Determination of tellurium by continuous hydride generation and atomic fluorescence spectrometry

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Abstract

It has been developed a simple method for the determination of Te(IV) and total tellurium in environmental samples by hydride generation and atomic fluorescence spectrometry (HG-AFS). For Te(IV) determination, acidified samples, aspirated in a carrier of 5 mol/L HCl, were merged with a $NaBH_4$ 1.2%(m/v) solution, with sample and $NaBH_4$ flow rates of 9.8 and 3.1 mL/min respectively. The hydride generated in a 100 cm reaction coil was passed through a gas-liquid separator and transported to the detector with an Ar flow of 400 mL/min. For total tellurium determination samples were heated, 10 min in a water bath at 60°C, after addition of 1.0 g NaBr to reduce Te(VI) to Te(IV). Solid NaBr was employed to avoid a long reduction step and the dilution of samples. The determination of total tellurium by atomic fluorescence was carried out as described above and Te(VI) was calculated as the difference between total tellurium and Te(IV). The limit of detection values obtained were between 0.4 and 0.7 µg/L and the calibration graph was linear up to 20 µg/L of tellurium. Recovery studies of different spiked concentrations of Te(IV) and Te(VI) in natural water samples were between 98 and 105% for Te(IV) and 99 to 109% for total tellurium. Furthermore, accuracy of the method was evaluated by using a sediment reference material with a known amount of tellurium after its leaching by means microwave treatment with 3 mol/L HCl.

Keywords: Atomic fluorescence spectrometry; continuous hydride generation; tellurium determination.

Determinación de teluro mediante generación contínua del hidruro y espectrometría de fluorescencia atómica

Resumen

Se ha desarrollado un procedimiento simple para la determinación de Te(IV) y teluro total por espectrometria de fluorescencia atómica y generación de hidruros (HG-AFS) en muestras ambientales. En la determinación de Te(IV), las muestras acidas, aspiradas en un portador de HCl 5 mol/L, confluyen con una disolución de $NaBH_4$ 1,2% (m/v), de flujos 9,8 y 3,1 mL/min respectivamente. El hidruro, generado en el bucle de reacción de 100 cm, se hace pasar a través de un separador gas-líquido y es trasportado al detector mediante un flujo de Ar de 400 mL/min. Para la determinación de Te total, las muestras se calientan por 10 minutos en un baño de agua a 60°C despues de la adición de 1,0 g de NaBr para la reducción del Te(VI) a Te(IV).

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Se emplea NaBr sólido para evitar la dilución de las muestras. La determinacion del teluro total mediante AFS se lleva a cabo como se indicó anteriormente y el Te(VI) se calcula como la diferencia entre el teluro total y el Te(IV). Los valores del límite de detección obtenidos se encuentran entre 0,4 y 0,7 µg/L y la curva de calibrado es lineal hasta los 20 µg/L de teluro. Los estudios a recuperación de diferentes concentraciones de Te(IV) y Te(VI) en aguas naturales estan entre el 98 y 105% para el Te(IV) y entre el 99 y 109% para el teluro total. Además, la exactitud del método fué evaluada empleando un material de referencia de sedimento con una cantidad conocida de Te, después de su extracción mediante tratamiento en microondas con HCl 3 mol/L.

Palabras clave: Determinación de Telurio; generación de hidruro continuo; espectrometría de florescencia atómica.

1. Introduction

Tellurium can be determined with high sensitivity and selectivity by atomic spectrometry after generation of its covalent-hydride through reaction with sodium borohydride. This strategy provides an excellent way for matrix isolation and increases the element intake inside the atomizer (1).

Using hydride generation, tellurium has been determined by atomic absorption spectrometry (2, 3), graphite furnace atomic absorption spectrometry (4, 5), inductively coupled plasma atomic emission (6, 7) and inductively coupled plasma mass spectrometry (8-10). In recent years, the development of simple atomic fluorescence spectrometers has provided a suitable tool for tellurium determination (11-20).

