



Valence properties of tellurium in different chemical systems and its determination in refractory environmental samples using hydride generation – Atomic fluorescence spectroscopy



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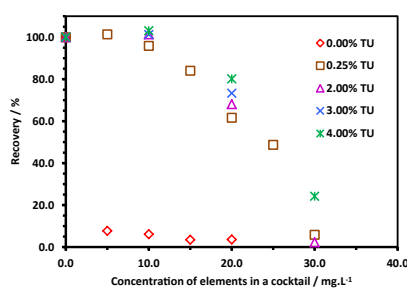
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HIGHLIGHTS

- HG–AFS is a powerful tool in studies of chemical valences and forms of Te in different conditions.
- Te can be lost in form of volatile species in presence of HCl at high temperature.
- Metal ions can be classified into 3 categories of interference; thiourea can effectively mask Cu^{2+} .
- A 2-step digestion allows to eliminate HF, reduce background and improve analytical precision.
- Matrix of sample can strongly influence Te chemical valence of Te and a pre-reduction is necessary.

GRAPHICAL ABSTRACT



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ABSTRACT

Using HG – AFS as a powerful tool to study valence transformations of Te, we found that, in presence of HCl and at high temperature, Te can form volatile species and be lost during sample digestion and pre-reduction steps. It was also noticed that the chemical valences of Te can be modified under different chemical and digestion conditions and even by samples themselves with certain matrices. KBr can reduce Te(VI) to Te(IV) in 3.0 M HCl at 100 °C, but when HNO_3 was >5% (v/v) in solution, Br_2 was formed and caused serious interference to Te measurements. HCl alone can also pre-reduce Te(VI) to Te(IV), only when its concentration was ≥ 6.0 M (100 °C for 15min). Among 10 studied chemical elements, only Cu^{2+} caused severe interference. Thiourea is an effective masking agent only when Cu^{2+} concentration is equal or lower than 10 mg/L. Chemical reagents, chemical composition of sample, as well as the modes of digestion can greatly affect Te valences, reagent blanks and analytical precisions. A protocol of 2–step digestion followed by an elimination of HF is proposed to minimize reagent blank and increase the signal/noise ratios. It is important to perform a preliminary test to confirm whether a pre-reduction step is necessary; this is especially true for samples with complex matrices such as those with high sulfide content. The analytical detection limits of this method in a pure solution and a solid sample were 100 ng/L and 0.10 ± 0.02 $\mu\text{g/g}$, respectively.

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1. Introduction

Tellurium (Te) is an element of very low abundance in the Earth's crust, at approximately $1\text{--}2 \times 10^{-9}$ g/g which is about 45–90 times lower than that of its close neighbor selenium [1], but similar to those of rhodium and rhenium. It is perhaps for this reason that this element has received so little attention in environmental studies and by analysts. Not only its health effects and biogeochemical behavior in environmental are scarcely known compared to Se, its chemical behavior in different systems is also poorly documented. Tellurium is widely used in photoelectrical devices, such as solar panels, infrared sensitive semiconductor materials and detectors, and the demand for Te increases sharply as more applications are found [2]. Tellurium has also found its ways in the areas such as metallurgy, anticancer function and drug development [3,4]. In studying a Te-tolerant fungus, Ramadan et al. [5] found that Te was incorporated in several types of proteins, detected as telluro-cysteine, telluro-cystine, telluro-methionine, and serine, indicating the possible involvement of this element in living systems. As the list of Te application grows, the potential risks in ecosystems also increases.

Tellurium exists in several oxidation states from the lowest reduced state (-II) as hydrogen telluride (H_2Te) to the higher oxidation states of tellurite TeO_3^{2-} (IV) and tellurate TeO_4^{2-} (VI). In 1997, D'Ulivo [6] wrote a comprehensive review on the determination of selenium and tellurium in environmental samples. The studies related to Te were then scarce compared to those of Se and this situation has not yet been improved since. Tellurium is considered as a difficult element to determine because of its lower instrumental sensitivity and a generally very low abundance in environmental samples. Inductively-coupled plasma – mass spectrometry is explored for the determination of Te. Casiot et al. [7] have demonstrated the possibility to determine Te(IV) and Te(VI) with capillary electrophoresis hyphenated with ICP – MS; however, the detection limits for both species (around 60 $\mu\text{g/L}$) are too high to be applicable to most real environmental samples. Other Te speciation methods, using ICP-MS as a detector, include specific retention of Te(IV) – pyrrolidine dithiocarbamate by C18 sorbent [8] and separation of Te(IV) and Te(VI) by ionic chromatographic column [9] prior to determination.

More studies have been carried out with electrothermal atomic absorption spectrometry combined with hydride generation [10–14]. Pre-concentration of hydride H_2Te by trapping on a Pt-coated W coil [13] and on ruthenium or palladium modified graphite tube [14] has greatly increased the sensitivity of the methods (limit of qualification 0.29 $\mu\text{g/L}$). Using the difference in redox potentials between Te(IV) and Te(VI) in formation of alloys with Hg electrode, Ghasemi et al. [15] achieved Te speciation by removing Te(IV) prior to measuring Te(VI) remaining in solution. The same research group [16] later used hollow fiber liquid phase micro-extraction based on the selective complexation between Te(IV) and ammonium pyrrolidine carbodithioate (APDC) to pre-concentrate Te and greatly decrease the detection limit (4 ng/L) while also performing Te speciation. To increase sensitivity, on-line solid phase extraction [17] and co-precipitation with various sorbents was also investigated [18,19]. However, any pre-concentration processes inevitably increase the complexity of the analytical work and possibly introduce analytical variations and errors.

Hydride generation coupled to atomic fluorescence spectroscopy (HG-AFS) is a more attractive technique to measure Te because of its high selectivity and sensitivity, and low cost in terms of instrumentation and operation. Unlike selenium, one of the most investigated hydride forming elements [20–23], studies on chemical behavior of tellurium in HG-AFS system have received little attention. D'Ulivo's research group [24] has provided evidence on

self-interference of Te and reported that KI could effectively eliminate this interference thus, improve dynamic range and at the same time reduce the concentration of sodium borohydride. In a complementary study [25], they showed that the combination of thiourea and KI in the analytical solution could effectively reduce the interference of foreign elements, but unfortunately, this system also strongly enhanced the rollover of Te calibration curves. Cava-Montesinos et al. [26] have studied optimal instrumental conditions, interference and effect of ascorbic acid on the determination of total Te and Se in milk with HG-AFS.

