# Determination of Tellurium by ETAAS With Preconcentration by Coprecipitation With Lanthanum Hydroxide

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## INTRODUCTION

Tellurium is a rare trace element and used as an additive to improve alloys. Powdered tellurium is employed as a secondary vulcanizing agent in various kinds of rubbers (natural rubber and styrene-butadiene rubbers) since it reduces curing time and endows the rubbers with increased resistance to heat and abrasion. Due to its photoelectric properties, tellurium and its compounds are also employed in the semiconductor and electronic industries (1). Because of the extremely low levels of tellurium in various matrices, a sensitive method is required for its determination.

In the past years, several methods have been developed for the determination of Te at low concentrations, among them anodic stripping voltammetry (2–4), inductively coupled plasma optical emission spectrometry (ICP-OES) (5,6), inductively coupled plasma mass spectrometry (ICP-MS) (7,8), and electrothermal atomic absorption spectrometry (ETAAS) (8–11).

Electrothermal atomic absorption spectrometry appears to be one of the most attractive approaches for trace element determination (12–14). However, the direct determination of ultratrace amounts of elements by ETAAS is usually difficult owing to an insufficient instrument detection power.

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## ABSTRACT

A procedure for the determination of traces of total tellurium is described which combines electrothermal atomic absorption spectrometry (ETAAS) with preconcentration of the analyte by coprecipitation. The samples, each spiked with lanthanum nitrate (20 mg L$^{-1}$), are introduced into the Amberlite XAD-4 resin, and mixed with ammonium buffer (pH 9.1). Tellurium is preconcentrated by coprecipitation with the generated lanthanum hydroxide precipitate. The precipitate is quantitatively collected in the resin, and subsequently eluted with 5% (v/v) nitric acid. The determination is developed with ETAAS.

Considering a sample consumption of 25 mL, an enrichment factor of 10 was obtained. The detection limit (3σ) was 0.04 µg L$^{-1}$ and the precision (relative standard deviation) was 3.5% (n=10) at the 10-µg L$^{-1}$ level. The calibration curve, using the preconcentration system for tellurium, was linear with a correlation coefficient of 0.9993. Satisfactory results were obtained for the determination of tellurium in the standard reference material NIST 1643d Trace Elements in Water and in a tap water sample.

Consequently, preconcentration procedures, such as ion exchange, adsorption, solvent extraction and coprecipitation, are often needed before ETAAS determination.

Separation and preconcentration techniques using sorption extraction (2–4), solvent extraction (10), ion exchange (9), and coprecipitation (6) have been employed for the preconcentration of tellurium in batch and flow injection modes.

The use of a knotted reactor (KR) as collector for precipitates has been found feasible in flow injection (FI) on-line precipitation-preconcentration systems. Besides, using KR, stainless-steel filters and packed-bed filters have also been used to retain precipitated compounds (15–17). Although XAD adsorption resins have been employed in on-line preconcentration systems for retaining soluble complexes (18–20), in a previous work we have reported the use of XAD-7 resin as a filter packing to retain Pb-diethyldithiocarbamate precipitate (21).

In the present work, a method for the preconcentration of tellurium and its determination by ETAAS is proposed. Tellurium was preconcentrated by coprecipitation with lanthanum hydroxide using a packed-bed filter with Amberlite XAD-4 resin packing. The methodology was applied for the analysis of tellurium in the standard reference material NIST 1643d Trace Elements in Water and in tap water.

## EXPERIMENTAL

### Instrumentation

The measurements were performed with a Shimadzu Model AA-6800 atomic absorption spectrometer (Tokyo, Japan), equipped with a deuterium background corrector, a Model 6500 electrothermal atomizer, and an ASC-6100

autosampler. Wall atomization with standard high-density graphite tubes (Shimadzu-Tokyo-Japan) was used. Some experiments were developed comparing the performance of high density graphite tube, pyrolytic graphite tube, and graphite tube with L'vov platform. Best results were obtained with the high density graphite tube. The use of a matrix modifier was not necessary because with the furnace program used there were no analyte losses. The introduction of oxygen was not necessary due to the simplicity of the matrix under study. A tellurium hollow cathode lamp (Hamamatsu Photonics K.K., Japan) was employed as the radiation source.

