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SCIENCE DIRECT®

Talanta 69 (2006) 199–203

Talanta

www.elsevier.com/locate/talanta

Thermal stabilization of tellurium in mineral acids solutions: Use of permanent modifiers for its determination in sulfur by GFAAS

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Received 9 August 2005; received in revised form 20 September 2005; accepted 20 September 2005
Available online 27 October 2005

Abstract

The aim of this work is the study of the best conditions for thermal stabilization of tellurium in graphite furnaces under different experimental conditions, including highly concentrated nitric and hydrochloric acids solutions as those resulting of drastic dissolution procedures. The influence of different noble metals used as matrix modifiers in solution or as permanent layers on the graphite furnace will be assessed.

Amongst the assayed matrix modifiers, iridium used as permanent has shown the best performance in high concentrations of mineral acids. The mass employed was 20 μg (for 1 ng of Te), with a maximal attainable pyrolysis temperature of 1400 °C without losses of the analyte or sensitivity (height, area and form of the atomization peak), being mo = 20 pg. Some speculations on the mechanisms of thermal stabilization of tellurium in graphite furnaces will be discussed.

The potentiality of ETAAS for tellurium determination in technical grade sulfur will be evaluated. Results involving characteristics mass, limit of detection and percentage of recovery of tellurium in a mineralized sulfur sample will be compared with those obtained through a working curve in absence of interferences.

Keywords: Tellurium stabilization; Matrix modifiers; Noble metals; Mineral acids; Determination in sulfur

1. Introduction

The limited information about the stabilization of tellurium in graphite furnaces [1–3], particularly in the presence of high concentration of mineral acids, makes this alternative not very attractive for the determination of microamounts of this analyte by electrothermal atomic absorption spectrometry (ETAAS). Consequently, studies on the best conditions for tellurium stabilization during an atomization cycle should help on the spreading of ETAAS as a standard technique for its determination at low concentration levels in different samples.

Studies on tellurium atomization recently presented by Muller-Vogt et al. [4] showed that the formation of tellurium oxides and their posterior reduction to elemental tellurium explain the appearance of atomic vapor. Losses of analyte at high temperature of pyrolysis were attributed to the volatilization of TeO(g). So, the employment of matrix modifiers is necessary in order to improve the thermal stabilization during pyrolysis.

Amongst matrix modifiers, palladium is well recognized due to its efficacy for thermal stabilization of a large number of analytes [5–7]. However, it is not a universal modifier and it is unworthy for some elements in some reaction media.

Recently, other noble metals such as Pt, Rh, Ru and Ir have been successfully applied to the determination of elements that form volatile oxides [8–12]. Experiments employing Mass Spectrometry [13], X-ray Photoelectron Spectrometry [14], Scanning Electron Microscopy [1] and Rutherford Backscattering Spectrometry [15] have shown that stabilization occurs through the entrapment of the analyte in droplets of the metallic reduced form of the modifier which produces a solid-phase solution and/or intermetallic compounds analyte-modifier.

Taking into account some negative side effects and limitations found with the employment of classical chemical modification,

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doi:10.1016/j.talanta.2005.09.027

the use of permanent modifiers became very popular during the last years [16].

The most attractive advantages of permanent modifiers include: simpler procedures for GFAAS determinations, increased sample throughput, reduction of reagent blanks, removal of unwanted modifier impurities previous to the analytical determination, higher compatibility with on-line and in situ enrichment, etc. However, drawbacks such as the appearance of multiple peaks resulting from imperfect coating and over-stabilization of some analytes need to be noticed [17,18].

Regarding ETAAS tellurium determination, neither the efficacy of different modifiers on its stabilization during pyrolysis nor the influence of high concentrated mineral acids on sensitivity have been emphasized in the literature up to date [3]. Both facts are surprising since tellurium determination in acid dissolved alloys is frequent and the finding of an improved sensitivity is always desirable.

Nowadays, a few publications involving the determination of traces of tellurium in alloys and semiconductors by ETAAS [19–21] have been reported. These works show that the high concentrations of mineral acids used for dissolution impoverish the sensitivity. Therefore, the study of the influence of these variables on the production of atomic vapor may provide relevant information.

The aim of this work is to study the stabilization of tellurium in highly concentrated nitric and hydrochloric acids. In all cases, matrix modification was performed through the addition of Pd, Rh and Ir in solution or as permanent layers on the graphite surface. The employment of the sodium salt of thioacetamide as non-conventional matrix modifier was also evaluated.