Among the studies related to Te determination by HG-AFS, only very few are related to refractory samples [25,27] and too little information is provided on the chemical valence of Te in different digestion systems. To dissolve refractory samples, high temperature and strong oxidative and destructive chemicals such as HNO_3 , HClO_4 , HF and HCl are often used in wet digestion techniques. It is therefore possible that Te is transformed to Te(VI) or other species rather than as Te(IV) under such harsh conditions, thus making a pre-reduction necessary. A detailed and systematic study on the chemical behavior of Te in analytical processes is essential for the quality of its determination.

2. Experimental

2.1. Reagents, solution preparation and instrumentation

Tellurium dioxide (TeO_2 , Aldrich 99+%) and telluric acid (H_6TeO_6 , Aldrich, 97.5–102.5%) were used to prepare standard solutions of Te (IV) and Te(VI), respectively. Sodium tetrahydroborate was purchased from Sigma-Aldrich (reagent grade >98.5%). Sodium hydroxide and hydrofluoric acid (28 M) were ACS grade, and hydrochloric acid (12 M), nitric acid (15 M) and perchloric acid (12 M) were Trace Metal grade from Fisher Scientific. The concentrated acids were used in all digestion tests. The masking agents were from The British Drug Houses Ltd. In the interference study, all standard solutions (Ni^{2+} , Co^{2+} , Cu^{2+} , MoO_4^{2-} , Mn^{2+} , Cr^{3+} , CrO_4^{2-} , Pb^{2+} , Fe^{3+} and Zn^{2+}) were prepared from their corresponding atomic spectroscopy standards of 10000 mg/L or salts. Te(IV) and Te(VI) standard stock solutions of 1000 mg/L (as Te) was dissolved in few milliliters of 12 M HCl or 15 M HNO_3 , respectively; then filled up with de-ionized water (DW) to obtain a final HCl or HNO_3 concentration of 3.0 M, respectively. They were stored in HDPE (high density polyethylene) bottles and kept in a refrigerator. The working standard solutions were prepared daily. A 0.7% (w/v) sodium tetrahydroborate solution was prepared in 0.1 M NaOH and it is stable at 4 °C for at least 1 month.

A Milestone Ethos 1600 URM, HPR 1000/10 (Bergamo, Italy) microwave (MW) digestion system was used for Te(VI) pre-reduction and digestion tests. A PSA 10.055 Millennium Excalibur equipped with a flow through injection –HG-AFS and a boosted Te Photron Super lamp was used. Instrumental working conditions included: sample flow rate 7.5 mL/min, NaBH_4 flow rate 4.5 mL/min, carrier solution 3.0 M HCl, argon inner pressure 30psi, carrier gas 300 mL/min, drying gas (Ar) 2.5 L/min, H_2 flow rate 120 mL/min, primary lamp current 15 mA, boost lamp current 15.7 mA. Delay, analysis and memory time were 13, 20 and 28 s, respectively. Peak height was recorded and signal magnification was 100.

2.2. Studies on species transformation of Te under different chemical conditions

2.2.1. Formation of volatile Te species

The potential loss of Te as volatile species was studied in a 3.0 M HCl medium under specific MW conditions, in which ten 25.00-mL aliquots of 10 $\mu\text{g/L}$ Te(IV) were equally divided into Group A and

Group B. As soon as the MW program was terminated (23 → 110 °C in 10min, at 110 °C for 10min and vented for 20min), the solutions in Group A were transferred in polypropylene tubes one after another, whereas the solutions in Group B were allowed to cool down thorough in an ice bath before being transferred. Te in these samples was determined by HG-AFS without further treatment.

2.2.2. Chemical valence transformation of Te under various digestion conditions

2.2.2.1. Te(IV) transformation in a closed microwave system ($Te^{IV}MW$). In a MW vessel containing an aliquot of 5.8 mL HNO_3 –1.7 mL $HClO_4$ –1.0 mL HF, or 3.0 mL HNO_3 –5.0 mL HCl –1.0 mL HF, 5.00 and 10.00 μg of Te(IV) standard solution were pipetted and microwaved (23 → 85 °C in 9min, 85 → 190 °C in 8min, kept at 190 °C for 20min and vented for 20min). After a thorough cooling, the digest was filled up to 50.00 mL with DW. An aliquot of this digestion was further diluted 50 times with 3.0 M HCl and Te was measured directly. Another aliquot of the digest with the same dilution was subjected to a pre-reduction step (see 2.3) before measurement.

2.2.2.2. Te(IV) and Te(VI) transformations in an open vessel digestion system ($Te^{IV}OV$). An aliquot of 25 μg standard solutions of Te(IV) or Te(VI) was pipetted into a 50 mL PTFE (polytetrafluoroethylene) beaker containing either (I) 5.0 mL HNO_3 –3.0 mL HF–2.0 mL $HClO_4$ or (II) 2.0 mL HNO_3 –5.0 mL HCl –2.0 mL HF. For digestion system I, the heating condition was 250 ± 20 °C for 50min, including a 25min fuming to remove HF. For digestion system II, the samples were heated at 180 ± 20 °C for 1h40min. Both the digests were filled up to 50.00 mL and stored in 10% (v/v) HCl. All the digestion tests were in duplicate. Te was determined in a 3.0 M HCl matrix after 50 times dilution without pre-reduction.

2.2.2.3. Chemical valence of Te(IV) in aqua regia under MW condition ($Te^{IV}ARMW$). To check whether some Te(IV) can be transformed to Te(VI) by aqua regia under MW heating, a test was carried out with 25.00 μg of Te(IV) in 2.0 mL HNO_3 –6.0 mL HCl and subjected to a MW program at a temperature of 170, 190 and 210 °C, respectively for 20min with a 5min preheating and 20min venting at the end. The samples were measured in 3.0 M HCl after an appropriate dilution without further treatment.

2.3. Studies on Te(VI) pre-reduction, metal ion interference and masking agents

Several commonly used reducing reagents, including KI (0.60 M), KBr (0.40 M), ascorbic acid (0.28 M) and oxalic acid (0.56 M), were first tested with a solution containing 60 $\mu g/L$ of Te(VI) at 20–22 °C for 24 h and their potential as reducing agents was evaluated. KBr was selected for further test with 10.0 $\mu g/L$ Te(VI) in 3.0 M HCl at different MW temperatures. The interference from HNO_3 in an analytical solution containing KBr at high temperature (110 °C, 10min) was also studied in a MW condition.

Pre-reduction tests of Te(VI) by HCl alone in a MW oven were conducted with 10, 30 and 50 $\mu g/L$ Te(VI) in different HCl concentrations, at different temperatures and for different times. The thorough cooling was performed before a vessel was opened. To test the adaptability of pre-reduction conditions in real samples, spiking standards of Te(VI) into refractory samples before the digestion was also performed.

