UNIVERSITÉ DE GENÈVE

Archive ouverte UNIGE

https://archive-ouverte.unige.ch

Article scientifique | Article | 2020

Published version | Open Access

This is the published version of the publication, made available in accordance with the publisher's policy.

A general strategy for the voltammetric trace determination of tellurium in geochemical and environmental matrices after arsenic coprecipitation and critical assessment of digestion schemes

Biver, Marc; Filella, Montserrat

How to cite

BIVER, Marc, FILELLA, Montserrat. A general strategy for the voltammetric trace determination of tellurium in geochemical and environmental matrices after arsenic coprecipitation and critical assessment of digestion schemes. In: Environmental Chemistry, 2020, vol. 17, p. 85–92. doi: 10.1071/EN19164

This publication URL: https://archive-ouverte.unige.ch/unige:126587

Publication DOI: 10.1071/EN19164

© This document is protected by copyright. Please refer to copyright holder(s) for terms of use.

SPECIAL ISSUE

CSIRO PUBLISHING

Environ. Chem. **2020**, *17*, 85–92
https://doi.org/10.1071/EN19164

Research Paper

A general strategy for the voltammetric trace determination of tellurium in geochemical and environmental matrices after arsenic coprecipitation and critical assessment of digestion schemes

Marc Biver[A] *and Montserrat Filella*[B,C]

[A]Bibliothèque Nationale de Luxembourg, Annexe Kirchberg, 31, Blvd. Konrad Adenauer, Luxembourg, L-1115, Luxembourg.
[B]Department F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, Geneva, CH-1205, Switzerland.
[C]Corresponding author. Email: montserrat.filella@unige.ch

Environmental context. Among chemical elements classified as elements of strategic importance, tellurium is rapidly becoming an emergent contaminant. There is, however, no accurate and sensitive method for measuring tellurium concentrations in environmental and geological samples (e.g., soils, sediments), and thus it is not possible to determine whether an ecosystem is being polluted by human activities. This study provides a reliable answer to this problem.

Abstract. A general method is proposed for the determination of tellurium in environmental and geochemical samples. Samples may be digested by any technique (acid or fusion digestion). The tellurium in the resulting solution is reductively coprecipitated with added arsenite by hypophosphorous acid, and the precipitate is redissolved and analysed by catalytic anodic stripping voltammetry. Several sample digestion techniques (acid and fusion digestions) are critically assessed. The method is applied to ore certified reference materials, with tellurium concentrations spanning three orders of magnitude, and sediment certified reference materials (ocean, lake and estuarine). An overall limit of detection (LOD) of 5 ppb is achieved. Acid digestion by H_2SO_4 and by $HClO_4$ or sintering with Na_2O_2 in glassy carbon crucibles are shown to be the most adequate sample digestion techniques.

Additional keywords: geochemical samples, sediments, solid sample digestion, voltammetry.

Received 4 June 2019, accepted 27 September 2019, published online 18 November 2019

Introduction

The element Te has recently been attracting attention because of its increasing use in technology and because of the general lack of information regarding its behaviour in the environment. Its history, occurrence and uses have recently been reviewed, alongside the formidable analytical problems posed by this element (Filella et al. 2019). Named 'problematic mineral' for good reason by its discoverer, von Reichenstein, its determination in the major environmental compartments has been hampered both by its extremely low natural concentrations (i.e. in the low ppb range and less) as well as by the scarcity of suitable analytical techniques.

The aim of the present work is two-fold:

1. The precise quantitation of Te at very low concentration levels in solid samples. This is not a routine task and could hitherto only be achieved by specialised inductively coupled plasma mass spectrometry (ICP-MS) techniques with instrumental parameters specifically tuned to this element (Filella and Rodushkin 2018). We have adapted a comparatively simple, low-cost voltammetric technique, previously developed for the analysis of Te in natural waters (Biver et al. 2015), to digestates of solid matrices. This is shown to be feasible if, following a method proposed by Luke (1959), Te is coprecipitated with added As^{III} by hypophosphorous acid.
2. The assessment of digestion methods. Published Te concentrations in soils and sediments led us to question the validity of the analytical results that were obtained subsequent to aqua regia digestion – we suspected analyte losses owing to volatilisation, as are known to occur with other elements, e.g. germanium (Biver and Filella 2018*a*). The volatility of Te from solutions has already been studied by Hoffmann and Lundell (1939) and Fujii et al. (2004). By application of several different digestion techniques to certified reference materials (CRMs), we seek to confirm if low values would indeed be obtained after aqua regia digestions and determine if it is possible to pinpoint better suited alternatives.