Data concerning optimal mass of modifier, maximal attainable pyrolysis temperature without losses of analyte and sensitivity (height, area and form of the atomization peak) for all the assayed modifiers will be presented. A critical comparison between the performances of each modifier will be given. The possibility for determining tellurium in technical grade sulfur – which implies its determination in a highly concentrated mineral acid media after dissolution – will be presented. Analytical figures of merit and recovery studies of the analyte in the sample will be also shown.

2. Experimental

2.1. Reagents

Te(IV) stock standard solution ($0.1\,\mathrm{g\,l^{-1}}$) in nitric acid was prepared by dissolving sodium tellurite (BDH) in HNO_3 5% (v/v) (Merck). Working solutions of Te(IV) were prepared by appropriate dilution with nitric acid at final concentrations ranging between 0.15 and 2 M.

Te(IV) stock standard solution ($0.1\,\mathrm{g\,l^{-1}}$) in hydrochloric acid was prepared by dissolving sodium tellurite (BDH) in HCl 5% (v/v) (Merck). Working solutions were obtained by dilution with hydrochloric acid at a final concentration ranging between 0.12 and 4.2 M.

Standard solutions of Pd ($1\,\mathrm{g\,l^{-1}}$) were prepared by dissolving $Pd(NO_3)_2$ (Merck) in HNO_3 15% (v/v). Rh solutions ($1\,\mathrm{g\,l^{-1}}$) were obtained by dissolving $RhCl_3{\cdot}3H_2O$ (Alfa Division) in HCl 20% (v/v). Ir solutions ($1\,\mathrm{g\,l^{-1}}$) were prepared from metallic Ir (Merck) in HCl 10% (v/v). Metallic Pd (Merck) 99.9% was employed for thermal evaporation experiments.

Sodium thioacetamide (Mallinkrodt) solutions were prepared by dissolving 0.1 g of the analytical reagent in 100 ml of water.

Doubly deionized water (DIW, $18\,\mathrm{M\Omega\,cm^{-1}}$) obtained from a Milli-Q water System (Millipore) was used throughout the experiments. All the reagents were analytical-reagent grade.

2.2. Instrumentation

A Shimadzu 6700 Atomic Absorption Spectrometer (Kyoto, Japan) equipped with a graphite furnace accessory GFA6000 and an autosampler ASC-6000 was used. A Hamamatzu hollow cathode lamp was employed as radiation source at 214.3 nm with a slit width of 2 nm and 8 mA lamp current. Measurements were performed in peak height and peak area (integrated absorbance) modes. A deuterium lamp was employed for background correction.

Tubes with pyrolytic graphite coating and integrated graphite platform were used throughout the experiments. High purity argon was used as internal gas (AGA, Argentina).

A thermal evaporator Model Auto 306 (Edwards, UK) was used for the physical deposition of Pd on the platform graphite surface.

A microwave digestion system CEM MDS 2000 (Matthews, NC, USA) was employed for sulfur dissolution.

2.3. Samples dissolution

Sulfur powder (250 mg) was treated with 6 ml of 70% (w/w) nitric acid in PFTE® vessels. The microwave digestion system provided by CEM was closed and the pressure conditions into the PFTE® vessels were automatically controlled. The dissolution program involves five steps: two steps of 3 min each and another three steps of 8 min each, all of them at a power of 600 W. The pressure was fixed at 20, 40, 85, 160 and 200 psi, respectively. Then the digestion vessels were cooled down to room temperature and the final clear solution was made up to 25 ml with DIW. Simultaneously, digestion blanks were prepared.

2.4. Procedure

The influence of different amounts of matrix modifiers on the absorbance of $0.1\,\mathrm{mg\,l^{-1}}$ Te(IV) in HNO_3 0.1% (v/v) was evaluated through the addition of Pd, Rh and Ir solutions. A mass of 1 ng of Te(IV) and 0.5–200 ng of each matrix modifier were injected into the coated tubes with pyrolytic graphite platforms for all absorption measurements.

The atomization profile of Te(IV) in the presence of HCl and HNO_3 in concentrations ranging between 0.12–4.2 and 0.15–2 M, respectively, was studied. A mass of 1 ng of Te(IV) was injected into the coated tubes with pyrolytic graphite platforms for all absorption measurements.

Table 1
Graphite furnace temperature program for conditioning graphite tubes with the permanent modifier

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow (ml $\min^{-1}$)
1	110	30	10	250
2	130	20	10	250
3	1200	30	10	250
4	1200	–	10	250
5[a]	2000	–	5	250

[a] Pd: 1500 °C.