The potential interferences of commonly encountered elements were studied with 10 $\mu g/L$ standard Te(IV) and different concentrations of foreign ions in 3.0 M HCl. To eliminate severe interference caused by Cu^{2+} , several potential masking agents such as 8-hydroxyquinoline, 1, 10-phenanthroline hydrate and thiourea

were examined.

2.4. Solid sample digestion

Refractory samples used in this study were a sediment sample from McFarlane Lake (Sudbury, Ontario) and a tailing sample from a tailing disposal field (Vale Canada Limited, Sudbury). Both samples were ball mill ground into very fine powders.

2.4.1. Solid sample digestion in a closed MW vessel (SSMW)

In this digestion test, 3 portions of 0.5000 g of sediment sample were weighed and spiked with 0.00, 5.00, and 10.00 μg of Te(IV), respectively. An aliquot of the mixed concentrated digestion acids of 5.8 mL HNO_3 –1.7 mL $HClO_4$ –1.0 mL HF or 3.0 mL HNO_3 –5.0 mL HCl –1.0 mL HF was added. The MW program was set at 190 °C for 20 (or 25) min with a pre-heating of 22 → 85 °C in 10 min, then to 190 °C in 10min and a 20min venting at the end. The digest was filled up to 50.00 mL with DW. The solution was diluted 50 times and measured directly in either 3.0 M HCl alone or a 3.0 M HCl –0.02 M H_3BO_3 matrix.

2.4.2. Solid sample digestion in an open vessel system (SSOV)

The tests were done in a 2-step digestion scheme: 0.3000 g of sediment (or tailings sample) was precisely weighed in quadruplicate and transferred into a 120 mL PFA (perfluoroalkoxy) digestion vessel where 0.00, 5.00, 10.00 and 20.00 μg of Te(IV) or Te(VI) was added respectively. In the first step, an aliquot of mixed acids (5.0 mL HNO_3 – 2.0 mL $HClO_4$) was added and the lid was loosely capped. The sample was digested at 170 °C for 1 h, then at 210 °C for 30min. In the second step, 3.0 mL HF was added and the lid was tightly closed and the digestion was continued at ca. 200 °C for one hour. When cooled down and with the lid open, the digest was heated at 210 °C for another 1h15min until nearly dried to eliminate HF. The digest, completely digested, was filled up to 50.0 mL with DW. One aliquot of 0.5 mL of the digest was diluted to 20.0 mL with 3.0 M HCl and analyzed directly by HG-AFS. Another aliquot of 0.5 mL of the digest was pre-reduced in 6.0 M HCl in MW before being measured.

2.4.3. Digestion of a certified sediment sample GBW07312 (SSCRM)

The 2-step oven vessel digestion was applied on the certified sediment sample GBW07312 and 0.2500 g of the sample was weighed in 6 replicates. In 3 of them, an amount of 0.15, 0.30 and 0.6 μg Te(VI), was spiked respectively, whereas the other three aliquots were non-spiked. Briefly, an aliquot of mixed acids (4.5 mL HNO_3 –1.7 mL $HClO_4$) was added first, the sample was digested for 1h30 min at ca. 200 °C. Then, 2.5 mL of HF was added and digested for an additional 2-h at 200–210 °C with the lid tightly closed. At the end, the excess of HF was evaporated (200 °C, 1 h). The digest was leached back and filled up to 25.0 mL with DW. The digest of 3 times dilution was pre-reduced by MW in 6.0 M HCl before the measurement. Analytical time of the instrument was set at 30sec due to a higher viscosity of this less diluted solution. A sand bath was employed in all open vessel digestion studies.

To facilitate the comparison to readers, sample treatment codes and brief descriptions of their experimental conditions are presented in Table 1.

3. Results and discussion

3.1. Studies on transformation of Te species under different conditions

3.1.1. Formation of volatile species in presence of HCl

It is known that, in presence of chloride ions, Se can form

volatile species and be lost under high temperature in a graphite furnace atomic absorption spectrometer and in a pre-reduction step. As a close neighbor, Te possesses many similar chemical properties as Se, thus could also form volatile chloride species.

A test in a 3.0 M HCl matrix and at 110 °C MW condition showed that, as the vessel temperature dropped from 60 °C at the end of MW program to room temperature (Group A), the loss of 10 µg/L of Te(IV) also dropped from 17.4, 12.1 and 3.7% compared to the average peak height measured in Group B (AVG = 149.6, SD = 2.04). As the operation proceeded to the 4th and 5th aliquots in Group A, the temperature of the digestion vessels had significantly dropped, thus no further loss was observed.

The formation of a volatile TeCl₂ species at an elevated temperature had been long suspected [28]. However, our results show that only a small fraction of Te(IV) was lost even in an open vessel system heated on the hot plate up to 200 °C for an extended period of time (Table 2). It is speculated that only lower isotopes of Te, such as ¹²⁰Te, ¹²²Te, ¹²³Te, ¹²⁴Te and ¹²⁵Te, could form volatile species, whereas the heavier ones, such as ¹²⁶Te, ¹²⁸Te and ¹³⁰Te, adding up to 84.7%, could not. Although all isotopes of the same element are expected to have exactly the same chemical properties, some difference in chemical reactivity has been observed before, where it was found that lighter isotope of ⁷⁶Se(VI) in suspension was preferentially consumed by green rust Fe(II) – Fe(III) compared to ⁸⁰Se(VI) in a reduction reaction from Se(VI) to Se(0) [31]. Further studies with Te isotopes should be performed to verify this hypothesis.

Nevertheless this loss would become more pronounced when the concentration of Te is very low in samples. Therefore the use of HCl in an open vessel digestion is not recommended. Furthermore, sample transfer in pre-reduction in 6.0 M HCl should be performed only when vessels are completely cooled down.

3.1.2. Chemical valence transforms of Te under various digestion conditions

3.1.2.1. Te(IV) transformation in a closed MW system (Te^{IV}MW).

In a chemical system of 5.8 mL HNO₃–1.7 mL HClO₄–1.0 mL HF, 5.0 and 10.0 µg of spiked Te(IV) were not found in any of these samples without a pre-reduction and even after a pre-reduction step, only about 15% of 10 µg Te(IV) was recovered (SD = 4.5%). However, in a 3.0 mL HNO₃–5.0 mL HCl–1.0 mL HF system, the spiked Te(IV) was recovered, but the analytical variability was very high, particularly when H₃BO₃ was not used. A further study with sediment samples (SSMW) is given below.