The instrument settings and furnace program are detailed in Table I. A Minipuls™ 3 peristaltic pump (Gilson, Villiers-Le-Bell, France) was used. A home-made microbore glass column (50 mm length; 3 mm internal diameter) fitted with porous 25 μm glass frits was used as the resin holder. Pump tubes, Tygon® type (Ismatec, Cole-Parmer Instrument Company, Niles, IL, USA), were employed to propel the sample, reagent, and eluent.

### Reagents

Amberlite XAD-4 resin (Rohm & Haas, Philadelphia, PA, USA) was used. The particle size was between 20 and 50 mesh with a surface area of 450 $m^2$ $g^{-1}$. Before use, the surface of the resin was activated by immersion in a solution of 4 mol $L^{-1}$ methanol/hydrochloric acid (1:1). Subsequently, the metal impurities were removed by further washing with 2 mol $L^{-1}$ HCl solution.

Tellurium standard solution was prepared by appropriate dilutions of a 1000 mg $L^{-1}$ stock solution (Merck, Darmstadt, Germany) immediately before use.

**TABLE I**
**Instrumental Operating Parameters and**
**Furnace Temperature Program for Te Determination**

| Parameters | |
| --- | --- |
| Wavelength | 214.3 nm |
| Spectral Bandpass | 0.2 nm |
| Lamp Current | 14 mA |
| Background Correction | Deuterium Lamp |

**Furnace Program**

| Stage | Temp. (ºC) | Time (s) Ramp | Time (s) Hold | Argon Gas Flow (L min$^{-1}$) |
| --- | --- | --- | --- | --- |
| Drying | 120 | 30 | - | 0.10 |
| | 250 | 10 | - | 1.0 |
| Pyrolisis | 600 | - | 20 | 1.0 |
| | 600 | - | 5 | 0.0 |
| Atomization | 2500 | - | 3 | 0.0 (Read) |
| Cleaning | 2600 | - | 2 | 1.0 |

Lanthanum nitrate solution (0.5% m/v) was made by dissolving 0.66 g of lanthanum nitrate hexahydrate in 100 mL of ultrapure water.

The buffer solutions used were in all instances 0.2 mol $L^{-1}$ ammonium chloride, adjusted to the appropriate pH (9.0–9.2) by addition of 0.2 mol $L^{-1}$ ammonia; the optimum pH was found to be 9.1.

Ultrapure water (18 MΩ cm$^{-1}$) was obtained from an EASY pure RF (Barnstedt, Dubuque, IA, USA).

All solvents and reagents were of analytical reagent grade or better, and the presence of tellurium was not detected in the working range.

### Sample Pretreatment

Water samples were filtered through a 0.45-μm pore size membrane filter. An appropriate amount of 0.5% lanthanum nitrate solution was added (so that each sample solution contained a final concentration of 20 mg $L^{-1}$ lanthanum nitrate) and then acidified to pH 3.0 with 0.1 mol $L^{-1}$ hydrochloric acid.

### Operational Procedure

A 25-mL sample and buffer solution at 5.0 mL min$^{-1}$ and 1.0 mL

min$^{-1}$ loading flow rates, respectively, was loaded by means of peristaltic pump into the column. The sample and buffer streams merged at a point about 1 cm upstream of the column. The precipitate, which is formed instantaneously after the merging point, was collected on the XAD-4 resin. The effluent emerging from the resin was discarded. The coprecipitated analyte was eluted from the resin with nitric acid up to a final volume of 2.5 mL.

After the preconcentration step, 50 μL of the analyte solution was automatically introduced into the graphite tube by means of the furnace autosampler. Then, the autosampler arm was moved back to the wash position and the atomization program was started. The absorbance measurements (peak height) were proportional to the tellurium concentration in the sample, and were used for all measurements. With respect to the characteristic mass for tellurium, the manufacturer does not report any value for this analyte. The characteristic mass obtained in our laboratory was 20 pg.

