolytic graphite surface*

Graphite surface of tube was modified with Ru as permanent modifier. For the coating of the surface, 50 μL of 100 mg/L Ru solution was injected into the graphite tube and complete drying–ashing–atomization cycle was applied as given in Table 2. This procedure was repeated five times to reach a total of 25 μg of the modifier deposited on the surface.

Pd was used as chemical modifier and 10 μL of 1000 mg/L solution was pre injected to the tube before each trapping cycle.

3.3. *Speciation strategy*

For the nonchromatographic inorganic speciation of tellurium, slow kinetics for hydride forming reaction of Te(VI) was used. It is well known from literature that only Te(IV) forms hydride upon reaction with $NaBH_4$ [16–19]. This principle has been used for the speciation analysis of inorganic Te. For the determination of Te(IV), samples were acidified and analyzed directly without applying a reduction procedure. For the total Te determination a reduction procedure was applied. The difference between the total Te and Te(IV) concentrations gave the concentration of Te(VI) species in the sample since Te(IV) and Te(VI) forms are known to be present as the dominant inorganic Te species in the nature [15].

For the reduction of Te(VI) to Te(IV) several procedures have been proposed in the literature [18,20–22]. Most frequently applied method is the heating of the sample in HCl solution. Open vessel reduction systems have the disadvantage that the sample and HCl loss occur during the heating step; consequently, the adjustment of acidity in the final solution is difficult. To overcome the disadvantages of open vessel reduction, a comparative study was performed.

3.4. *Microwave assisted reduction of Te(VI) to Te(IV)*

For the reduction of Te(VI) species 5.0 mL of sample solution and 5.0 mL of concentrated HCl solution were placed in the PTFE digestion bomb of microwave digestion system (Ethos Plus, Milestone). The bomb was closed and placed into the microwave oven that is operating at 700 W. First, contents are heated to 100 °C within 3 min and held at this temperature for 3 min. Following this step, temperature is further increased to 150 °C in 3 min and held for 3 min at this temperature. Following the digestion/reduction process, the sample solution was transferred to a volumetric flask using a PTFE funnel. Solutions were diluted to appropriate volume by adding acid and water so that the final solution contains 4.0 mol/L HCl.

Table 3
Temperature program applied for the *in situ* trapping of H_2Te in pyrolytic coated, Pd and Ru modified graphite tubes.

Step	Function	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow (L/min)
1	Preheating	95	5.0	5.0	0.30
2	Preheating	120	5.0	5.0	0.30
3	Trapping	300	5.0	Variable	0
4[a]	Atomization	Variable	0.5	1.0	0
5	Cleaning	2100	0.5	2.0	0.30

[a] Readings were taken at this step.

3.5. *Graphite tube trapping system*

Outlet of the GLS in hydride generation system was connected to the autosampler arm of graphite furnace. Sample and reductant flow rates and stripping Ar flow were set to optimized values for each case. Peristaltic pumps were turned on and the temperature program given in Table 3 was initiated. When the temperature was elevated to 300 °C, *i.e.* step 3, autosampler arm was manually inserted into the graphite tube through injection port and was kept inside during the *trapping* period. After the trapping step, the autosampler arm was removed, temperature was elevated rapidly to the *atomization* stage, step 4, and a transient signal was obtained. Both peak area and peak height values of the signals were collected.

For trapping of Te species in Pd modified graphite tube a slightly modified procedure was applied. Ten microliters of 1000 mg/L Pd modifier were injected into the graphite tube using a micropipette. Sample flow rate was adjusted to 3.2 mL/min and Ar flow of HGAAS system was set to 133 mL/min. After the injection of modifier, peristaltic pumps were turned on and temperature program was initiated. An initial 30 s drying step was added to the temperature program. When temperature was reached to trapping temperature, autosampler arm was placed into the graphite tube and kept there for an optimized trapping period. Then the arm was removed just before atomization step.