3.1.2.2. Te(IV) and Te(VI) transformation in an open digestion system (Te^{IV,VI}OV).

In an open vessel digestion system, the final valence of spiked Te(IV) appeared very different from that of a pressurized MW vessel. In the acid mixture I (HNO₃–HF–HClO₄), even under a very high temperature and strong oxidative conditions, the spiked Te(IV) was completely recovered without pre-reduction, meaning that neither formation of volatile Te species nor that of Te(VI) had occurred. However, in the acid mixture II (HNO₃–HCl–HF), about 12% of spiked Te(IV) was lost, which further confirmed the formation of volatile Te compound observed in 3.1.1. In both chemical systems, only a minor percentage of the spiked Te(VI) was measured without a pre-reduction, suggesting that the majority of spiked Te(VI) still remained as Te(VI) (Table 2).

It is interesting to note that in a pressurized vessel (Te^{IV}MW), only 15% of spiked Te(IV) was detected in the HNO₃–HClO₄–HF system even after a pre-reduction, whereas in an open vessel system a total Te(IV) recovery was found without pre-reduction. This indicates that under pressurized conditions, Te(IV) was not simply converted to Te(VI). It is likely that under such a condition, ClO₄[–] and F[–] could have reacted with some Te(IV) and formed a chemical compound inactive to sodium borohydride. It was also noticed that in an open digestion system, the chemical condition was not strong enough to oxidize Te(IV) to Te(VI) by HClO₄ at 190 °C.

3.1.2.3. Chemical valence of Te(IV) in aqua regia under MW condition (Te^{IV}ARMW).

Aqua regia is a common oxidizing system to dissolve organic rich solid samples, therefore the potential conversion of Te(IV) to Te(VI) in *aqua regia* could occur. Our studies show that the spiked Te(IV) (25 µg) cannot be converted to Te(VI) by *aqua regia* in a pressurized MW condition at a temperature as high as 210 °C. The recoveries of Te(IV) at 170, 190 and 210 °C were found to be 101.9% (SD = 0.9%, n = 3), 100.2% (4.1%) and 101.9% (4.4%), respectively, demonstrating that no Te(IV) had been converted to Te(VI) or lost in the process, which indicates that the oxidation potential of *aqua regia* is not strong enough to oxidize Te(IV) to Te(VI) under the tested conditions.

3.2. Studies on Te pre-reduction

In aqueous solutions, Te(IV) and Te(VI) are both present as oxyanions (TeO₃^{2–} and TeO₄^{2–}) and only TeO₃^{2–} can form tellurium hydride upon reaction with sodium borohydride. Thus, to measure TeO₄^{2–} a pre-reduction is needed.

It was found that at room temperature, Te(VI) (60 µg/L) could not be reduced by either KI (0.60 M), ascorbic acid (0.28 M) or oxalic

Table 1

Summary of major experimental conditions used in this study. The experimental details can be found in Section 2.

Experiment code	Sect.#	Major experimental conditions		
		State of analyte	Chemical reagents	Treatment
Te ^{IV} MW	2.2.2	Te ^{IV} std soln	HNO ₃ –HClO ₄ –HF & HNO ₃ –HCl–HF	Microwaved at 190 °C 20min. One aliquot measured directly; another measured after pre-reduction.
Te ^{IV,VI} OV	2.2.2	Te ^{IV} std soln or Te ^{VI} std soln	I: HNO ₃ –HF–HClO ₄ II: HNO ₃ –HCl–HF	Open vessel. I: 250 ± 20 °C, 40min. II: 180 ± 20 °C, 100min. Measured without pre-reduction.
Te ^{IV} ARMW	2.2.2	Te ^{IV} std soln	<i>Aqua-regia</i> (1HNO ₃ :3HCl)	Microwaved at 170, 190 and 210 °C, 20min. Measured without pre-reduction.
SSMW	2.4.1	Sediment with spiked Te ^{IV} std soln	HNO ₃ –HClO ₄ –HF & HNO ₃ –HCl–HF	Microwaved at 190 °C, 20 (or25) min. Measured without pre-reduction; with or without H ₃ BO ₃ .
SSOV	2.4.2	Sediment (or tailing) with spiked Te ^{IV} (or Te ^{VI}) std soln	Step1: HNO ₃ –HClO ₄ ; Step2: HF	Step 1: lid loosely capped, 170 °C, 1 h; then 210 °C, 30min; Step 2: lid tightened, 200 °C, 1 h. Open lid to eliminate HF (210 °C, 75min), Measured with and without pre-reduction.
SSCRM	2.4.3	GBW07312 with spiked Te ^{IV} std soln	Step 1: HNO ₃ –HClO ₄ Step 2: HF	Step1: lid loosely capped, 200 °C, 90min; Step2: lid tightened 200 °C, 2 h. Open lid to eliminate HF (200 °C, 60min), measured with pre-reduction.

Table 2

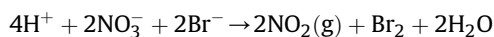
Studies of Te chemical valence in an open vessel digestion with two different chemical systems (Te^{IV, VI}OV): 25.00 µg of Te(IV) or Te(VI) was spiked in a PTFE beaker, and Te was determined in 3.0 M HCl after dilution without pre-reduction. Two individual digestions and triplicate analyses per digestion were performed under each condition.

Chemical reagents	(I) 5.0 mL HNO ₃ –3.0 mL HF–2.0 mL HClO ₄	(II) 2.0 mL HNO ₃ –5.0 mL HCl–2.0 mL HF
Digestion conditions	250 ± 20 °C for a total 85min	180 ± 20 °C for a total 1hr45min ^a
Spiked Te(IV)		
Te found/µg	24.34	21.93
SD/µg	1.20	0.81
Recovery %	97.4	87.7
Spiked Te(VI)		
Te found/µg	1.48	2.31
SD/µg	0.58	0.84
Recovery %	6.91	10.13

^a The digestion temperature was set lower due to the consideration of higher volatility of HCl in this system.

acid (0.56 M) in a 3.0 M HCl matrix after setting for 24 h, with the only exception of KBr (0.43 M) where 10% Te(VI) was measured as Te(IV). It was also found that at a temperature of 100 °C, KBr could quantitatively convert Te(VI) to Te(IV) in 3.0 M HCl in 10min (Fig. 1). The coexistence of both Te(VI) and Te(IV) at 3.0, 5.0, 7.0 and 10.0 µg/L for each species was also tested under this condition and it was found that before the pre-reduction, only Te(IV) was quantitatively detected, whereas after treatment, the sum of Te(IV) and Te(VI) were recovered to nearly 100%.