The proposed quantitation methodology can be applied to samples containing Te concentrations spanning several orders of magnitude. This is achieved by developing two variants adapted to the level of Te in the sample. When needed, differences between the two variants are clearly explained in the experimental part. They concern: volumes used in the measuring step, the procedure followed to achieve a suppression of Te in blanks and manipulations needed in the coprecipitation

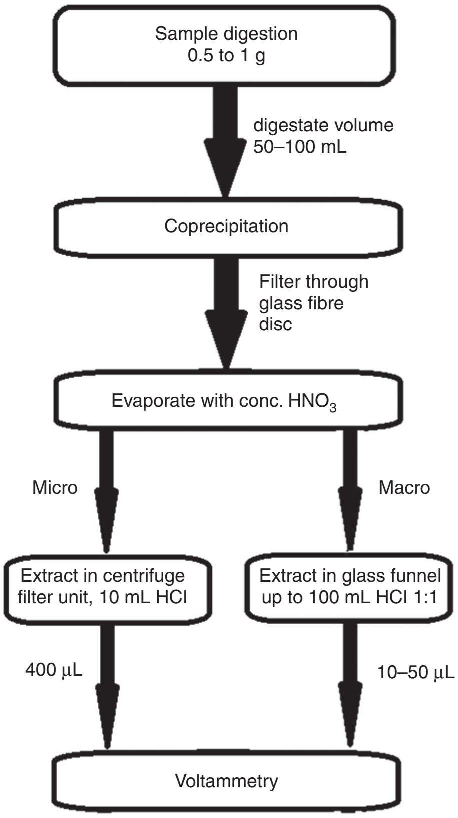

Fig. 1. Summary of the analytical procedure.

step. The experimental procedure is summarised in Fig. 1. Digestion procedures are described in great detail because of the importance to understand the advantages and limitations of the different treatments as a function of the sample characteristics.

Experimental

Reference materials

The reference materials were ore samples from OREAS (Ore Research and Exploration P/L, Australia): OREAS 603, an Au-Ag-Cu ore consisting of epithermal sulfide minerals in a matrix of argillic rhyodacite; OREAS 600, essentially the same composition as OREAS 603 but with a much smaller ore to rhyodacite ratio; OREAS 522, prepared from iron oxide Cu-Au ore and altered porphyritic volcanic rock; OREAS 135, a Zn-Pb-Ag ore consisting of sulfides with graphitic slate, pyrrhotite and pyrite as gangue material; and OREAS 903, consisting of transitional Cu ore (sulfides to oxides). Detailed documentation on the elemental concentrations, mineralogical composition, experimental uncertainties, analytical techniques and participating laboratories are available from the manufacturer's website (www.ore.com.au). Sediment samples were MESS-3 (ocean sediment from the Beaufort Sea); PACS-2 (ocean sediment from the harbour of Esquimalt, British Columbia) issued by the National Research Council of Canada; fresh water lake sediment BCR-701 from lake Orta (Italy), issued by the European Commission's Joint Research Centre (ECJRC, formerly Bureau Communautaire de Référence, BCR); and an estuarine sediment that is in the process of being certified. Its issuing authority requested that the identity and origin of the sample not be disclosed until the certification process is completed. The OREAS materials were chosen so as to cover a range of Te concentrations as wide as possible (from 57 ppm to 34 ppb). Certified Te concentrations do not exist for the sediments.

Reagents

The purity and origin of reagents are given in parentheses when they are first mentioned. All solutions were prepared with ultrapure water (0.055 µS cm^{-1}) from a reverse osmosis unit (TKA Genpure, ThermoFisher, Germany).

Digestion procedures

Our suite of digestion procedures comprised acid digestions by H_2SO_4, HNO_3, $HClO_4$, two commonly used protocols of aqua regia extraction, as well as fusion experiments with $LiBO_2$, NaOH, Na_2O_2 and $KHSO_4$. Digestion techniques are described in standard texts on analytical geochemistry (Jefferey and Hutchinson 1981; Johnson and Maxwell 1989; Heinrichs and Herrmann 1990; Potts 1992); for a modern review, the reader is referred to Cotta and Enzweiler (2012). We chose to avoid the use of HF because we felt that for virtually any sample matrix, alternatives can be found that are less hazardous for both the environment and laboratory personnel. Since the strength of the coprecipitation–voltammetry approach described here lies in its independence of the initial digestion scheme, an HF digestion could well be envisaged if it really were unavoidable for a particular sample. Note that care should be exercised when heating concentrated acids to boiling and handling molten salts. Aqua regia gives off toxic vapour even in the cold and should only be prepared and used in a fume hood. $HClO_4$ is potentially explosive. Inexperienced personnel should familiarise themselves with the special precautionary measures in relation to this compound.

H_2SO_4 digestion

The use of boiling H_2SO_4 on its own is uncommon, yet we chose to include it because it has been specifically recommended for Te determination in minerals (Jankovsky and Kšir 1960).

Procedure. Depending on the expected Te concentration, 0.5 to 1 g of sample were weighed into a 100-mL Kjeldahl flask, together with 3.5 to 7 mL of concentrated H_2SO_4 (95 % (m/m) suprapure) and a few glass beads, and heated to gentle boiling for 5 min over a Bunsen flame. It may be assumed that the temperature at which the digestion took place was that of boiling sulfuric acid, i.e. 335 °C.