4. Results and discussion

4.1. *Optimization of hydride generation system*

Optimization of hydride generation system was performed in continuous flow mode. In these studies, the hydride generation AAS system described in Experimental section was employed. The optimized parameters then were modified and used for trapping system. For the optimization of $NaBH_4$ and HCl concentrations a 3-D plot shown in Fig. 2 was constructed. Analytical signal increases in general with decreasing reductant concentration and reaches a maximum at 0.5% (m/v) $NaBH_4$ concentration. This behavior can be attributed to the dilution effect of H_2 gas produced as a result of the reaction between HCl and $NaBH_4$. Best signal was observed between 0.5–1.0% (m/v) $NaBH_4$ and 3.0–6.0 mol/L HCl concentration ranges. Although 4.0 mol/L HCl and 0.5% $NaBH_4$ concentrations were selected as the optimum working concentrations for this work, it can be concluded from the data that H_2Te can be studied over a wide range of acid and reductant concentrations without any significant loss of sensitivity. This would be particularly useful for multielemental analysis.

Second step was the optimization of sample and $NaBH_4$ solution flow rates. It was observed that analytical signal was much more dependent on the sample flow rate rather than that of $NaBH_4$. This can be clearly seen from Fig. 3. To keep the sample consumption at reasonable levels, 6.5 mL/min sample flow rate was selected as the optimum value. It was also observed from the plot that increasing reductant flow rate decreased the analytical signal probably due to the dilution effect of excess H_2 formed.

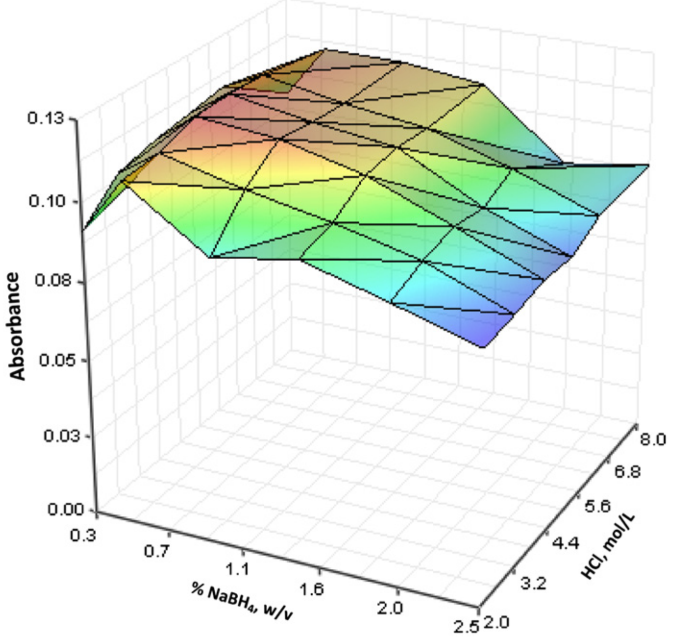

Fig. 2. Variation of continuous flow HGAAS signal with $NaBH_4$ and HCl concentrations for 20 ng/mL Te(IV) sample solution. Sample and reductant flow rates were adjusted to 2.9 and 3.1 mL/min, respectively. All other parameters are given in Table 3.

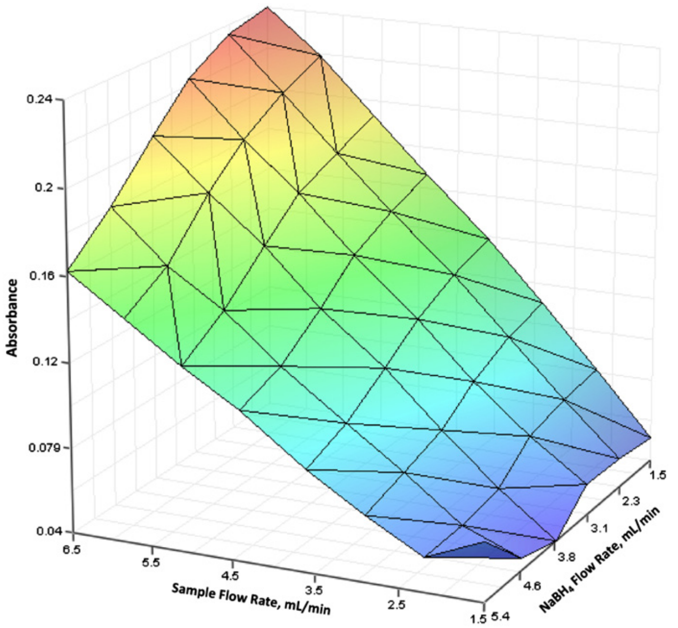

Fig. 3. Effect of sample and $NaBH_4$ flow rates on the continuous flow HGAAS signal of 20 ng/mL Te(IV) solution. Other parameters are given in Table 3.