However, it was found that, in the co-presence of KBr and HNO₃ and at an elevated temperature (110 °C for 10min), the solution turned to brown and a high reagent blank was generated. The reagent blank value increased as HNO₃ concentration increased in solution and the results also deteriorated. For instance, the recovery of 10.0 µg/L Te(VI) was around 101% in 5% (v/v) HNO₃ and 55.7% in 10.0% (v/v) HNO₃ after subtraction of the reagent blanks. This is very likely due to formation of Br₂ by the reaction:



Therefore, when a digestion system contains a high concentration of strong oxidant such as HNO₃, the use of KBr as a pre-reducing agent should be avoided.

Although HCl has been used before to convert Te(VI) to Te(IV) [1,14], there is no systematic study to support the proposed conditions which varied widely from 4.5 M to 6.0 M HCl and from boiling temperature to 150 °C and some authors [25,27] did not even perform a pre-reduction step at all. It was found in our studies that both temperature and HCl concentration affect Te(VI) conversion greatly. At 100 °C and 6.0 M HCl, a satisfying pre-reduction was achieved in 15min (Fig. 2). A separate study showed that, with 5.0 M HCl, the Te(VI) pre-reduction was not better than 87%, even when the temperature was increased to 130 °C; however when [HCl] reached 6.0 M, a 90% reduction of Te(VI) was achieved at 100 °C in only 5 min (Fig. 3), which shows the importance of HCl concentration in the pre-reduction step. To guaranty a complete pre-reduction in samples with complex matrices, an optimal pre-reduction was decided as 6.0 M HCl at 110 °C for 20min. The enhancement of Te(VI) conversion to hydride forming species Te(IV) in a higher HCl concentration is possibly due to the formation of hydroboron intermediates and analytical substrates which could in turn activate the formation of hydride of Te(IV) [21].

Kuldvere [32] noticed that Se(VI) could even be reduced to Se(IV) in an *aqua regia* or in a reversed *aqua regia* system, and the author argued that this was attributed to the presence of high concentrations of both H⁺ and Cl⁻ in the system that drove the equilibrium toward left:

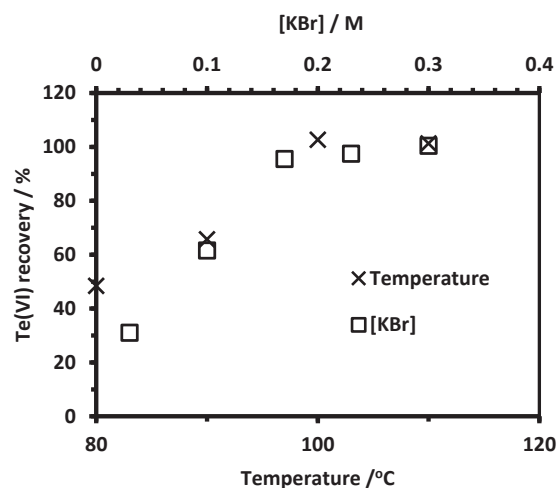
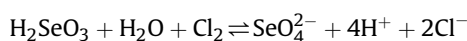


Fig. 1. The pre-reduction conditions of Te(VI) by KBr as reducing agent ([Te(VI)] = 10.0 µg/L, 3.0 M HCl). When the temperature effect was studied (x temperature), [KBr] = 0.17 M. When the [KBr] was examined (□ [KBr]), temperature = 100 °C. The MW program was 23 °C to a given temperature in 10min and kept at that temperature for 10min, followed by a 20-min venting.

Since Te is a close neighbor of Se, it would not be surprising that Te(IV) could still remain as Te(IV) in *aqua regia*. The intact Te(IV) in *aqua regia* and MW condition at 190 °C (Te^{IV}ARMW, 3.3.1) seems also to support this hypothesis.

3.3. Metal ions interference and masking agents

The interference on Te determination by foreign ions during hydride formation has been only scarcely studied [10,25]. It is known that the interfering phenomenon is heavily dependent on the instrumental setup and precise chemical conditions (see discussion in section 3.4); it is necessary to take the literature information with precaution.

When individual concentrations of Zn²⁺, MoO₄²⁻, Mn²⁺ and Cr³⁺ were up to 500, 500, 500 and 2000 mg/L, the recoveries of 10 µg/L Te(IV) in 3.0 M HCl were 106.0, 104.9, 95.2 and 102.3%, respectively, therefore, this group of elements can be classified as non-interfering elements. Ions CrO₄²⁻, Ni²⁺, Co²⁺, Pb²⁺ and Fe³⁺ belong to a group that did not interfere with Te(IV) signal at a low concentration range (≤10 mg/L), but did at a higher concentration range. The Cu²⁺ ion clearly exhibited the worst interference to Te(IV) determination. When its concentration in solution was 5, 10, 30 and 70 µg/L, the Te(IV) signal dropped by 5, 7, 10 and 16%, respectively (Fig. 4). The interference mechanism of the first 5 metal ions

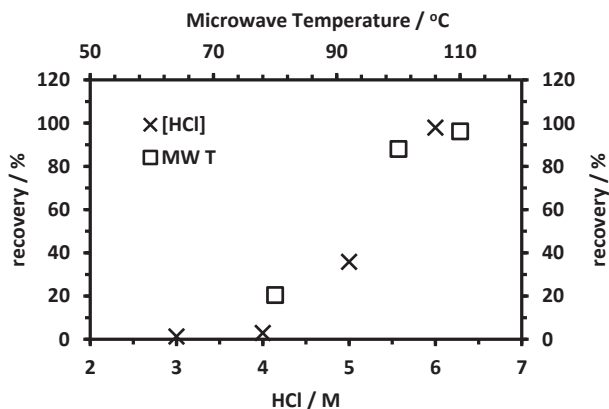


Fig. 2. The effect of HCl concentration and temperature on pre-reduction of Te(VI) in a MW oven. In the test with HCl concentration (x [HCl]), $T = 100\text{ }^{\circ}\text{C}$ and $[\text{Te(VI)}] = 10.0\text{ }\mu\text{g/L}$. In the test of pre-reduction temperature (\square MW T), $[\text{HCl}] = 6.0\text{ M}$ and $[\text{Te(VI)}] = 50\text{ }\mu\text{g/L}$. The microwave program was $23\text{ }^{\circ}\text{C}$ to a given temperature in 10min and kept at that temperature for 15min, followed by a 20-min venting.