$HClO_4$ digestion

$HClO_4$, either on its own or in various combinations with other acids (e.g. the so-called 3-acid or 4-acid digestions), is a popular digestion reagent. The boiling mixture of $HClO_4$ with H_3PO_4 has been recommended as a reliable reagent especially for the analysis of sulfides, because no losses of sulfur occur (Hoyle and Diehl 1971). H_3PO_4, either on its own or in conjunction with $HClO_4$, has recently been discussed as an alternative to HF for the determination of rare earth elements (REE) in a variety of matrices (Hannaker and Hou 1984; Bezerra de Oliveira et al. 2019).

Procedure. 0.25 to 0.5 g of sample were weighed into a 100-mL Kjeldahl flask and heated with equal volumes (3.5 to 7 mL) of concentrated $HClO_4$ (70 % (m/m) suprapure) and H_3PO_4 (85 % (m/m) analytical grade) for 5 min with a few glass beads over a Bunsen flame. After 5 min, the mixture boiled at a constant temperature of 210 °C (i.e. much lower than concentrated H_2SO_4).

In both H_2SO_4 and $HClO_4$ digestions, the Kjeldahl flask was chosen because its long neck facilitates the condensation of vapours and thus avoids the loss of volume and of the active (and volatile) digestion reagents. Both digestates were rinsed from the flask into beakers containing ~50 mL of water, boiled briefly to help dissolve any precipitated sulfates or phosphates and filtered from any undigested material.

HNO_3 digestion

Boiling HNO_3, used on its own, is an equally uncommon digestion reagent, but it was used in an early survey of Te concentrations in rocks and in the solubilisation of elemental Te or pure Te compounds for the preparation of standard solutions (Watterson and Neuerburg 1975).

Procedure. Approximately 0.5 g of sample were weighed into a glass evaporating bowl and covered with 10 mL of concentrated HNO_3 (69 % (m/m) suprapure) and taken to dryness on a boiling water bath.

Aqua regia

Aqua regia is likely the most popular reagent for pseudo-total digestion of soils and sediments. However, the lack of procedural standardisation also makes it the most problematic. Protocols may differ in many respects, such as the sample to reagent ratio, whether the system is open or closed to the atmosphere, temperature and duration of the digestion itself, recovery of vapours and so forth, and very often, experimental details are not communicated, so that results obtained by aqua regia digestion obtained in different laboratories may not be fully comparable. Experience has shown that for some elements, the final recovery may be greatly affected by the choice of experimental conditions and this could be an issue with Te analysis (Filella et al. 2019). Hence, we opted for an 'open beaker' protocol of the type frequently used in soil science (Chen and Ma 2001), and the closed system approach taken by the ISO protocol 11466 (ISO 1995) and recommended by the European Commission–Joint Research Centre (ECJRC) as a quasi-total digestion for soils and sediments. The protocol is used for the 'residual' fraction of the BCR sequential extraction scheme (Ure and Davidson 2002).

Procedures. The 'open' protocol involved weighing ~0.5 to 1 g of sample into a 250-mL beaker and covering the material with 3 mL of concentrated HNO_3 (69 % (m/m) suprapure) and 9 mL of HCl (35 % (m/m) suprapure) and leaving the covered beaker on a hotplate set at 110 °C. After 3 h, the cover was removed and the temperature was increased so as to evaporate the contents to (near-)dryness. The cooled residue was taken up in 1 : 1 HCl (suprapure), heated gently and filtered if insoluble material remained. According to the ISO 11466 protocol (ISO 1995), 1 g of sample was introduced into a 250-mL flat-bottom round flask with a ground neck and 21 mL of HCl (35 % (m/m) suprapure) and 7 mL of HNO_3 (69 % (m/m) supra) were added. The flask was fitted with a reflux condenser and left for 16 h, then refluxed for 2 h. Aqua regia digestates needed treatment with formic acid (Healy 1958) to destroy excess HNO_3 that would be undesirable in the reductive coprecipitation step. 5 mL of formic acid (analytical grade, Roth) were sufficient in the 'open' variant, and 50 mL were added to the digestate of the ISO protocol. After formic acid addition, the solutions were heated gently until the evolution of gas just commenced and the heat source was removed, as the reaction quickly became uncontrollable and spitting out of the beaker was observed. When the evolution of gas subsided, the solutions were gently evaporated to ~100 mL before reductive coprecipitation.

All acid digestions (except the aqua regia 'open beaker' variant in some cases) were incomplete in that a solid residue remained. Therefore, the supernatant was diluted by 50 to 100 mL of water and filtered before further processing through fluted filter paper (Macherey and Nagel, finest porosity).

$LiBO_2$ fusion digestion

Lithium metaborate and tetraborate and mixtures thereof are near-universal fluxes for total digestions of silicates, and we felt that at least one true total digestion technique was needed to assess the Te recovery that other digestions were able to achieve.

Procedure. 0.25 to 0.5 g of sample were mixed with ~2 g of $LiBO_2$ (puratronic, >99.997 %, Alfa-Aesar), well homogenised with the aid of a rounded agate spatula in a Pt crucible (99.7 % Pt + 0.3 % Ir, OEGUSSA, Austria). The covered crucible was heated in a muffle furnace to 800 °C and left at that temperature for 30 to 45 min. The melt was leached in a mixture of 12.5 mL of HCl (36 % (m/m) suprapure) and ~100 mL of water.