Stripping Ar flow rate is another important parameter for the performance of the hydride generation analytical system. Lower Ar flow rates results in high signal with low reproducibility and fluctuations in signal shapes were observed. As the Ar flow rate increases, signals decreased but the repeatability of the signal was improved. Higher Ar flow rates result in low signal but high precision (Fig. 4). For the continuous flow mode 435 mL/min was selected as the optimum value. This value was varied for the

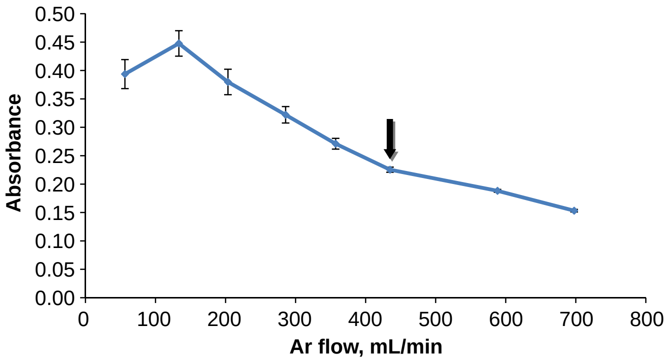

Fig. 4. Effect of stripping Ar flow rate on HGAAS signal of 20 ng/mL Te(IV) solution. Sample solution was prepared in 4.0 mol/L HCl solution and pumped at 6.5 mL/min flow rate. 0.5% (w/v) $NaBH_4$ was used at a flow rate of 1.5 mL/min.

Table 4
Optimized parameters for continuous flow hydride generation system.

Parameter	Optimum value
HCl concentration	4.0 mol/L
$NaBH_4$ concentration	0.5% (m/v)
Ar flow rate	435 mL/min
Sample flow rate	6.5 mL/min
$NaBH_4$ flow rate	1.5 mL/min
NaOH concentration	0.5% (m/v)
Stripping coil length	30 cm
Reaction coil length	30 cm

trapping system as will be discussed later in the text. Experiments showed that stripping coil and reaction coil lengths had negligible effect on signals over the range 10–50 cm. Optimized parameters for continuous flow hydride generation system are given in Table 4.

4.2. Reduction studies

As can be seen from Fig. 5, heating with 5.0 mol/L HCl was sufficient to quantitatively reduce all Te(VI) species with the given temperature program. Considering the real samples that may have highly oxidizing character, reduction in 6.0 mol/L HCl was chosen as the optimum value.

In order to see the efficiency of reduction, a set of solutions were prepared with different Te(IV) and Te(VI) contents. Solutions were analyzed using HGAAS before and after the application of the reduction procedure; the results are given in Table 5.

From the data it was observed that the significant fraction of analytical signal was originated from Te(IV) species before applying the reduction and Te(VI) was quantitatively reduced to Te(IV) with the proposed reduction technique.

4.3. Trapping temperature

Trapping temperature is one of the key parameters affecting the sensitivity of the system. Performance characteristics of untreated pyrolytic coated graphite tube, Pd pretreated graphite tube and Ru modified graphite tubes were studied; the summary of the results are given in Fig. 6.