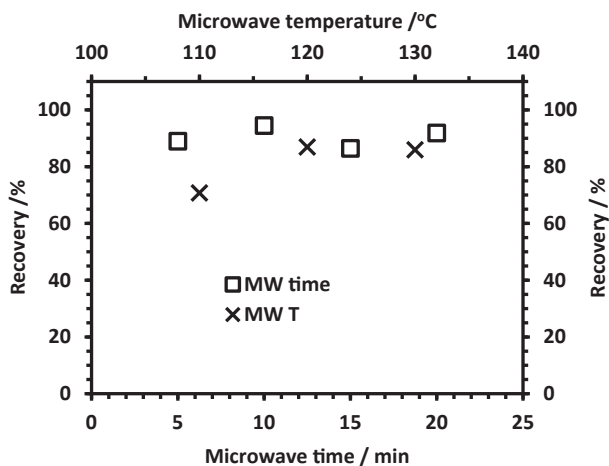


Fig. 3. In the study of Te(VI) pre-reduction under different temperature (x MWT), $[\text{HCl}] = 5.0\text{ M}$ and $t = 20\text{ min}$. In the study of microwave time (\square MW time), $[\text{HCl}] = 6.0\text{ M}$ and $T = 110\text{ }^{\circ}\text{C}$. In these tests, $[\text{Te(VI)}] = 30\text{ }\mu\text{g/L}$, the preheating and venting was 10 and 20min, respectively.

can be interpreted as competition for the reducing agent sodium borohydride, since the interference appeared only when their concentrations were high. The mechanism of interference caused by Cu^{2+} was clearly different, as interference started at a very low level. It is likely that copper can react directly with tellurium as indicated by Kirkbright & Taddia [29]. The exact mechanism of the interference is not yet clear but it is possible that the formation of a charge neutral tellurium–copper colloidal compound (CuTe) could occur, as it is known that in reacting with NaBH_4 , Cu^{2+} tends to form Cu^0 . A sharp interference by Cu^{2+} was also observed by Marcucci et al. [25].

Potassium iodide (3% w/v), 8-hydroxy-quinoline (1.0% w/v), L-cysteine (2.0% w/v), L-ascorbic acid (2.0% w/v), 1,10-phenanthroline (1.0% w/v) and thiourea (0.25% w/v) were tested as masking agents in a solution of $10.0\text{ }\mu\text{g/L}$ Te(IV) and 5.0 mg/L Cu^{2+} in 3.0 M HCl , but only thiourea was found promising. When the concentration of Cu^{2+} increased to more than 10 mg/L in the tested solution, thiourea seemed to have lost its masking capacity, which could not be improved by simply increasing its concentration (Table 3). This looks very similar as using thiourea to mask Cu^{2+} in Se(IV) determination [25].

To test the masking capacity and check the possible interactions of thiourea with other metal ions, a series of cocktail solutions of metal ions and thiourea were prepared and the recoveries of $10\text{ }\mu\text{g/L}$ Te(IV) in such solutions were examined. It showed that without masking agent, the recoveries of Te(IV) signal were extremely low. In presence of 0.25% (w/v) thiourea, the interference was free until the concentration of the mixed solution reached 10 mg/L per element. Beyond this concentration, the masking capacity dropped remarkably, even with increased concentrations of thiourea (Fig. 5). Cu^{2+} is most likely the responsible species for this drop, as 10 mg/L coincides with that in the single Cu^{2+} study (Table 3). Thus, it can be concluded that when an analytical solution contains Cu^{2+} at less than 10 mg/L , thiourea can be considered as a good masking agent.

3.4. Refractory sample digestions and analysis

3.4.1. Effect of reagent blanks on low Te samples

Because of the low Te concentration in most natural refractory samples and its relatively low sensitivity with HG–AFS compared to other hydride forming elements, it is not possible to reduce sample matrix by simply using dilution. The potential interference from the matrix could then become a serious problem, however, this concern has never been addressed before [27,30].

First, three series of standard calibration solutions prepared in 5.0, 10.0 and 15.0% (v/v) HNO_3 –5.0 M HCl were compared to that prepared in pure 3.0 M HCl and the average standard calibration equation of these four standard series was $Y_{\text{avg}} (n=4) = 4.1611(\pm 0.0209)x + 4.4325(\pm 0.8907)$, $R^2 = 0.9992 (\pm 0.00079)$, indicating that there is no visible difference between these 4 matrices and that HNO_3 , at a concentration below 15% (v/v), does not affect the Te signals. The standard calibration equations obtained from standard series prepared in 3.0 M–6.0 M HCl were also very close.

In our various digestion trials, it was observed that reagent blanks varied significantly from one digestion system to another. In general, a closed vessel digestion produced remarkably higher reagent blank readings compared to an open vessel digestion. The open digestion system of HNO_3 – HClO_4 –HF had a lowest background value (Table 4). It was also found that the reagent blank of a closed system was usually greater in less diluted solution. The presence of excessive HF in digested solutions seems to contribute greatly to this variation. The addition of boric acid to sequester excessive HF somewhat improved the Te(IV) recovery and the

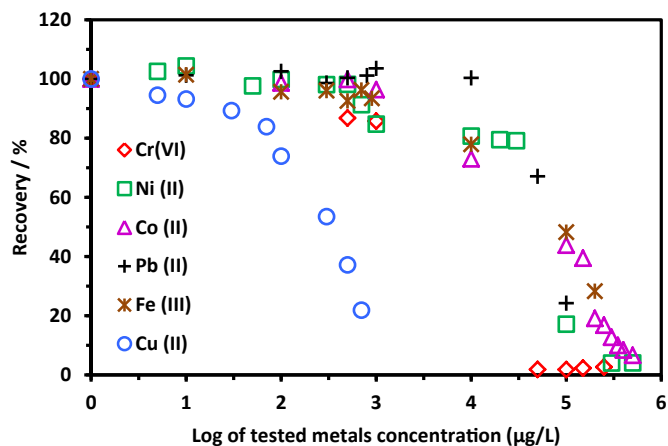


Fig. 4. The interference study with Ni^{2+} , Co^{2+} , CrO_4^{2-} , Fe^{3+} , Pb^{2+} and Cu^{2+} in presence of $10.0\text{ }\mu\text{g/L}$ of Te(IV) in 3.0 M HCl . In this set of tests, a single element was present in the testing solution.

Table 3

Study of masking capacity of thiourea in the solutions containing different concentrations of Cu^{2+} and thiourea, expressed as the recovery (%). $[\text{Te(IV)}] = 10.0 \mu\text{g/L}$ in 3.0 M HCl.