## RESULTS AND DISCUSSION

### Effect of pH and Lanthanum Concentration

Preliminary experiments showed that the pH and the lanthanum concentration in the sample were critical for the precipitation reaction itself and the subsequent recovery of tellurium. Measured on standards all containing 10 µg L$^{-1}$ of tellurium, the absorbance remained almost constant in the pH ranges of 9.0–9.2. The results obtained are shown in Figure 1. Moreover, the lanthanum nitrate concentration was within the range: 15–30 mg L$^{-1}$. In the present work, 20 mg L$^{-1}$ lanthanum nitrate and a pH of 9.1 were selected for subsequent studies. These results are in agreement with those obtained by Tao et al. (15) who used knotted reactors for the determination of Se .

### Selection of Resin

A resin Amberlite XAD-4 packing filter allowed the tellurium present in the samples to be efficiently preconcentrated. This might have been due not only to retention by filtration of the precipitate, but also possibly due to adsorption effects of the precipitate on the resin surface. The resin size constitutes an important parameter, since it must allow appropriate precipitate retention with low hydrodynamic impedance. The particle size used in this work (20–50 mesh) permitted us to obtain optimum retention (95%) at sample flow rates of 5 mL min$^{-1}$.

### Sample Loading Rate

The sample flow rate through the column is one of the steps that controls the  preconcentration time. In this study it was verified that with flow rates up to 5.0 mL min$^{-1}$ there is no effect on analyte recovery, which under optimum conditions is 95%. Figure 2 shows that at higher flow rates the recovery decreases.
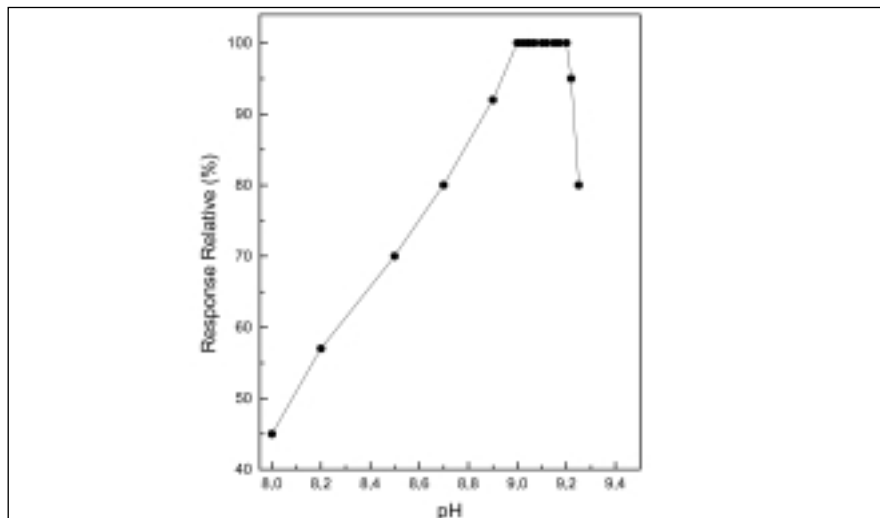