It was observed that when a pyrolytic coated graphite tube surface was used, hydride species were efficiently trapped in a rather narrow temperature range of 200 and 400 °C. When a Pd pretreated tube surface was used, the analytical responses stay constant in a broader range of approximately 100–1000 °C. This result indicates that interaction of H_2Te with the Pd surface is strong and is not significantly affected from temperature variations. For Ru modified graphite surface, analytical response stays almost the same between 200 °C and 500 °C; an increase in analytical signal was observed for higher temperatures. Blank studies revealed that this increase was not due to an increase of the trapping efficiency but it was rather originating from a carryover effect. Most probable explanation of this behavior was that at high furnace temperatures quartz capillary, which was used for the introduction of the hydrides, was functioning as a trap since it is also heated by the tube that is in close proximity during the trapping period. Use of heated quartz surfaces for atom

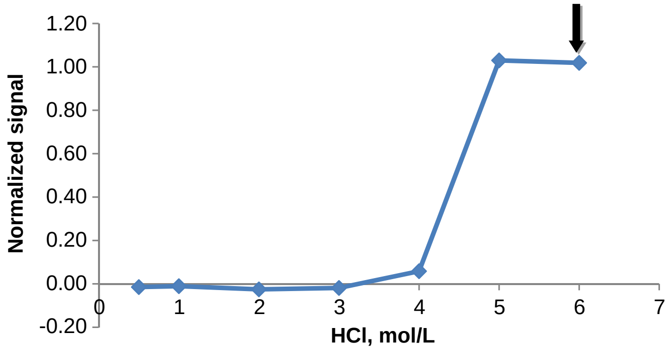

Fig. 5. Effect of HCl concentration on the reduction of 20 ng/mL Te(VI) to Te(IV) using microwave assisted reduction system. Optimized parameters given in Table 3 were used. RSD values are better than 5% for all cases.

Table 5
HGAAS results for the performance of procedure used for the reduction of Te(VI) to Te(IV).

Te(IV) (ng/mL)	Te(VI) (ng/mL)	Total Te (ng/mL)	Absorbance, HGAAS	
			Before reduction[a]	After reduction[a]
0	20.0	20.0	0.00	0.22
4.0	16.0	20.0	0.04	0.21
8.0	12.0	20.0	0.08	0.21
10.0	10.0	20.0	0.10	0.21
12.0	8.0	20.0	0.12	0.21
16.0	4.0	20.0	0.17	0.21
20.0	0	20.0	0.21	0.21

[a] RSD is 5% or lower, $N = 3$.

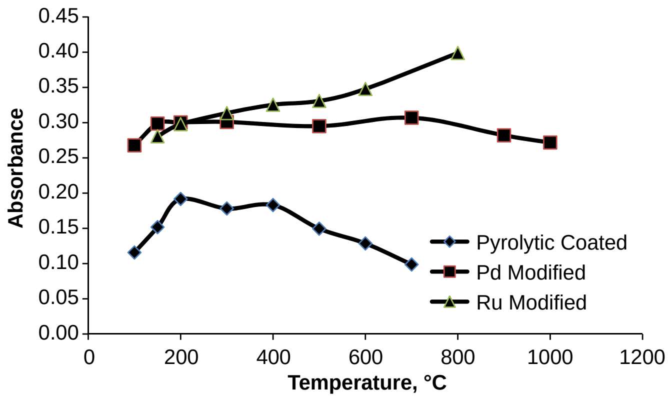

Fig. 6. Optimization of trapping temperature for pyrolytic coated, Pd modified and Ru modified graphite cuvette surfaces for HG-ETAAS; peak height values were used. Other parameters are given in Table 5. RSD values are better than 7% for all cases.

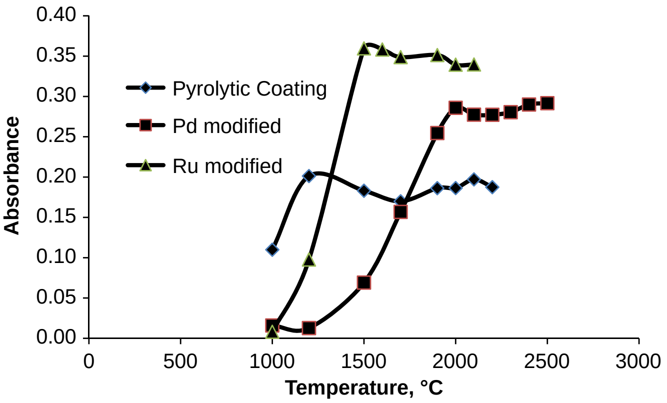

Fig. 7. Optimization of atomization temperature for pyrolytic coated, Pd modified and Ru modified graphite cuvette surfaces for HG-ETAAS; peak height values were used. Other parameters are given in Table 5. RSD values are better than 5% for all cases.