Tellurium has been determined by HG-AFS in metals and alloys (11-15), water (16, 17), urine (18), milk (19) and geological samples (20).

From studies reported in the literature for Te determination in waters by HGAFS it can be noticed that a high limit of detection (80 µg/L) was found in spite of the use of a preconcentration through cation exchange (16). On the other hand, total Te can be determined after reduction of Te(VI) with citric/tartaric acids, obtaining a limit of detection of 0.1 µg/L in the diluted solution (17).

The aim of this paper is to develop a simple method for the direct determination of trace amounts of tellurium, by continuous hydride generation and atomic fluorescence spectrometry, in environmental samples. The sensitivity and limit of detection of HGAFS were improved by selecting the appropriated operational conditions. On the other hand, for total tellurium determination, Te(VI) was reduced to Te(IV) by using solid sodium bromide as reductant in order to avoid sample dilution. The developed method was evaluated by the analysis of a reference material (SGR-1).

2. Experimental

2.1. Apparatus

An Unicam VP-90 continuous-flow vapour system equipped with a B-type gas-liquid separator (Cambridge, UK) and a Permapure drier tube from PS Analytical (Sevenoaks, Kent, UK) was used for hydride generation. An Excalibur atomic fluorescence detector PSA 10033 from PS Analytical, equipped with a tellurium boosted discharge hollow cathode lamp (BDHCL) from superlamp Photron (Victoria, Australia), an hydrogen diffusion flame, a series of lenses and a specific filter and a solar blind photomultiplier, was employed for tellurium fluorescence measurements at the 214.3 nm resonance wavelength.

Flexible polyvinyl-chloride peristaltic pump tubes of 1.85 mm and 1.14 mm id

were employed to transport HCl and NaBH$_4$ respectively. All tubes employed to construct the manifold were from 0.8 mm id. polytetrafluoroethylene (PTFE).

For sample digestion, a domestic LG microwave oven, model MS 1905-C (Manchester, U.K.), with a magnetron frequency of 2450 MHz and a maximum exit power of 750 W was used.

2.2. Reagents and standards

All the reagents used were of the highest purity available, and reagent-grade water, obtained from a Milli-Q water purification system Millipore (Bedford, MA) with a resistivity of 18 M/cm, was used for preparation of standards and samples.

A 0.1221 g/L Te(IV) standard stock solution was prepared by dissolving Na$_2$TeO$_3$ Aldrich Chem. Co, (Milwaky, WI) in deionized water. A 0.1228 g/L Te(VI) stock standard solution was prepared in deionized water by dissolving H$_2$TeO$_6$ Fluka (Buchs, Switzerland). The calibration solutions were prepared daily by dilution of stock standard ones with 5.0 mol/L HCl which was prepared from 37% d= 1.18 g/mL HCl Fluka (Buchs, Switzerland). For total tellurium determination 1.0 g of sodium bromide Panreac (Barcelona, Spain) was dissolved, in acidified samples and standards, and employed as reductant.

Sodium tetrahydroborate was prepared from Fluka (Buchs, Switzerland) and dissolved in 0.5% (m/v) NaOH Probus (Barcelona, Spain). This solution was prepared daily and filtered before use with a nylon 0.45 µm pore-size mesh from Lida (Kenosha, WI), and was used as the reducing reagent and as H$_2$ source for the diffusion flame.

Argon C-45 (purity 99.995%) and synthetic air C-45, obtained from Carburos Metalicos (Barcelona, Spain), were used to transport the hydride generated to the atomiser flame and to dry the vapour phase in the Perma Pure drier tube respectively.

2.3. Sample conditioning

Mineral and drinking water samples were obtained from the local market in Morocco (Sidi Ali, Sidi Harazem) and Spain (Bejis) and tap waters taken from several towns near Valencia (Burjassot, Els Pous). Samples, collected in polyethylene bottles, were acidified with concentrated HCl to obtain a pH near 1.2 to minimize adsorption of trace elements on the bottle walls and microorganisms proliferation and were stored in the dark.