Table 2
Graphite furnace temperature program for studies of tellurium stabilization

Step	Temperature (°C)	Ramp time (s)	Hold time (s)	Ar flow (ml $\min^{-1}$)
Drying	120	30	10	250
Pyrolysis	400–1400	20	10	250
Pyrolysis	400–1400	–	30	250
Pyrolysis	400–1400	–	5	0
Atomization	2500	–	5	0

The influence of matrix modification (classic way) on the atomization profile of Te(IV) in the presence of HCl (0.12–4.2 M) and HNO_3 (0.15–2 M) was observed by injecting 1 ng of tellurium and 100 ng of each modifier onto the coated tubes with platforms.

Permanent modification of the graphite surface was obtained by injecting 20 μl of 1.000 g l^{-1} solutions of the respective noble metals onto the coated tubes with platforms. Tubes were dried and thermally treated (Table 1) in order to obtain the metals in their reduced form. Afterwards, a mass of 1 ng of Te(IV) was introduced onto the platform in the presence of different concentrations of hydrochloric acid (0.12–4.2 M) and nitric acid (0.15–2 M) for all measurements. The furnace temperature program for the different studies is given in Table 2.

Tellurium determination in sulfur was performed by injecting 10 μl of sample into the iridium coated graphite furnace. The obtained signal (peak area) was interpolated in a standard addition curve obtained by spiking a tellurium free sulfur sample with Te(IV) working standard solutions ranging between 10 and 50 ng ml^{-1}.

3. Results and discussion

3.1. Influence of minerals acids on tellurium atomization

Fig. 1 shows the curves A versus t at two concentrations of hydrochloric acid. At low concentration, the signal appears distorted by the presence of double peaks suggesting the existence of two mechanisms for atomization. The first peak of the absorbance profile could be attributed to the conversion of TeO(g) into Te(g). This assumption is in line with the gas phase dissociation of volatile oxides proposed by Droessler and Holcombe [22] as one of the routes for atomic vapor production. The second part of the atomization profile corresponds to the desorption of tellurium from the graphite surface.

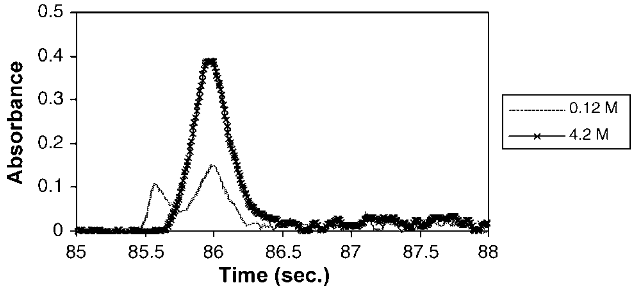

Fig. 1. Absorbance profiles for the atomization of 1 ng of Te(IV) in hydrochloric acid (pyrolysis at 600 °C, atomization at 2400 °C).

When the concentration of acid is increased from 0.12 up to 4.2 M, the first peak diminishes whilst the second grows. Finally, at the highest concentration only one symmetric peak is observed. This behavior could be attributed to the formation of stable complexes between Te(IV) and chloride instead of TeO as the previous step for conversion into metallic tellurium.

The experiments performed at different concentrations of nitric acid show profiles slightly more irregular and broader suggesting a higher interaction with the graphite surface. No significant differences in the form of the signals were observed at all the acid concentrations assayed.

3.2. Effect of the presence of thiocetamide on tellurium atomization characteristics

Thioacetamide is a known chemical reagent usually employed in qualitative analysis. In the presence of acid, it hydrolyses into sulfide ions which react with numerous metals to form highly insoluble metallic sulfides.

The addition of a solution of thioacetamide together with the Te(IV) solution produces an increment of sensitivity together with the removal of the double peak. This analytically desired change should be explained through an atomization mechanism where thiocetamide promotes the formation of tellurium sulfide which is re-converted during the pyrolisis step into elemental sulfur and metallic tellurium. Therefore, tellurium desorption from the graphite furnace should be responsible for the production of the atomic vapor. In this way, the formation of TeO is prevented and the losses of tellurium are minimized.

3.3. Effect of the presence of noble metals as matrix modifiers on tellurium atomization characteristics

The modifiers were applied as follows:

1. The modifier solution was introduced onto the graphite surface simultaneously with the aliquot of the tellurium solution (no previous reduction of the noble metal solution on the graphite surface was performed).
2. The modifier solution was injected, dried and pyrolysed to obtain the respective noble metal in its reduced form, the sample was injected and analysed once obtained the permanent modification of the graphite surface.