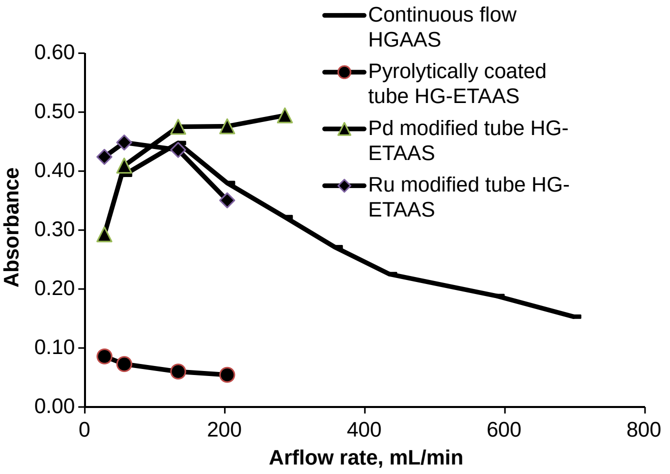

Fig. 8. Effect of Ar flow rate on the analytical signals from HG-ETAAS using untreated pyrolytic coated surface, palladium modified surface and Ru modified surface; HGAAS data are given for reference. Collection period was 60 s; concentration was 2.0 ng/mL for HG-ETAAS and 20 ng/mL for HGAAS. RSD values for trapping systems are better than 7% for all cases.

Table 6
Optimized parameters for HG-ETAAS system for three cuvette surfaces.

Parameter	Pyrolytic coated graphite surface	Pd pretreated graphite surface	Ru modified graphite surface
Stripping Ar flow rate (mL/min)	53	133	133
Sample flow rate (mL/min)	1.6	3.2	3.2
Trapping temperature (°C)	300	300	300
Atomization temperature (°C)	1900	2300	2000

trapping has been previously reported [23]. The possible trapping by the quartz capillary surface might be taking place in a way similar to these atom traps. Therefore, the trapped analyte species might have been carried over to the next measurements. This behavior was facilitated in the presence of Ru since no similar carryover effect was observed for pyrolytic coated and Pd modified surfaces. A similar effect was observed by Liao and Haug for Ir coated graphite surface [13].

4.4. Atomization temperature

Atomization temperatures for all three surfaces were studied over a reasonable range of temperature. Results are given in Fig. 7. Lowest atomization temperatures were attained with pyrolytic coated graphite surface. This is due to rather low interaction between H_2Te and the pyrolytic graphite surface. Stabilizing effect of Pd was higher than that of the pyrolytic coated and Ru modified surface. Relatively high temperature values were needed for the atomization of Te when Pd pretreated graphite tube was used. Peak shapes revealed that atomization behavior of the hydride trapping system is different than that of the ETAAS analysis (not shown here) which indicates that Te may have been deposited as different species on the surface. Signal half widths in ETAAS analysis are 1.5 times wider as compared to those by hydride trapping system.

Considering the performance characteristics of three surfaces, Ru modified surface showed the best signal with relatively low atomization temperature. This behavior does also have a positive effect on the lifetime of the tube.

4.5. Effect of carrier gas flow rate

Another important parameter was the carrier Ar flow rate during the collection-trapping stage. Different behaviors were observed for all the graphite surfaces used as seen in Fig. 8. Effect of Ar for continuous flow hydride generation system was added for comparison. Here, the two parameters, namely the residence time and the transport efficiency, compete with each other. As Ar flow rate decrease, residence time increases, hence trapping efficiency should increase since atoms spend a longer period of time in the trapping zone. On the other hand, low Ar flow rates resulted in a rather lowered transport of formed hydrides as seen from signals obtained using the continuous flow HGAAS system. Stripping Ar flow should be as low as possible to increase the residence time but it should be high enough to efficiently strip and transport the formed volatile analyte species to the trapping medium.