Cu(II) (mg/L)	Thiourea % (w/v)		
	0.5	0.75	1.0
0.0	100	100	100
10.0	102	103	96
20.0	50.9	61	65
30.0	1.7	23	33

analytical precision (Table 5). However, a larger quantity of H_3BO_3 can produce a jelly like texture of digest and could produce unwanted effects, particularly when a larger dilution is not possible.

It should be mentioned that this high reagent background was not observed by D'Ulivo et al., and their detection limit was also significantly lower [24,25]. It is due to the fact that their light source was an EDL lamp where, unlike a hollow cathode lamp (HCL) and boosted HCL, the power is modulated; therefore, it can effectively eliminate the background noise from the flame. It was found that when using boosted HCL, the emission of CO_2 in the flame could interfere with the determination of selenium in HG-AFS [33]. In addition the boosted HCL usually emits more spectral lines than the EDL, therefore the probability of molecular emission of compound in the flame also increases the background noise.

3.4.2. Effects of sample matrix and HF on Te valence and its determination in a two-step digestion system

Hydrofluoric acid is a most frequently used acid in wet digestion of refractory aluminosilicate samples, but it seriously deteriorates the Te signals and increases the blank values. The spiked Te(IV) in sediment sample (SSMW, 2.4.1) was also un-measurable in a pressurized digestion system of $\text{HNO}_3\text{--HClO}_4\text{--HF}$, as those in the study of section 3.1.2 (Te^{IV}MW), and only a small fraction could be detected even after a pre-reduction step, whereas in $\text{HNO}_3\text{--HCl--HF}$ system, the spiked Te(IV) was recovered, but with large analytical variation (Table 5).

It was found that a 2-step digestion, first with $\text{HNO}_3\text{--HClO}_4$ at a high temperature to mineralize organic matter, then with HF present in a closed system, followed by an open vessel digestion to thoroughly eliminate excessive HF, was ideal for digestion of refractory samples rich in organic matter (SSOV, 2.4.2). This allowed a total sample digestion, reduced reagent background and improved

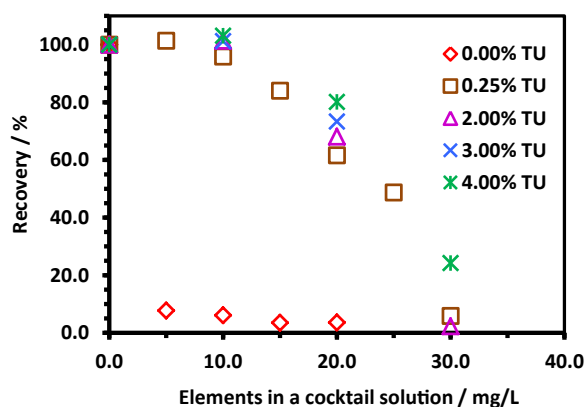


Fig. 5. The effect of thiourea (TU) concentration on masking effectiveness in presence of a series of cocktail solutions containing Co^{2+} , CrO_4^{2-} , Cr^{3+} , Cu^{2+} , Fe^{3+} , Mn^{2+} , Pb^{2+} , MoO_4^{2-} , Zn^{2+} and Ni^{2+} in which the concentrations of each element were identical. $[\text{Te(IV)}] = 10.0 \mu\text{g/L}$ in 3.0 M HCl.

analytical precision. After the total elimination of HF, the introduction of H_3BO_3 became unnecessary, which would further reduce reagent background signals. Once HF was introduced, the lid of the vessel should be closed to avoid a quick evaporation of the acid under high temperature and enhance sample dissolution. In addition, the absence of HCl in the digestion eliminated any concern on Te loss as volatile compounds.

In the studies with two types of refractory samples, we found that the chemical composition of a sample can strongly influence the valence of Te in a digestion (SSOV, 2.4.2). A lake sediment with a high natural organic matter (30% w/w in loss on ignition) and a tailing sample with high sulfide (34% w/w in S) were used in the 2-step digestion test. Different quantities of Te(IV) or Te(VI) were spiked prior to digestion. The purpose of spiking Te(IV) or Te(VI) in these samples was to study possible valence modification of these species in given chemical conditions and sample matrices, and to further test the robustness of digestion and pre-reduction protocols. The results are summarized in Table 6. No Te was detected in the original lake sediment and tailing sample. In the sediment sample, the spiked Te(IV) was satisfactorily found at all levels with and without pre-reduction. It shows that in such a digestion system, $\text{HNO}_3\text{--HClO}_4$ did not convert Te(IV) to Te(VI), or to a volatile species, which have also been demonstrated in Table 2 (chemical reagent I). This shows that for some samples, the pre-reduction is unnecessary. The Te(VI) spiked in the samples was satisfactorily recovered after pre-reduction. It is noted that about 25–40% of spiked Te(VI) was found in the sediment samples without a pre-reduction step, which is significantly higher than those found in Table 2, suggesting that a relatively reducing environment was created in such digestion system possibly due to the presence of high organic matter in the sample.

However, in the tailing sample the chemical environment created during digestion appeared completely different (Table 6). A good recovery of spiked Te(IV) can only be achieved after a pre-reduction step, indicating that some of Te(IV) was oxidized in such a system, which is likely due to the presence of high concentration of sulphide in the sample. It is known that S^{2-} is converted to SO_4^{2-} or SO_3^{2-} in the first digestion step and they, as strong acidic oxidants at high temperature, could oxidize Te(IV) to its higher valence. In the digests of the tailing sample, a formation of yellow elemental sulphur agglomerates was observed during the first digestion step, probably due to deficiency of oxygen. However, the formation of S^0 did not seem to affect Te determination and could be avoided by introducing more O_2 at this step.

These results show that sample matrix, chemical reagents and digestion mode can all strongly influence the chemical conditions of a digestion system and make it more or less oxidative. For a sample of unknown chemical nature, a preliminary study should be conducted to confirm if a pre-reduction should be carried.

3.5. Determination of Te in certified sediment sample GBW07312 (SSCRM)

The total Te in a certified sedimentary rock sample GBW 07312 was measured with the 2-step digestion protocol. The results were obtained based on an external calibration curve and are presented in Table 7. It was found that when the analytical time of the instrumental condition was set at 20sec, the recovery of the spiked Te(VI) was less satisfactory. However when the analytical time increased to 30sec, the recoveries of the spiked Te(VI) were improved, which could be explained as a higher viscosity of the less diluted samples (three times) requires a longer analytical time to establish a stable reading in a continuous flow injection instrument. The certified value of Te in this sample is $0.30 \pm 0.07 \mu\text{g/g}$, therefore the result is considered satisfactory.