Sediment reference material SGR-1 was obtained from U.S. Geological Survey.

Table 1
Operating conditions for HG-AFS determination of tellurium

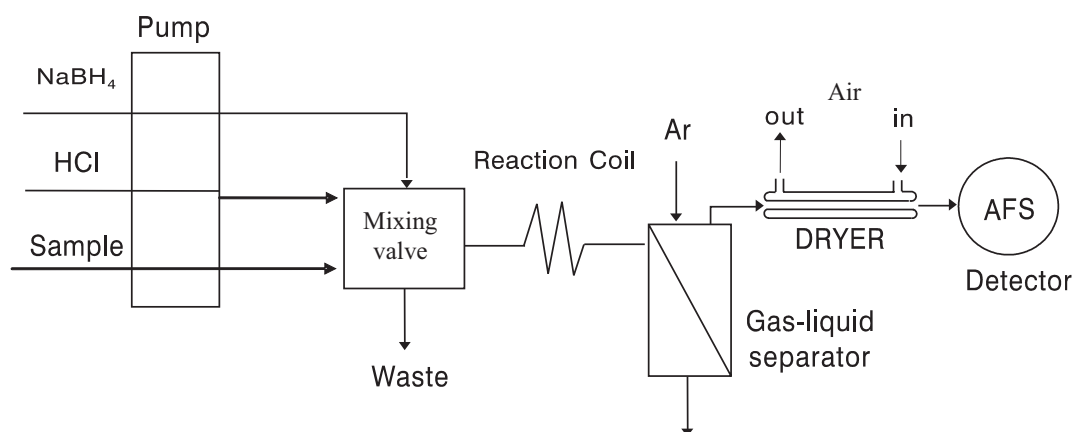| Parameter	
Spectrometer operating conditions	
Resonance wavelength/nm	214.3
Bandpass/nm	0.5
Primary current/mA	15.0
Boost current/mA	17.5
Gain	6.0
Potentiometer	6.0
Hydride generation conditions	
Reagent concentration	
HCl / mol/L	5.0
NaBH$_4$ /% (m/v)	1.2
NaBr /% (m/v)	4
Reagent flow rate	
Sample/HCl / mL/min	9.8
NaBH$_4$ / mL/min	3.1
Argon / mL/min	400
Air / L/min	3.0
Reaction coil length /cm	100

Figure 1.   Manifold employed for the on-line HG-AFS determination of tellurium.

2.4. Analytical procedure

Table 1 summarises the instrumental and experimental conditions for tellurium determination, and Figure1 shows the manifold employed in this study.

For Te(IV) determination, a water sample volume of 12.5 mL was acidified with concentrated HCl and diluted to 25 mL with deionized water obtaining a 5.0 mol/L HCl solution.

Standard solutions, reagent blank and samples, transported at a flow rate of 9.8 mL/min, were merged with a 1.2% (m/v) $NaBH_4$ solution, in 0.5% (m/v) NaOH, with a flow rate of 3.1 mL/min, to produce the tellurium hydride. The hydride was generated in a reaction coil of 100 cm, and the reagents mixture passed to the gas-liquid separator, being transported the Te hydride to the detector by an argon flow rate of 400 mL/min.

For the total tellurium determination in water, the aforementioned procedure was used after a previous reduction of the samples. 1.0 g of NaBr was added to the acidified samples and then the solution heated at 60°C during 10 minutes inside a water bath. All solutions were further cooled to room temperature before reaction with $NaBH_4$ for hydride generation.

2.5. Microwave-assisted leaching procedure

For quantitative leaching of tellurium from sediments, 200 mg of sediment were weighed and introduced into a 115 mL PTFE reactor. A volume of 3 mL of different concentrations of HCl (from 1 to 6 mol/L) was added to the sample and the reactor was closed hermetically and irradiated in a microwave oven, operated at 750 W, during three steps of 1 minute. After that, the reactor was let to cool and the partially dissolved sample was dispersed to 25 mL with water. 5 mL of the supernatant solution were diluted to 25 mL with HCl to obtain a final concentration of 5 mol/L and the Te determination was carried out as indicated before. Acid solutions were employed as standards for the analysis of leached samples and results were compared with the standard addition procedure to prevent possible matrix interference.