As shown in Fig. 8, for the untreated pyrolytic coated graphite surface, HG-ETAAS signal steadily decreased with increasing Ar flow, although transport efficiency is lower. This result indicated that residence time dominates the trapping process for pyrolytically coated graphite surface. For the Pd pretreated graphite surface, analytical signal was increasing up to 133 mL/min Ar flow. After this point, signal values reached a plateau. It could be concluded that analytical signal was dominated by transport efficiency rather than residence time for Pd pretreated graphite surface.

When permanent modification with Ru was used, the behavior was somewhat different and a mixture of both effects, residence time and transport efficiency, was observed in data. The maximum signal was obtained near 133 mL/min Ar flow rate where the two mentioned effects are optimized.

Summary of the optimized parameters for three different surfaces are given in Table 6.

4.6. Comparison of analytical performances for different surfaces using HG-ETAAS

Limit of detection (LOD), characteristic concentration (C_0) and characteristic mass (m_0) values were calculated under optimized conditions and given in Table 7. Overall trapping efficiency was calculated as the ratio of the characteristic masses of ETAAS

Table 7
Analytical performance for Te determination by HG-ETAAS using pyrolytic coated, Pd modified and Ru modified graphite cuvette surfaces.

Atomization device	Signal	LOD, N=7, ng/mL	C_0, ng/mL	[a]Overall trapping efficiency, %
Pyrolytic coated graphite tube (60 s trapping)	Peak area	0.27	0.18	15
	Peak height	0.086	0.045	17
Pd Modified Graphite tube (180 s trapping)	Peak area	0.014	0.0088	50
	Peak height	0.0064	0.0031	40
Ru Modified Graphite tube (180 s trapping)	Peak area	0.0074	0.010	33
	Peak height	0.0022	0.0025	37
Pyrolytic Coated Graphite tube, ETAAS (20 μL)	Peak area	1.7	2.1	–
	Peak height	0.49	0.61	–
Pd Modified Graphite tube, ETAAS (20 μL)	Peak area	0.57	1.5	–
	Peak height	0.17	0.44	–
Ru Modified Graphite tube, ETAAS (20 μL)	Peak area	0.59	1.6	–
	Peak height	0.17	0.43	–
Continuous flow HGAAS		0.19	0.38	–

[a] RSD is 4% or lower, $N = 7$.

Table 8
Comparison of the performances of the systems.

System	E with respect to ETAAS[a]	E with respect to HGAAS[a]	E_t with respect to ETAAS[b]	E_v with respect to ETAAS[c]
ETAAS	1.0	0.6	–	–
Continuous flow HGAAS	1.6	1.0	–	–
Pyrolytic coated graphite HG-ETAAS, 60 s trapping	14	8.4	14	14
Pd modified graphite HG-ETAAS 180 s trapping	142	122	47	15
Ru modified graphite HG-ETAAS, 180 s trapping	172	152	57	18

[a] E, enhancement, ratio of characteristic concentrations of the two methods to be compared.
[b] E_t, enhancement factor for the unit time, in units of min^{-1}.
[c] E_v, enhancement factor the unit volume, in units of mL^{-1}.

analysis and HG-ETAAS system using peak area signals. Under the optimized conditions, RSD value was calculated below 5% ($N = 7$) for all the cases. Although the method proposed in this study covers the nonchromatographic speciation for Te(IV) and Te(VI) species, a single set of LOD, LOQ and C_0 values were provided. Because, the values obtained for continuous flow HGAAS system were almost the same for Te(IV) and Te(VI). For Te(IV) and Te(VI); LOD values were 0.19 and 0.18 ng/mL and C_0 values were 0.38 and 0.41 ng/mL, respectively.

Accuracy of the method was tested by NIST 1643e "Trace elements in water" SRM. Before the analysis, reduction procedure given before was applied. Direct calibration method was used with three parallel samples. Using Student's t-test at 95% confidence level no significant difference was found between the obtained results of 1.30 ± 0.13 ng/mL and 1.17 ± 0.10 ng/mL for Pd modified and Ru modified tubes, respectively, and the certified value 1.09 ± 0.11 ng/mL.