NaOH and Na_2O_2 fusion digestions

Total digestions of silicates are also possible by fusing the sample with NaOH in Ag crucibles (Heinrichs and Herrmann 1990), or by fusing or sintering with Na_2O_2 in Ni, Zr or glassy carbon crucibles (Meisel et al. 2002; Bokhari and Meisel 2017). These alkaline and oxidative fluxes were included because they allow for a complete digestion at much lower temperatures than that of $LiBO_2$, which makes volatilisation losses of Te appear less likely.

NaOH fusion procedure. A sturdy silver crucible with a silver lid, which was loaded with ~0.25 g of sample and 4 g of NaOH (>99.99 %, Alfa-Aesar), was used. The crucible was heated to 600 °C in a muffle furnace for 1 h. The cooled crucible was leached with ~100 mL of water and 20 mL of HCl (35 % (m/m) suprapure). Undigested material was separated from the solution by filtration.

Na_2O_2 fusion procedure. 0.25 to 0.5 g of sample and ~3 g of Na_2O_2 were homogenised and the mixture was fused in a Ni crucible. The clear melt was leached in ~200 mL of water and acidified with ~30 mL of HCl (35 % (m/m) suprapure) before processing further. The resulting solution contained high concentrations of Ni^{2+} but, fortunately, they did not affect the analysis. The choice of crucible material and flux reagent purity posed a problem for this particular digestion; this is thoroughly discussed in a dedicated section below.

Sintering with this flux was carried out as follows: Approximately 0.5 g of sample were weighed directly into a glassy carbon or zirconium crucible, ~3 g (accurately weighed) of Na_2O_2 were added and well mixed with an agate spatula. The Na_2O_2 was not ground to a fine powder, but used in the granular form (i.e. as supplied), to avoid further contamination. The crucible was heated in a muffle furnace from ambient temperature to 480 °C, which took ~25 min, and held at that temperature for 30 min. The crucible was allowed to cool and was covered in a beaker with ~100 mL of water and heated gently (not boiled) to aid dissolution once the initially lively reaction had subsided. The solution was rendered acidic by the addition of 25–30 mL of HCl (35 % (m/m) suprapure). The volume of the resulting clear solution was reduced to ~100 mL by gentle evaporation, during which time unreacted peroxide was also decomposed. Even though coarse-grained Na_2O_2 was used, complete sample digestions and complete destruction of organic matter could be achieved. Excessive volume reduction is undesirable to avoid the precipitation of sodium chloride at later stages. The sample solution should not be left for too long before proceeding with the reductive coprecipitation, as silica tends to precipitate out of the hydrochloric solution after a few minutes. It is best not to let the solution cool at all and to complete the whole analysis without interruption.

$KHSO_4$ fusion digestion

$KHSO_4$ forms pyrosulfate when heated and the melt may be used as an 'acidic' flux, in quartz crucibles, to digest refractory oxides of trivalent and quadrivalent metals and other phases that resist alkaline fluxes (Heinrichs and Herrmann 1990). It is thus an important complementary reagent to the latter and was therefore included in this study. 0.5 g of sample were weighed into a quartz crucible and ~5 g of crystalline $KHSO_4$ (analytical grade, Roth) were added on top. Homogenisation proved unnecessary, as the sample was not digested immediately when the flux melted, but rather settled to the bottom of the crucible in the molten salt. Heating was continued until sulfur trioxide fumes started to be evolved and the melt was kept at a temperature such that fuming did not become excessive (so as not eliminate the active decomposing agent SO_3). This was best done manually over an open gas flame, while rotating the crucible. A clear melt was not always obtained. After 5 min, the crucible was allowed to cool somewhat and then leached with boiling dilute sulfuric acid (10 mL of concentrated suprapure and 100 mL of water). The leachate was separated from undigested material by filtration.

Coprecipitation

The idea to use As as a precipitant for Te (and Se) was developed by Luke (1959). The original procedure calls for a precisely defined solution composition before the precipitation is carried out. We observed that the actual acid and salt concentrations could be varied broadly, as long as some excess of HCl was present. In the absence of HCl, precipitation was extremely slow. All other acids resulting from the digestions could be tolerated in virtually any concentration. Even high concentrations of $HClO_4$ did not hinder the reduction, neither did any dissolved salts. Undigested organic matter, however, should be absent. While organic matter did not interfere with the As precipitation as such, it was partly carried over with the precipitated As into the final sample solution and depressed the voltammetric peak intensities. The only other undesirable component was HNO_3, which is why the aqua regia solutions were treated with formic acid beforehand.

A sodium arsenite solution was prepared by dissolving 10 sodium hydroxide pellets (analytical grade, Roth) in 10 mL of water. To the warm lye, 250 mg of arsenious oxide (99.5 %, ACROS, USA) were added, dissolved by swirling, and the volume completed to 200 mL.