Fig. 1. Effect of pH of loading solutions. Sample loading volume 25 mL, loading flow rate 5 mL min$^{-1}$, elution flow rate 1.5 mL min$^{-1}$, Te concentration 10 µg L$^{-1}$, lanthanum nitrate concentration 20 mg L$^{-1}$.
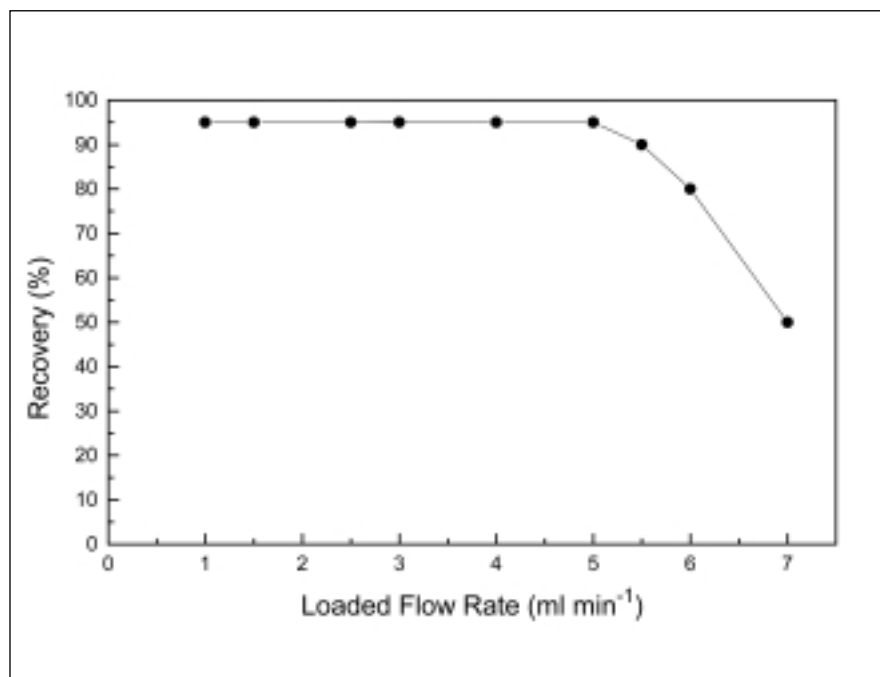


Fig. 2. Analysis of sample loading rate. Sample loading volume 25 mL, elution flow rate 1.5 mL min$^{-1}$, Te concentration 10 µg L$^{-1}$, lanthanum nitrate concentration 20 mg L$^{-1}$.

## Effect of Eluent

A satisfactory eluent should effectively dissolve the precipitate with a discrete volume in order to obtain a better enrichment factor. Nitric acid turned out to be a good eluent for the tellurium coprecipitate with lanthanum hydroxide. It was found that 5% (v/v) nitric acid was the minimum concentration necessary to obtain best response. The optimum flow rate of the eluent used was 1.5 mL min$^{-1}$.

## Interference Studies

The proposed coprecipitation system can tolerate the presence of ions at the concentration levels that may be found in natural water samples. Thus, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$, $Ni^{2+}$, $Co^{2+}$, $Mn^{2+}$, and $Fe^{3+}$ could be tolerated up to at least 2500 µg L$^{-1}$. Commonly encountered matrix components, such as alkali and alkaline earth elements, are not retained on the column.

## Analytical Performance

The time required for the preconcentration of 25 mL of sample (5.0 min, flow rate of 5 mL min$^{-1}$), elution (1.7 min, flow rate of 1.5 mL min$^{-1}$), and conditioning (0.2 min) was about 6.9 min. Additionally, the time required for the ETAAS determination was about 1.0 min, resulting in a sample throughput of seven samples per hour.

A 10-fold total enrichment factor for a sample volume of 25 mL was obtained with respect to the tellurium determination by ETAAS without preconcentration.

The relative standard deviation (RSD) for 10 replicates containing 10 µg L$^{-1}$ of Te was 3.5%. The calibration curve was linear, with a correlation coefficient of 0.9993. The detection limit (DL), calculated as the amount of Te required to yield a net peak equal to three times the standard deviation of the background signal (3s), was 0.04 µg L$^{-1}$.

### TABLE II
### Recovery Study

| Aliquots | Base Value (µg L$^{-1}$) | Te Added (µg L$^{-1}$) | Te Found (µg L$^{-1}$) | Recovery (%)[a] |
|---|---|---|---|---|
| 1–6 | – | 0.0 | 0.0 | – |
| 7 | 0.0 | 1.0 | 0.95 | 95.0 |
| 8 | 0.0 | 2.0 | 1.98 | 99.0 |
| 9 | 0.0 | 3.0 | 3.06 | 102.0 |
| 10 | 0.0 | 5.0 | 5.0 | 100.0 |

[a] 100 x [(Found-Base)/Added].

In comparison to our method, the procedure of multiple injections would be too time-consuming. Besides, it would require 10 injections of 50 µL each to obtain a signal comparable with that of the preconcentation procedure. On the other hand, we believe that a drying stage would be indispensable in order to inject 500 µL due to the limited capacity of the graphite tube (approximately 100 µL).