4.7. Evaluation of system performance

Developed methods were compared in terms of sensitivity enhancement. Enhancement was calculated as the ratio of characteristic concentrations of the two methods to be compared.

Table 9
Comparison of other methods from the literature with the current study using HG-ETAAS.

Method of preconcentration/detection	LOD	Reference
Integrated atom trap AAS	0.9 ng/mL	[25]
Hollow fiber liquid phase microextraction ETAAS	4.0 ng/L	[26]
Electrodeposition-ETAAS	2.0 ng/mL	[22]
Magnetic separation-ICP-MS	0.079 ng/L	[27]
HG-AFS (no preconcentration)	23 ng/L	[19]
HG-ETAAS	0.5 pmol/L	[28]
Ru modified graphite surface HG-ETAAS	2.2 ng/L	This study
Pd pretreated graphite surface HG-AAS	6.4 ng/L	This study

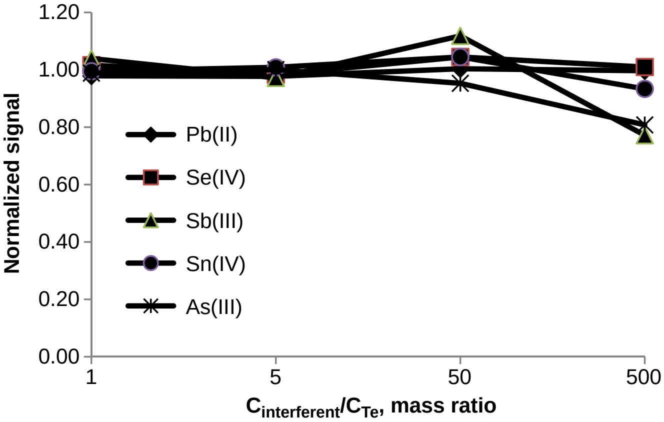

Fig. 9. Effect of hydride forming elements on the analytical signal of 50.0 ng/mL Te solution by direct ETAAS analysis.

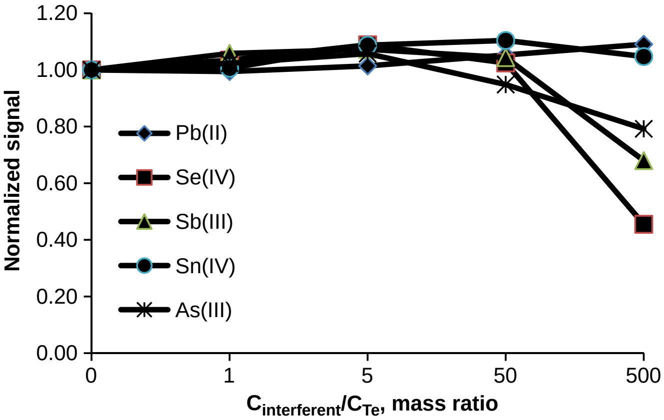

Fig. 10. Effect of hydride forming elements on the HG-ETAAS signal of 1.0 ng/mL Te(IV) solution trapped over 60 s.

In many cases, enhancement factor became insufficient for the comparison of two methods since sample consumption and/or time of integration may vary significantly from one method to the other. Since both time and sample volume involved are usually important and relevant parameters to indicate the performance of any preconcentration technique, a normalization is necessary regarding the cases where these parameters are different. Ataman suggested two novel terms that normalize the sensitivity enhancement with respect to time consumed and volume of the sample spent [24]; E_t was defined as enhancement factor for the unit time and E_v is defined as enhancement factor the unit volume where these terms have the units of min^{-1} and mL^{-1},

Table 10
Results of the spike recovery tests using *in situ* trapping HG-ETAAS.