To the digestate, which should have a volume of 50 to 100 mL and must contain some HCl, 2 mL of sodium arsenite solution were added, followed by 15 mL of aqueous hypophosphorous acid (H_3PO_2, 50 % (m/m) Alfa-Aesar). The mixture was swirled, heated to boiling with a few glass beads to control bumping and kept boiling gently for exactly 5 min, where the timing was started from incipient precipitation (when the solution began to darken). This was left to cool to a temperature between 80 and 60 °C and the then aggregated precipitate of elemental As was separated by filtration. The concentration of HCl in the initial digestate was not at all critical, as long as some was present. We typically added ~20–30 mL of concentrated HCl (except to aqua regia digestates which already contained HCl). Note that in the complete absence of HCl, no precipitation occurred.

In the *macro* variant, a binder free glass fibre filter pad (Ø 12 cm, Macherey and Nagel) supported on a coarse ashless paper filter (Ø 5.5 cm, Macherey and Nagel), for reasons of mechanical stability, in a glass funnel was used, with both filter discs folded – not fluted – in the traditional way. The precipitate was washed thrice with HCl (1 : 1), followed by water. The filter disc was transferred to a glass evaporating bowl (using ceramic tweezers) and covered with 5 mL of HNO_3 (69 % suprapure). The acid was gently evaporated to complete dryness on a boiling water bath (this took ~1 h). The dried filter was covered by ~25 mL of HCl (1 : 1) and left for at least 1 h, after which, the acid extract was filtered through a glass wool plug in the stem of a glass funnel into a volumetric flask (100 mL). This step was repeated once, without waiting for another hour. The evaporating bowl, glass rod and the glass fibre pulp were rinsed copiously with water and the volume was made up to the mark. Suitable volumes of this solution, which depended on the expected Te content, were directly used for voltammetric analysis. The solutions were stable at room temperature for at least three weeks.

In the *micro* variant, the As was precipitated in exactly the same fashion, but a smaller, folded glass binder free fibre filter was used (Ø 7 cm, Macherey and Nagel), supported on a folded paper filter (Ø 5.5 cm, Macherey and Nagel) in a small glass funnel. The glass fibre disc was treated by HNO_3 exactly as described above. The dried filter was removed from the evaporating bowl and placed in a 5-mL centrifuge filter insert (Oxy Fil® Midi, 0.45 µm), which was contained in a 14-mL disposable PP centrifuge tube. The bowl was rinsed with 3 mL of 1 : 1 HCl and the acid was left in the bowl, with occasional swirling, for ~1 h. The acid was poured on top of the fibre filter and left to act on it for another hour. Filtration was then carried out by centrifugation (EBA 200, Hettich, Germany) at 6000 rpm, corresponding to 3461 *g*, for 2 min. The evaporating bowl was rinsed with two more 2-mL portions of the dilute acid and a third time with 3 mL of water, poured into the centrifuge tube and filtered immediately by centrifugation. The exact volume of the recovered extract ($\approx$ 10 mL) may easily be determined gravimetrically by its specific gravity, if a tared centrifuge tube is used. The centrifuge filter insert was discarded with its contents and the solution containing the Te was stored in the centrifuge tube. We also used 2-mL filter inserts (Merck-Millipore UltraFree-CL, 0.22 µm) as the Oxy Fil inserts are no longer marketed; the extraction was then carried out by 4 × 2 mL of acid (centrifugation time 5 min) and 2 mL of water (centrifugation time 10 min).

Several spike-recovery experiments were conducted to confirm that the whole coprecipitation procedure was quantitative for Te concentrations of the order of those encountered in our samples. No losses were observed.

Instrumentation and voltammetric method

The voltammetric method was implemented on a Computrace VA797 (Metrohm, Switzerland), equipped with a standard three electrode assembly, which consisted of a hanging mercury drop (HMDE) working electrode, a Pt rod as auxiliary electrode and an Ag/AgCl reference electrode with 3 mol L^{-1} KCl as a bridge electrolyte. Nitrogen or argon (99.999 % from L'Air Liquide, Luxembourg) were used for degassing the electrolyte and

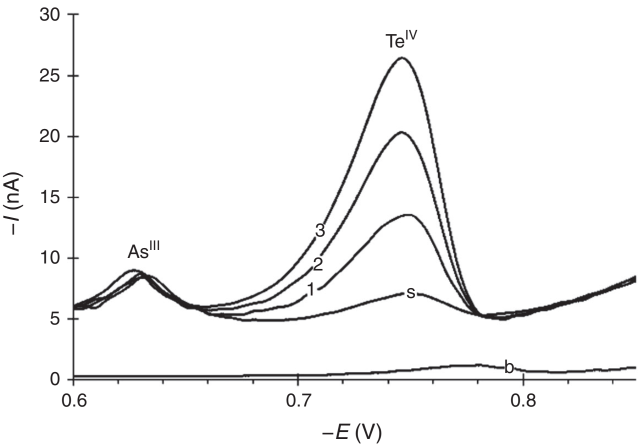

Fig. 2. Differential pulse (DP) voltammograms for Te determination, deposition time 50 s. Curve 'b' represents the blank with a 263 pA signal to be subtracted, curve 's' is the sample voltammogram (500 μL^{-1} sample solution added, Te concentration in the electrolyte 4.96 $\mu g\ L^{-1}$). Curves 1, 2 and 3 obtained after standard additions (3×10 µL of 1 $mg\ L^{-1}$ Te solution). $R^2 > 0.9989$. Initially solid sample concentration calculated to be 17.3 ppb.

operation of the tapping mechanism of the HMDE. The instrument was interfaced to a laptop computer running the manufacturer's software for data acquisition and processing.