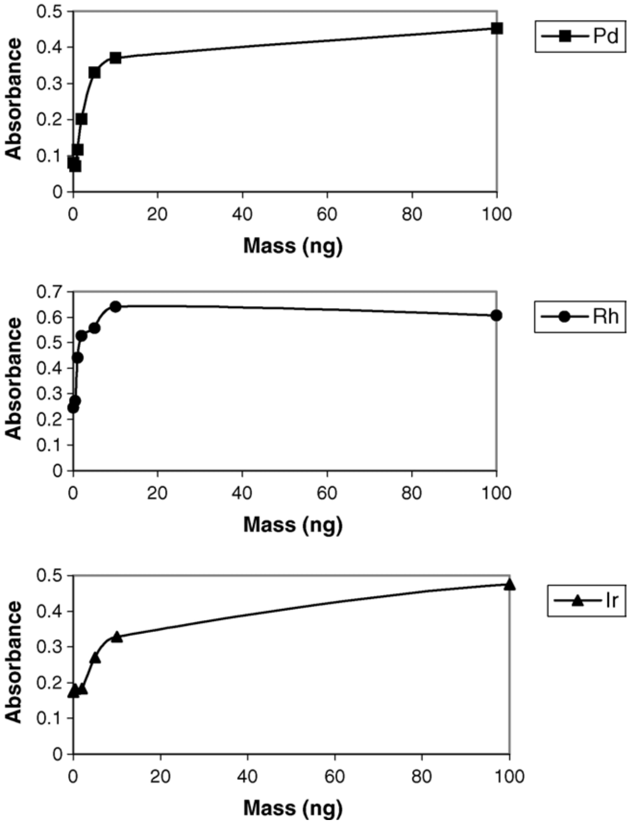

Fig. 2. Stabilization effect of different masses of Pd, Rh and Ir on 1 ng Te(IV) pyroysed at 600 °C and atomized at 2400 °C.

Firstly, the influence of Pd, Rh and Ir introduced in the graphite furnace as non reduced modifiers was investigated.

Fig. 2 shows the effect of the mass of added modifier (palladium, rhodium or iridium) on the pyrolysis behavior of 1 ng of tellurium. Stabilization of the analyte is improved up to the addition of 100 ng of each metal. From this value onwards, no significant changes are observed. Consequently, 100 ng of Pd, Rh or Ir were chosen as suitable amounts for obtaining the optimal pyrolysis behavior of 1 ng of Te and then, the pyrolysis curves. These amounts correspond to molar ratios Pd:Te, Rh:Te and Ir:Te equal to 1:3, 1:4 and 1:10, respectively. Our findings show that unlike selenium which stabilizes at a molar ratio 1:1 [23], tellurium requires a larger excess of modifier in order to obtain an efficient stabilization.

The influence of the pyrolysis temperature on the absorbance was studied in the range from 600 to 1500 °C, with atomization temperature set for 2400 °C. The maximum pyrolysis temperatures obtained were 1200 °C in the presence of Pd, 1300 °C in the presence of Rh and 1400 °C in the presence of Ir in concordance with the melting points of the metals.

The same noble metals were also assayed as permanent layers showing a similar behavior.

3.4. *Influence of noble metals modifiers on the atomization of tellurium in acidic media*

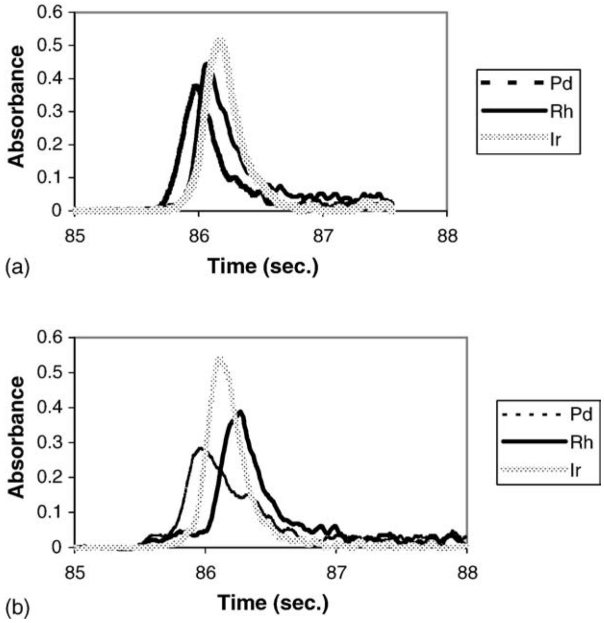

Fig. 3. (a) Absorbance profiles for the atomization of 1 ng of Te(IV) in hydrochloric acid 4.2 M in the presence of 20 μg of Pd, Rh and Ir (added as a permanent layer). (b) Absorbance profiles for the atomization of 1 ng of Te(IV) in nitric acid 2 M in the presence of 20 μg of Pd, nRh and Ir (added as a permanent layer).

