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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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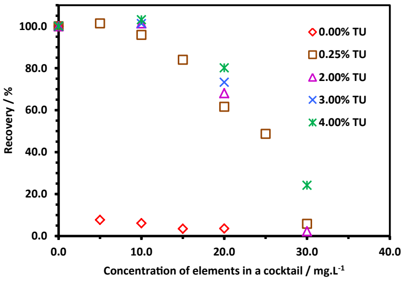
HIGHLIGHTS

- 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 μg/g, respectively.

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1. Introduction

Tellurium (Te) is an element of very low abundance in the Earth's crust, at approximately 1–2 x10^{-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 μg/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 μg/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 μg/L Te(IV) were equally divided into Group A and