The measuring voltammetric method was essentially that described earlier (Biver et al. 2015), with deposition times considerably shortened to reduce sensitivity. The base electrolyte consisted of 10 mL of water to which 100 µL of HCl (35 % (m/m) suprapure) and (optionally) 0.5 mL of 0.1 mol L^{-1} Na_2H_2EDTA (analytical grade, Roth) had been added. The purpose of the EDTA addition was the chelation of Fe^{III}, small amounts of which were carried over into the sample solution through the coprecipitation scheme. If the kinetic blank suppression method (see below) is used, in the course of which Fe^{III} is formed by oxidation of Fe^{II}, the addition of EDTA is mandatory.

We developed two versions of this technique, a *macro* method for the determination of high Te concentrations in the ppm range (with respect to the initial solid sample) and a *micro* version if much smaller Te concentrations (i.e. in the ppb range) were anticipated. Both procedures are described above.

The electrolyte was sparged with N_2 or Ar (99.999 %, L'Air Liquide, Luxembourg) for 180 s and a blank voltammogram was recorded. After introduction of the sample, typically 10–100 µL in the *macro* variant of the extraction procedure or 400 µL in the *micro* variant, the solution was again sparged for 90 s and the sample voltammogram recorded. Then, 3–4 standard additions of 10 µL of 1 mg L^{-1} Te standard (*macro* variant) or 10 µL of 100 µg L^{-1} Te standard (*micro* variant) were made with 20 s sparging after each addition. The standard solutions were prepared by dilution of a commercial AAS standard (SpecPure Alfa-Aesar, Germany) in water containing a little HCl (suprapure).

The instrumental parameters were as follows: deposition potential −0.5 V, deposition time 10 s (*macro* variant) to 50 s (*micro* variant), followed by 10 s equilibration time. The potential was then scanned in the cathodic direction from −0.6 to −0.9 V in differential pulse mode, with a pulse amplitude of 25 mV and pulse duration of 0.5 s. The voltage increment was 5 mV every 2 s (resulting in a sweep rate of 2.5 mV s^{-1}). The Te peak appeared at −0.750 V. Peak evaluation was by height above a linear baseline. Representative voltammograms are shown in Fig. 2.

Kinetic blank suppression

Care must be taken that, in the blank voltammogram, no Te is discernible. A Te peak appearing in the blank voltammogram can be subtracted from the subsequent sample and standard addition voltammograms in the *macro* variant of the method only. In the *micro* variant, this cannot be done because, as the sample volume is larger and has a high ionic strength, the sensitivity of the method would be greatly altered upon addition of the sample aliquot to the base electrolyte. We observed blank peaks with intensities of the order of 10 pA that were proposed to arise from contaminations of the instrument and its ancillary equipment and proved impossible to suppress by cleaning. In our determination of Nb by cathodic stripping voltammetry, we noted that the interfering catalytic Te peak could be suppressed by oxidation (Biver and Filella 2018*b*); the same approach was used here by the addition of 10 µL of 0.1 mmol L^{-1} $KMnO_4$ before the initial sparging, which oxidised any Te^{IV} present in the electrolysis cell to the electroinactive Te^{VI}. The excess of $KMnO_4$ must obviously be quenched before introduction of the sample. This was achieved by adding 10 µL of a 1 mmol L^{-1} $FeSO_4 \cdot 7H_2O$ (analytical grade, Roth) solution containing a little H_2SO_4 (suprapure) 60 s after the addition of permanganate, and proceeding normally with the method from then on. Even though the electrolyte contained HCl, the reduction of Te^{VI} is so slow at room temperature that the contaminating Te does not contribute to the signal intensity over the duration of the experiment. A blank was nevertheless recorded every time to confirm successful blank suppression.

Results and discussion

Figures of merit and interferences

The sensitivity of the voltammetric method was found to be approximately $\beta = 1.3 \times 10^{-2}$ A L g^{-1} ($= 1.3 \times 10^7$ nA/[g L^{-1}] or 1.66 A L mol^{-1}) for a 50 s deposition time, with some variation among individual determinations, and the standard deviation of the signal current at the peak potential (−0.746 V) was $\sigma = 40.5$ pA for 10 successive blank voltammograms. This led to a limit of detection (LOD), calculated as $LOD = 3\frac{\sigma}{\beta}$ (IUPAC 1978), of 9.6×10^{-9} g L^{-1} ($= 7.5 \times 10^{-11}$ mol L^{-1}) for Te in the electrolyte on which the voltammetry was performed. The electrolyte volume in the electrolysis cell was 11.02 mL and it contained typically 400 µL of sample solution. With an initial solid sample aliquot of ~500 mg and an approximate total volume of 10 mL of solution resulting from the extraction of the coprecipitated Te ('sample solution'), the overall LOD of Te with respect to the solid sample was ~5 ppb. As a cross validation (Ehrlich and Danzer 2006), we computed, for selected determinations, the variance of the regression residuals σ_y after successive standard additions fitted to a linear model:

$$\sigma_y = \sqrt{\frac{1}{N-2}\sum_{i=1}^{N}(y_i - \hat{y}_i)^2}$$

where y_i and $\hat{y}_i$ stand for the ith experimental and predicted signal currents respectively, and N is the number of data points. σ_y may be regarded as a proxy for σ, a useful approach in cases where the absolute intensity of the blank signal is subject to strong variance, yet the intensities of added sample and standard additions behaved perfectly additively with well reproducible sensitivity. This approach yielded LODs of the same order, though generally a few ppb higher. Similarly, if the macro

Table 1. Certified and measured Te concentrations in OREAS certified reference materials according to digestion procedure and method variant
All concentrations in ppm; number of replicates *N* in parentheses. Uncertainties reflect 95 % confidence level except where stated otherwise. Blank cells mean that the digestion procedure was not applied because of expected poor performance. n/a, not applicable

	Digestion technique	OREAS 603	OREAS 600	OREAS 522	OREAS 135	OREAS 903
Certified values	Aqua regia	57	6.80	1.11	0.19	0.034
	4-acid digestion	56	7.34	1.14	n/a	n/a
Acid digestions	H_2SO_4	59.5 ± 2.0 ($N = 6$)	6.68 ± 0.71 ($N = 6$)	0.93 ± 0.05 ($N = 6$)	0.18 ± 0.01 ($N = 6$)	0.035 ± 0.006 ($N = 5$)
	$HClO_4/H_3PO_4$	58.2 ± 3.3 ($N = 6$)	6.96 ± 0.19 ($N = 5$)	1.24 ± 0.07 ($N = 5$)	0.24 ± 0.01 ($N = 5$)	0.045 ± 0.003 ($N = 4$)
	Open aqua regia	53.3 ± 1.6 ($N = 7$)	7.21 ± 0.44 ($N = 6$)	1.19 ± 0.07 ($N = 5$)	0.222 ± 0.009 ($N = 5$)	0.019 ± 0.001 ($N = 4$)
	ISO aqua regia	61.6 ± 1.0 ($N = 3$)	7.62 ± 0.26 ($N = 5$)	0.71 ± 0.06 ($N = 4$)	0.176 ± 0.004 ($N = 4$)	0.048 ± 0.004 ($N = 3$)
	HNO_3	47.9 ± 2.8 ($N = 4$)	3.69 ± 0.15 ($N = 3$)			
Fusion digestions	Na_2O_2	57.9 ± 4.5 ($N = 5$)	7.57 ± 0.28 ($N = 5$)	1.16 ± 0.05 ($N = 4$)	0.207 ± 0.007 ($N = 6$)	0.037 ± 0.001^{A} ($N = 4$)
	$KHSO_4$	57.1 ± 3.3 ($N = 6$)	6.27 ± 0.24 ($N = 5$)	0.97 ± 0.05 ($N = 5$)	0.14 ± 0.01 ($N = 4$)	0.035 ± 0.003 ($N = 6$)
	$LiBO_2$	53.5 ± 0.2 ($N = 4$)	6.22 ± 0.17 ($N = 6$)			
	NaOH	21.2 ± 4.6 ($N = 4$)				
Method variant		*macro*	*macro*	*micro*	*micro*	*micro*

[A] Combined error on mean.

variant is adopted with a 0.5 g sample mass, 100 mL digestate volume and 50 µL aliquot added to the voltammetric cell, the LOD is 0.44 ppm.

We did not explore how much the LOD (5 ppb) could be improved by further reduction of the extract volume or increase of sample aliquot as that already achieved appeared sufficiently low for the samples studied here (the lowest Te concentration to be measured in this work was 34 ppb, in OREAS 903).

Since Se is also coprecipitated with As, we checked whether Se^{IV} interfered in the voltammetric determination: the addition of a large excess (25 µg L^{-1}) of selenite to the base electrolyte did not cause any additional or overlapping peaks, only a slight depression of the catalytic Te peak was noted. A steep shoulder observed in the region of interest in the sample voltammogram, effectively masking the catalytic Te peak, arose from traces of nitrite ion remaining from the acid digestion of the precipitated As (i.e. the acid had been removed incompletely on the water bath). The problem could be corrected by dissolving a few crystals of sulfamic acid (analytical grade, Roth) in the sample solution.