3. Results and discussion

3.1. Effect of hydrochloric acid and sodium tetrahydroborate concentrations on Te fluorescence

The study of the HCl concentration effect on the atomic fluorescence signal for Te(IV), showed in Figure 2, indicated that signals obtained are strongly influenced by HCl concentration in the range between 0.5

and 7 mol/L. However, HCl did not influence blank signals. The increase of HCl increases Te fluorescence signal up to reach a maximum value for 6.0 mol/L HCl, and it was observed a strong reduction of Te(IV) fluorescence for a 6.5 mol/L HCl. So a HCl concentration of 5.0 mol/L was selected. Moreover, a 10 ng mL Te(VI) standard solutions gives the same fluorescence signal as the blank in the HCl range studied.

Previous experiments demonstrated that a $NaBH_4$ concentration higher than 1% (m/v) was required to maintain the hydrogen flame. Figure 3 summarizes studies carried out about the influence of $NaBH_4$ concentration, on the Te(IV) hydride fluorescence using a 3.0 mL/min $NaBH_4$ flow. As can be seen, it was observed a dramatic influence of the $NaBH_4$ concentration on the Te(IV) and blank fluorescence signals, being found at 1.8% $NaBH_4$ the maximum fluorescence. However, to obtain a good signal to noise relationship, and in order to obtain the best analytical performance, a $NaBH_4$ concentration of 1.2% (m/v) was selected for Te(IV) determination.

3.2. Effect of carrier and sodium tetrahydroborate flow rates on Te hydride generation

The effect of the sample flow rate on the tellurium hydride generation was studied between 4.0 to 12.5 mL/min. Results shown in Figure 4 indicate that tellurium fluorescence signal increases on increasing the flow rate up to reach a maximum value for 10.5 mL/min whereas the blank signal remains constant in all the range studied. Furthermore, the use of higher flow rates causes an increasing unstability of signals and was not recommended. So, to obtain the best signal to noise relationship, a 9.8 mL/min flow rate was considered as the most appropriate.
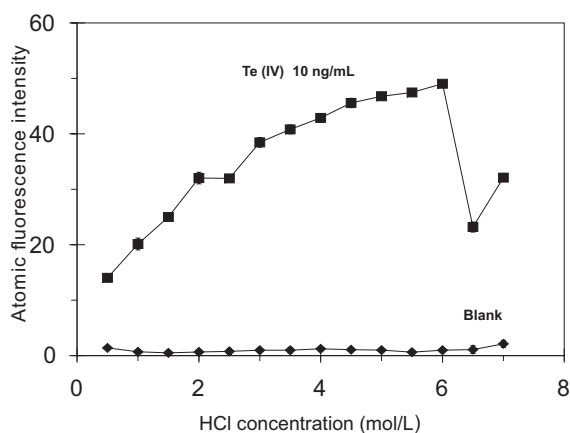

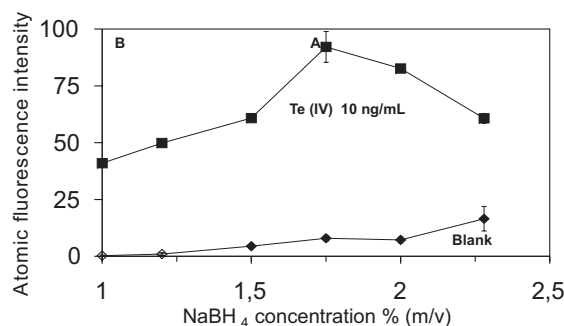Figure 2.   Effect of HCl concentration on the fluorescence of 10 ng/mL Te(IV).