Table 4

Comparison of reagent blank signals (at the same magnification) in different digestion systems. All the reagent blanks are followed the same protocol as samples. After digestion treatment, they are filled up to 50.0 mL with DW and the readings are recorded in 3.0 M HCl after a 50 times dilution ($n = 3$). No H_3BO_3 was added in these tests.

Chemical reagents in digestion system	Close vessel microwave oven			Open vessel on hot plate		
	3.0 mL HNO_3 – 5.0 mL HCl – 1.0 mL HF	5.8 mL HNO_3 – 1.7 mL $HClO_4$ – 1.0 mL HF	2.0 mL HNO_3 – 6.0 mL HCl	2.0 mL HNO_3 – 2.0 mL HF	5.0 mL HCl- 3.0 mL HF	5.0 mL HNO_3 – 2.0 mL $HClO_4$
Average pk ht)	21.13	8.25	9.85	2.10	2.23	
SD (pk ht)	1.61	0.75	0.97	2.27	0.63	

Table 5

Recoveries (%) of spiked Te(IV) in a closed MW vessel containing 0.5000 g lake sediment and 3.0 mL HNO_3 –5.0mLHCl–1.0mLHF (SSMW). The digests were analyzed after 50 times dilution without pre-reduction. The spiked Te(IV) in analytical solutions were 2.0 and 4.0 $\mu\text{g/L}$. Calculation is based on the slopes of both external and standard addition calibration curves (n is number of measurements).

H_3BO_3 in analytical solution	0.0 M		0.02 M		
	5.0 μg	10.0 μg	5.0 μg	10.0 μg	
External calibration	Avg recovery (%)	119.17	69.49	106.54	95.07
	SD ($n = 3$)	17.31	42.59	4.85	6.30
Standard addition	Avg recovery (%)	174.9	102.0	118.89	112.52
	SD ($n = 3$)	25.42	70.52	5.41	7.04

Table 6

Studies of a 2–step digestion: first with HNO_3 – $HClO_4$, then HF and followed by an elimination of HF (SSOV). 0.3000 g samples were weighed and digest was fixed to 50.00 mL and diluted 40 times before analyzed. No H_3BO_3 was added. The pre-reduction was done in 6.0 M HCl at 110 °C for 20min.

Measured without pre- reduction					Measured after pre- reduction				
Spiked Te/ μg	0.00	5.00	10.00	20.00	Spiked/ μg	0.00	5.00	10.00	20.00
McFarlane Lake Sediment					Te (IV)				
Te (IV)					Found/ μg	N.D.	4.01	9.42	20.54
Found/ μg	N.D.	4.35	11.10	19.61	SD ($n = 4$)	–	0.24	0.68	0.69
SD ($n = 4$)	–	0.34	0.70	0.29	Recovery%	–	80.27	94.16	102.69
Recovery%	–	87.07	110.97	98.07	Te (VI)				
Te (VI)					Found/ μg	N.D.	4.82	10.56	19.76
Found/ μg	N.D.	1.97	2.78	4.98	SD ($n = 4$)	–	0.43	0.66	1.47
SD ($n = 3$)	–	0.72	0.7	0.34	Recovery%	–	96.42	105.60	98.82
Recovery%	–	39.40	27.84	24.90	Pulverized Tailing Sample				
Te (IV)					Te (IV)				
Found/ μg	N.D.	2.51	4.85	15.81	Found/ μg	N.D.	5.04	9.92	20.03
SD ($n = 4$)	–	0.30	0.56	0.31	SD ($n = 4$)	–	0.77	0.37	1.11
Recovery%	–	50.19	48.47	79.05	Recovery%	–	100.83	99.20	100.15
Te (VI)					Te (VI)				
Found/ μg	N.D.	0.19	0.1	0.47	Found/ μg	N.D.	5.04	9.92	20.03
SD ($n = 4$)	–	0.05	0.13	0.07	SD ($n = 4$)	–	0.34	0.49	0.79
Recovery%	–	4.47	2.72	9.31	Recovery%	–	102.62	104.11	98.81

N.D. – not detected.

4. Conclusion

Although a 0.17 M KBr solution can reduce Te(VI) to Te(IV) in 3.0 M HCl at 100 °C, at this temperature Br^- is oxidized to Br_2 by HNO_3 in solution and interfere severely with the analysis. KBr can be used in pre-reduction if the solution does not contain HNO_3 . Alternatively, an optimal condition for Te(VI) pre-reduction for refractory samples was found to be in 6.0 M HCl solution and at 110 °C for 20min. It is important to note that the loss of Te in volatile form in the presence of HCl can occur at a higher temperature; therefore HCl should not be used in an open vessel digestion. When using HCl to pre-reduce Te(VI), a thorough cooling should be employed before opening a digestion vessel. Only Cu^{2+} interferes with the Te signal severely among 10 tested ionic species. A 0.25%(w/v) thiourea in the analytical solution can eliminate the interference of Cu^{2+} up to 10 mg/L.

The valences of Te are strongly affected by the modes of digestion (closed vs. open vessel), digestion reagents, and even chemical composition of refractory samples. In a closed MW system and with

mixed reagents of HNO_3 – $HClO_4$ –HF, the spiked Te(IV) was unmeasurable with or without pre-reduction step. When $HClO_4$ was replaced by HCl in a MW system, Te(IV) was measured without pre-reduction, but the analytical precision was poor. The presence of HF in an analytical solution appears to interfere with measurement and cause high reagent background and analytical variation. A 2-step digestion scheme was then proposed for refractory samples,

Table 7

Determination of total Te in certified sedimentary rock sample GBW07312 (SSCRM) and the recovery of Te(VI) spiked before digested. The dilution factor was 3 and the analytical time was 30sec. The pre-reduction was done in 6.0 M HCl at 110 °C for 20min.

Certified Te $0.30 \pm 0.07 \mu\text{g/g}$	GBW07312 ($\mu\text{g/g}$)	Spiked Te(VI) (μg)		
		0.15	0.30	0.60
Average found	0.32	0.13	0.27	0.54
SD ($n = 3$)	0.04	0.023	0.014	0.016
Recovery/%	–	86.7	91.2	90.1

which allows a total destruction of organic matter and dissolution of aluminosilicate. Due to the elimination of HF, the reagent background of the analytical solution was remarkably diminished and the analytical precision increased. Because the chemical composition of sample can strongly affect the valence of Te in the digest, a study should always be conducted to decide whether a pre-reduction step is necessary.

Acknowledgments

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