In order to study the probable interaction between mineral acids and the noble metals used as modifiers, the experiments above were repeated in the presence of hydrochloric and nitric acid.

Results show that for noble metals introduced in the classical way similar profiles were obtained for all modifiers and acids assayed. However, when the modifier was used as permanent layer significant differences were observed.

In the presence of Ir, highly symmetrical and narrow peaks with no tailing were obtained in the presence of both acids.

Conversely (see Fig. 3), in the presence of rhodium – particularly at high concentrations of nitric acid – the signal was broader and showed an important tailing similar to the atomization profile of elements that form refractory compounds.

The advantages of Pd, Rh and Ir as modifiers seem to be based on the formation of intercalation compounds (ICC) and a subsequent activation of these ICC [24]. It is proposed that the activated metals atoms develop strong covalent bonds with the easily volatile atoms of the analyte, which leads to their stabilization at high pyrolysis temperatures. Experiments performed by X-ray emission showed that in the case of Pd, these ICC penetrate during pyrolysis up to 30 μm into the graphite surface [10]. The strong bonding between the analyte and the modifier in this structure reduce the mobility of the analyte. Hence, the analyte atoms cannot diffuse further into the graphite or into the inner tube surface. So, neither broadening of the atomization peak nor analyte losses are observed.

However, a pronounced interaction between Rh and graphite could produce a deeper penetration of the intercalation compound into the surface of the graphite. This process could be accelerated at high concentrations of nitric acid due to corrosion effects on the surface. This circumstance should explain the tailing observed for Rh. A similar observation was reported for arsenic by Volynsky and Wennrich [25].

More evidence of the formation of ICC was supported by experiments where Pd was deposited on the graphite surface by physical vapor deposition (PVD) instead of thermal reduction. It is reasonable to think that the dense layers obtained by PVD are not favorable for ICC formation as they probably block the carbon active surface. As a matter of fact, our studies on the aptitude of physical vapor deposition of Pd showed important losses of sensitivity.

According to the observations described above, Iridium allows one to obtain the best performance for tellurium atomization independently of the way it is employed: in solution or as permanent layer on the graphite surface. So, it was selected for further experiments in real matrices.

3.5. *Determination of Te in sulfur*

The microwave assisted dissolution of sulfur in nitric acid produces sulfate which is a serious interference in the determination of elements by ETAAS. In order to study the effect of sulfate on tellurium atomization when Ir is employed as permanent modifier, a Te free sulfur sample was spiked with different amounts of tellurium ranging between 0.1 and 1 ng in order to obtain a standard addition curve through ETAAS. The absence of tellurium in the sulfur sample (LOD = 1 ng ml^{-1}, $k = 3$) was established by hydride generation atomic absorption spectrometry [26].

Values of slopes, characteristic masses and limits of detection of tellurium were found from both, the standard addition curve and a working curve obtained for tellurium in nitric acid. The range of tellurium concentrations and the nitric acid concentration were kept the same for both curves. The slope of the standard addition curve was 0.0017 ml ng^{-1} and that of the working curve was 0.0026 ml ng^{-1}. Characteristics masses of tellurium were 20 and 28 pg in the presence and absence of sulfate, respectively. Regarding limits of detection ($k = 3$), calculated values were 4.2 ng ml^{-1} (sulfate matrix) and 2.6 ng ml^{-1} (absence of sulfate).

This indicates that the sulfate matrix significantly suppresses Te signal and, thus, the method of standard addition needs to be used for quantification purposes.

Recovery studies were carried out in order to test the method for the determination of tellurium in sulfur. The percentage recovery ranged from 98.0 to 99.5%. The precision was 6.6% (R.S.D., $n = 10$, for a solution of 50 ng ml^{-1} of tellurium). The detection limit based on three times the standard deviation of the blank was estimated to be 0.4 μg g^{-1} ($k = 3$, $n = 11$).

4. Conclusions

It can be concluded that high concentrations of hydrochloric acid improve considerably the thermal stabilization and the atomization profile of tellurium. The same is observed with the employment of thioacetamide.

All modifiers assayed showed a similar behavior when used in the classic way. However, when applied as permanent modifier only iridium showed an optimal performance in all the acidic media under study.

GFAAS with permanent modifiers seems to be a good alternative for tellurium determination in highly concentrated acid media.

Acknowledgment

To UBACyT, CONICET and INQUIMAE for financial support. To Prof. Ernesto Calvo and Mario Tagliazzuchi for PVD facilities.

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