## Recovery and Validation Studies

Since tellurium was not detected in the tap water samples, we spiked the samples with a known quantity of tellurium and applied the preconcentration procedure.

In order to evaluate the tellurium recovery of this method, 250 mL of tap water sample was collected in our laboratory and divided into 10 portions of 25 mL each. The proposed method was applied to six portions and the average quantity of tellurium obtained was taken as the base value. Then, increasing quantities of tellurium were added to the other sample aliquots and tellurium was determined by the same method. The results obtained were between 95–102 % (Table II). Even though the method of standard addition is not as useful as the method of validation; it is considered as a method of validation (22).

Additionally, the proposed method was applied to a standard reference material, NIST SRM 1643d Trace Elements in Water, with a reference tellurium content of 1.0 µg L$^{-1}$. The density of the SRM 1643d sample at 22ºC was 1.016 g mL$^{-1}$. Using our method, the tellurium concentration found in this SRM was 1.1 ± 0.1 µg L$^{-1}$.

## CONCLUSION

Although the proposed methodology was not completely automated, the on-line preconcentration system increases the speed of the preconcentration and analysis process.

The preconcentration procedure with lanthanum hydroxide using a packed-bed filter with Amberlite XAD-4 resin packing and coupled to ETAAS allowed better detection limits, approximately 10-fold, in comparison to tellurium determination without preconcentration. The recovery studies performed indicate that the method shows good reproducibility and accuracy.

## REFERENCES

1. H.G. Seiler, A. Sigel, and H. Sigel, Handbook on Metals in Clinical and Analytical Chemistry, Marcel Dekker, New York (1994).

2. J. Wang and J. Lu, Electroanalysis 6, 405 (1994).

3. T. Ferri, S. Rossi, and P. Sangiorgio, Anal. Chim. Acta 361, 113 (1998).

4. M. Baldelli, T. Ferri, A. Liberatori, and B.M. Petronio, Analusis 22, 147 (1994).

5. P. Fodor and R.M. Barnes, Spectrochim. Acta 388, 229 (1983).

6. L. Halicz and G.M. Russell, Analyst 111, 15 (1986).

7. A.G. Coedo and M.T. Dorado, J. Anal. At. Spectrom. 9, 1111 (1994).

8. S.K. Aggarwal, M. Kinter, J. Nicholson, and D. Herold, Anal.l Chem. 66, 1316 (1994).

9. M. Grotti and A. Mazzucotelli, J.f Anal. At. Spectrom. 10, 325 (1995).

10. V.G. Torgov, G.A. Vall, M.G. Demidova, and V.T. Yatsenko, Chem. Geol. 124, 101 (1995).

11. T. Wickstrom, W. Lund, and R. Bye, Analyst 120, 2695 (1995).

12. R.E. Sturgeon, Fresenius' J. Anal. Chem. 355, 425 (1996).

13. E. Vereda Alonso, A. García de Torres, and J.M. Cano Pavón, Talanta 55, 219 (2001).

14. Z-L. Fang, Spectrochim. Acta Part B 53, 1371 (1998).

15. G. Tao and E. Hansen, Analyst 119, 333 (1994).

16. S. Nielsen, J.J. Sloth, and E. Hansen, Analyst 121, 31 (1996).

17. Z-L. Fang, Flow Injection Separation and Preconcentration, VCH, Weinheim, Germany (1993).

18. V. Porta, C. Sarzanini, E. Mentasti, and O. Abollino, Anal. Chim. Acta 258, 237 (1992).

19. R.G. Wuilloud, H.A. Acevedo, F.A. Vazquez, and L.D. Martinez, Anal. Letters 35, 1649 (2002).

20. S. Moyano, R.G. Wuilloud, R.A. Olsina, J.A. Gásquez, and L.D. Martinez, Talanta 54, 211 (2001).

21. R.G. Wuilloud, J.A. Salonia, J.A. Gásquez, R.A. Olsina, and L.D. Martinez, Anal. Sciences 17, 457 (2001).

22. E. Prichard, G.M. MacKay, and J. Points, Trace Analysis: A structures approach to obtaining reliable results, The Royal Society of Chemistry, UK (1996).