Figure 3.   Effect of $NaBH_4$ concentration on the fluorescence of 10 ng/mL Te(IV).
Hydride generation conditions: Standard/sample carrier flow 7.5 mL/min, HCl 5.0 mol/L, $NaBH_4$ flow 3.0 mL/min, Ar flow 300 mL/min, reaction coil length 100 cm.

Further studies on the efficiency of the hydride generation for different flow rates of $NaBH_4$, between 2.0 and 5.5 mL/min, were carried out. The flame was extinguished when flow rates lower than 2.0 mL/min were employed. The maximum signal was obtained for a 3.1 mL/min flow rate, being observed that the use of higher than 3.1 mL/min $NaBH_4$ values only increases the unstability of blank signals.

3.3. Effect of reaction coil length on fluorescence signals

The reaction coil length controls the hydride generation time, for a fixed flow rate, and it can affect the fluorescence signal depending on the speed of tellurium hydride formation. For a fixed total carrier flow of 11.9 mL/min it was evaluated the effect of the reaction coil length, from 50 to 300 cm using a PTFE tube of 0.8 mm of internal diameter. As can be seen in Figure 5, the increase of coil length from 50 to 100 cm increases slightly the tellurium hydride signal. On the other hand, coils longer than 100 cm cause signal decreasing, possibly due to the increase of dispersion and thus, a 100 cm coil was selected. Moreover, blank signal do not varies as a function of the coil length changes.

3.4. Effect of Argon flow rate on fluorescence signals

The increase of the Ar flow rate increases the tellurium fluorescence signal up to reach a maximum value for a value of 400 mL/min. The fluorescence of the blank remains practically independent on the Ar flow. On the other hand, the use of an Ar flow higher than 500 mL/min extinguished the flame, and when Ar flow rates employed were lower than 200 mL/min the flame can not be ignited. According to that an Ar flow of 400 mL/min was chosen as the most adequate for tellurium determination.

3.5. Reduction of Te(VI)

It is important to note that, in the conditions previously selected for Te(IV) hydride generation, Te(VI) solutions do not give any fluorescence signal. Because of that, the effect of a previous reduction step on the fluorescence intensity of tellurium was investigated in order to obtain as higher as possible signals from Te(VI).

Some papers have reported the use of concentrated HCl (21), 4 M HCl (18), 3 M HCl (22) 20% HCl (23) or 0.5 M HCl (20) for the reduction of Te(VI) to the Te(IV). Other authors employed KI and ascorbic acid (9,
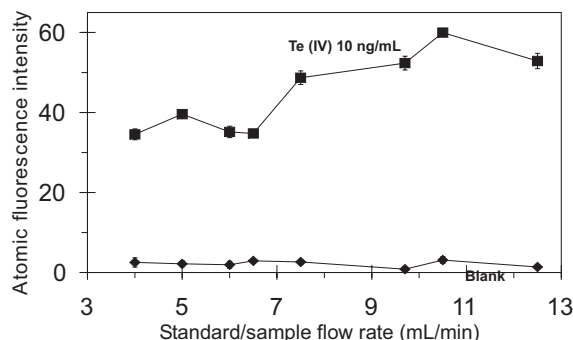

Figura 4. Effect of the standard/sample carrier flow on the fluorescence of 10 ng/mL Te(IV). Hydride generation conditions: HCl 5.5 mol/L, NaBH$_4$ 3% (m/v) on NaOH 0.5% (m/v), NaBH$_4$ flow 1.4 mL/min, Ar flow 400 mL/min, reaction coil length 150 cm.
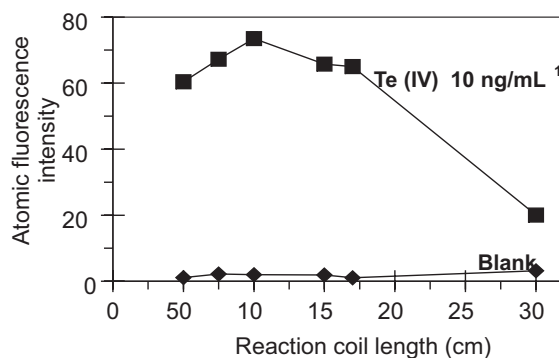

Figura 5. Effect of reaction coil length on the fluorescence of 10 ng/mL Te(IV). Hydride generation conditions: NaBH$_4$ flow 1.4 mL/min, HCl 5.5 mol/L, NaBH$_4$ 3 % (m/v) on NaOH 0.5% (m/v), Standard/sample carrier flow 10.5 mL/m, Ar flow 400 mL/min.