System	Spiked (ng/mL)		Found (ng/mL)		
	Te(IV)	Te(VI)	Te(IV)	Te(VI)	Te (total)
Drinking water	0.100	0.100	0.098 ± 0.005	0.095 ± 0.012	0.193 ± 0.011
Tap water	0.100	0.100	0.109 ± 0.005	0.081 ± 0.016	0.190 ± 0.015
Sea water	0.100	0.100	0.097 ± 0.007	0.107 ± 0.014	0.204 ± 0.012
Mineral water brand 1	0.100	0.100	0.100 ± 0.011	0.091 ± 0.019	0.191 ± 0.015
Mineral water brand 2	0.100	0.100	0.095 ± 0.009	0.100 ± 0.014	0.195 ± 0.010

respectively. The higher E_t and E_v values indicate better preconcentration performance regarding the unit time and unit sample volume, respectively. The relevant results are given in Table 8.

We can conclude from the values in Table 8 that Ru modified graphite surface has the highest overall efficiency among the others. In addition, there is no need for high temperature cleanup stage as in the case of Pd modified surface. Therefore, the overall lifetime of the tube is higher. Under optimized conditions, Ru coating is stable over 250 cycles with 10% performance lost after this limit. Recoating of the surface regenerates activation.

Comparison of the developed system with other systems from literature is given in Table 9.

4.8. Interferences

To see the interference effect of hydride forming elements, Te solutions were prepared in 1:1, 1:5, 1:50 and 1:500 mass ratios of analyte/interferent for As(III), Sb(III), Pb(II), Se(IV) and Sn(IV) ions. For direct ETAAS system 50 ng/mL Te was used and 1.0 ng/mL Te was used for HG-ETAAS system. Results for direct ETAAS analysis and hydride generation *in situ* trapping AAS (HG-ETAAS) are given in Figs. 9 and 10, respectively.

It was observed that in the presence of As(III) the Te signal was reduced by around 20% at 500 fold excess of interferent for both ETAAS and HG-ETAAS cases. In the presence of Se(IV), Te signal was reduced only for HG-ETAAS case which implies liquid phase interference rather than gas phase interference. Another observation was that Sb(III) caused a decrease in the peak height signal by 20% for direct ETAAS and about by 30% for hydride trapping case. However, peak area values were not affected for both cases. Since splitting of the peaks was also observed, the presence of different analyte species may be suggested. Most probably Sb partially forms an alloy with Te on the graphite surface and thus the atomization profile was altered.

In addition to common hydride forming elements, effect of Al, Ca, Cd, Cr, Fe, Hg and Mn was studied. None of these elements caused significant interference on the analytical signal of Te within the range studied up to 500-fold excess.

4.9. Analysis of samples and recovery studies

Among the methods developed, using Ru modified graphite tube was selected as the easiest method and sea water (Marmaris, Turkey), drinking water (Bursa, Turkey), tap water (Middle East Technical University Campus, Turkey) and commercially available mineral water samples were analyzed by this method. In the samples analyzed neither Te(IV) nor Te(VI) was detected. In order to show the applicability of the method, a series of spike recovery tests were performed. Results are given in Table 10. Te(IV) amounts were determined by direct analysis of samples without applying a prereduction step. Total Te was determined after the application of a prereduction step. Te(VI) was determined as the difference between total Te and Te(IV). Three parallel samples were analyzed.

5. Conclusion

HG-ETAAS *in situ* trapping of H_2Te in pyrolytic coated, Pd modified and Ru modified graphite surfaces was demonstrated to be an efficient method for the determination of ultra trace levels of Te. It was observed that trapping efficiency of Pd modified and Ru modified graphite surfaces are better as compared to untreated pyrolytic coated graphite surface. This result was attributed to the stabilizing effect of Pd and Ru on Te. Pd modified graphite tube exhibits better resistance to variations in Ar flow regarding trapping efficiency as compared with the other two.

Developed methods were applied for the speciation of Te in several water matrices. No Te was detected in the samples studied. A recovery study was performed and good recovery values were obtained for sea water, drinking water, tap water and mineral water samples.

As a conclusion, developed method offers a highly sensitive and low cost method for the speciation of Te in water samples. This is especially useful for laboratories where rather costly hyphenated speciation systems, such as HPLC-ICPMS, are not available. Results demonstrate that developed method is compatible with other methods in literature.

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