24) as reductant reagents before hydride generation. However, experiments carried out with 5 M HCl heating at 50°C and 70°C during 1 hour, do not provide evidences on reduction of Te(VI) to Te(IV).

Table 2

Effect of temperature, heating time and NaBr concentration on the hydride fluorescence signal ratio obtained from Te(VI) and Te(IV).

Time (min)	Fluorescence ratio (in%) between signals found from Te(VI) and Te(IV)				
	50°C 2% NaBr	50°C 4% NaBr	60°C 2% NaBr	60°C 3% NaBr	60°C 4% NaBr
0	12 ± 9	14 ± 2	12 ± 9	10 ± 3	14 ± 2
5	–	27 ± 9	–	–	63 ± 2
7	–	–	–	–	80 ± 1
10	26 ± 9	50 ± 10	56 ± 6	77 ± 4	97 ± 9
15	–	80 ± 10	–	–	96 ± 5
20	20 ± 5	61 ± 3	82 ± 7	97 ± 6	104 ± 4
25	–	90 ± 10	–	–	87 ± 6
30	40 ± 10	80 ± 5	89 ± 3	104 ± 4	98 ± 2
40	–	–	98 ± 1	95 ± 5	–
50	–	–	105 ± 3	–	–
60	93 ± 3	95 ± 5	99 ± 5	–	–

Sodium bromide is an efficient reductant for Te(VI) as can be seen in Table 2. This Table shows the ratio between Te(VI) and Te(IV) fluorescence signals from solutions of the same concentration that undergoes the same reduction procedure, that is, same temperature, heating time and NaBr concentration. Nevertheless, the reduction of Te(VI) to Te(IV) depends on both, NaBr concentration and temperature, being observed that using a 4% NaBr concentration and 50°C, 20 minutes are enough to obtain comparable results between fluorescence of tellurium hydride obtained from Te(IV) and Te(VI) solutions. On the other hand, the increase of temperature till 60°C provides a quantitative reduction of Te(VI) to Te(IV) in 10 minutes, thus offering the same fluorescence for solutions of 5 µg/L tellurium obtained from Te(IV) and Te(VI). So, the aforementioned conditions were selected in order to obtain accurate results in total tellurium determination in aqueous or dissolved samples.

3.6. Analytical figures of merit

Typical calibration lines obtained for the two species considered, when standards were prepared without any previous reduction for Te(IV) and with the previous reduction step for Te(VI), correspond to equations:

IF = 6.79 (Te(IV)) - 0.719; r = 0.994

IF = 7.10 (Te(VI)) + 0.453; r = 0.998

As it has been indicated before, without a previous reduction step the fluorescence signal obtained from Te(VI) was practically undetectable. However, as can be seen from equations, the slope of calibration lines obtained from both, Te(IV) and Te(VI) after reaction with NaBr, were statistically comparable.

Using the operating conditions indicated in Table 1, the calibration graphs were linear up to a concentration of 20 µg /L, but could be enlarged if the sensitivity of the instrument was reduced. The detection limit,

established as $3s_b$/slope, where s_b is the standard deviation of 10 blank measurements, were in the range between 0.4 and 0.7 µg/L for Te(IV) and from 0.4 to 0.9 µg/L for Te(VI) determination. The coefficient of variation, evaluated from the relative standard deviation of 3 independent determinations of a same sample in the whole range of calibration varied between 1 and 16% for Te(IV) and from 0.2 to 13% for Te(VI).

The accuracy of the method was evaluated by recovery experiments carried out using water samples spiked with known concentration of Te(IV) and Te(VI) at different concentration levels from 0.4 to 2.0 µg/L and from 1.0 to 3.0 µg/L respectively. As can be seen in Table 3, the analytical recovery values achieved were closed to 100% in all the experiments.

3.7. Determination of total tellurium in sediments

Additional experiments were carried out to confirm the accuracy of the developed procedure, and it was determined the total tellurium concentration in a certified sample (SGR-1 USGS).

To get the quantitative tellurium leaching from sediment, a microwave assisted treatment at 750 W was employed. From studies carried out, a three minutes digestion with HCl 6 mol/L, in 1 minute steps, was considered adequate. Results obtained were 0.250 ± 0.003 ng/g in front of the 0.248 ng/g proposed value in the certified sample.

On the other hand, to reduce the pressure problems produced from the high HCl concentration employed, it was studied the leaching effectiveness of HCl concentration, maintaining constant the heating steps. Figure 6 shows the obtained results and, as can be see, a 3 mol/l concentration of HCl is enough to achieve the quantitative leaching of tellurium from sediment. Additional experiments, in which slopes of external calibration and standard addition calibration were compared, for sediment analysis, evidenced that the HCl concentration and sample matrix do not affect the fluorescence measurements, obtaining slope ratios between 94 and 102%.

4. Conclusión

Hydride generation atomic fluorescence provides a sensitive methodology for direct determination of Te(IV) and total tellurium at µg/L levels. The LOD obtained,

Table 3

Analytical recovery of Te (IV) and Te (VI) in mineral[a] and drinking[b] waters at different levels of concentration

Water	Te(IV)		Te(VI)	
	Added (ng/mL)	R (%)	Added (ng/mL)	(R%)
I	0.4	100 ± 2	2.0	95 ± 4
II	0.8	98 ± 4	2.0	98 ± 2
III	0.8	105 ± 5	1.0	107 ± 7
IV	0.4	103 ± 3	1.0	100 ± 9
V	2.0	102 ± 3	3.0	108 ± 6
VI	1.6	103 ± 6	3.0	100 ± 1

[a]Mineral waters: I, Bejis; II, Sidi Ali; III, Sidi Harazem.   [b] Tap waters: IV, Pous; V, Burjassot 1; VI, Burjassot 2.
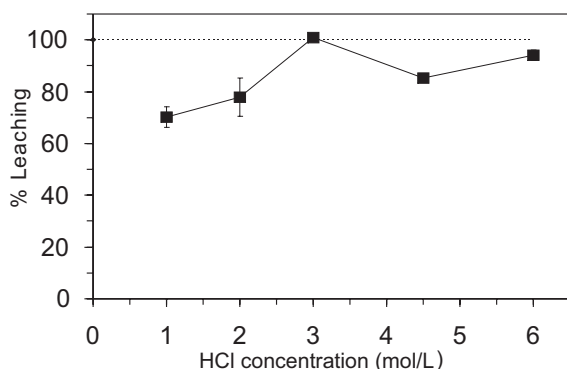R (%): Recovery values obtained from three replicates ± standard deviation.

Figura 6. Effect of HCl concentration on leaching percentage of total tellurium from sediment sample during microwave-assisted sample treatment (n=3).

0.4 to 0.7 ng/mL, are of the same order or better than those found in the literature, 0,1 ng/mL (17) and 80 ng/mL (16). However, the concentration of Te(IV) and Te(VI) present in natural waters make necessary the use of a preconcentration step before the determination of these species in waters. The use of a prereduction step, based on the use of solid NaBr, provides a way to do the determination of Te(IV) and total tellurium, being confirmed by the recovery studies carried out on spiked water samples. On the other hand, the developed procedure for the determination of tellurium by HG-AFS has been validated analyzing a sediment that has a Te concentration level higher than that found in natural and mineral waters.

Acknowledgments

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