Procedural and reagent blanks

All of the reagents used in this work, with the exception of sodium peroxide, proved sufficiently pure so that no blank values needed to be subtracted. None of the labware used for digestions (except Ni crucibles) nor the filter materials gave rise to procedural blanks. Thus, only the fusion or sintering experiments with sodium peroxide require discussion: when analysing samples that contained less Te than 1 ppm, it became clear that the purity of the flux as well as Te leached from the Ni crucible (99.5 %, Roth) itself were a problem. A typical fusion experiment in a Ni crucible dissolved 300 to 400 mg of Ni, with the crucible material containing 110.6 ± 9.2 ($N = 3$) ppb of Te. This finding ruled out the use of Ni crucibles. Initially, we used an older sample of Na_2O_2 (>93 %, ACS grade, Alfa-Aesar) that contained no detectable Te. Newly purchased batches of the same material from Alfa-Aesar and from Roth, however, contained too much Te (4.6 ± 0.2 ppb, $N = 5$ and 3.5 ppb, $N = 1$ respectively). A batch from Fluka (Switzerland) was found to be the only suitable one with 1.5 ± 0.1 ($N = 8$) ppb of Te. The apparent Te content of this reagent rose to 6.2 ± 0.6 ($N = 3$) ppb on sintering in a Zr crucible (Alfa-Aesar), but to only 2.2 ± 0.2 ($N = 11$) ppb when a glassy carbon crucible (Sigradur, Germany) was substituted for Zr. Digestions with Na_2O_2 were therefore conducted exclusively using this method (Bokhari and Meisel 2017). The mass of flux used in each digestion was accurately weighed and a blank Te value subtracted from the determination. Note that there is no conflict between the Te concentrations in this section and the LOD given above. The Na_2O_2 batches were analysed by the *micro* variant with sample masses ~6 times larger than those of the analysed CRMs, to which the LOD of 5 ppb applies.

Extraction efficiencies of the individual digestion procedures

The recoveries of several methods on available standard reference materials were compared to determine the methods suitable for Te determination in environmental matrices (Table 1).

The H_2SO_4 digestion protocol yielded consistently good recoveries over the whole concentration domain studied, with the exception of OREAS 522, where only ~80 % of the certified values were recovered. The peculiarity of this sample was its high iron oxide content. Note that the H_2SO_4 method was the only acid digestion method to perform well with the least concentrated CRM, OREAS 903. Advantages of this procedure are its rapidity (the digestion itself takes little more than 5 min) and simplicity (only a Kjeldahl flask and a Bunsen burner needed), which make it well amenable to automation.

The HNO_3 showed insufficient recovery (~80 %) with the very first, most highly concentrated sample, OREAS 603, and failed altogether for the second one (~50 % recovery), OREAS 600. Evaporation with HNO_3 alone cannot be recommended for the determination of Te and older results obtained in this way should be viewed with caution. Note that we did confirm, however, that pure elemental Te, TeO_2 and the Te coprecipitated with As are quantitatively recovered.

$HClO_4$ in conjunction with H_3PO_4 performed about as well as the H_2SO_4 procedure, which included the case of OREAS 522, with recoveries slightly above the certified values obtained by aqua regia digestions. This may mean that digestion by $HClO_4$ is more complete than by aqua regia, although in the case of OREAS 135, both digestions (by $HClO_4$ and by the 'open' aqua regia variant) returned much higher values than the certified values (~120 %). Whether these are genuine or as a result of undetected contaminations in the course of the experiment could not be determined. As far as rapidity, expediency and simplicity were concerned, the method was comparable to H_2SO_4 digestion.

Table 2. Measured concentrations of Te in sediment certified reference materials (after peroxide sintering)

All values in ppb; error margins reflect the combined error on the mean of *N* replicates. Certified values for Te do not exist. The estuarine sediment sample is in the process of being certified, with a provisional concentration of 45 ± 8 ppb ($N = 3$, 95 % confidence level); our value is not yet included

Estuarine sediment	PACS-2	MESS-3	BCR-701
41.1 ± 1.1 ($N = 5$)	48.3 ± 0.9 ($N = 5$)	56.0 ± 1.0 ($N = 5$)	105.4 ± 1.1 ($N = 4$)

The ‘open beaker’ aqua regia digestion performed very well for OREAS 603, 600 and 522. An unusually high recovery was obtained with OREAS 135 (near 120 %). The particular ‘open beaker’ variant adopted here (Chen and Ma 2001) was a particularly aggressive one, as it involved evaporation to (near-)dryness of the aqua regia-sample mixture. We noted that, more often than not, this resulted in complete solubilisation of the sample, while an aqua regia digestion that is not taken to dryness, such as the ISO protocol, invariably left an undissolved residue. The OREAS 135 results could therefore mean that this material contained Te in phases that were not targeted by milder variants of aqua regia digestion. We suspected that adsorption of Te to graphite might play a role. OREAS 135 contains an unusually high concentration of this mineral, and it could be identified in the solid residue of the H_2SO_4 aqua regia ISO digestions, as well as in that of pyrosulfate fusion digestion. We demonstrated, in an independent experiment, that tellurite was strongly adsorbed onto natural graphite even in moderately acidic solutions. Tellurium could thus be lost by adsorption to graphite during the leaching step, following digestion procedures that do not or only incompletely oxidise graphite. However, an anomalously low recovery was found for the least concentrated sample (OREAS 903). Overall, the results obtained by the ‘open’ aqua regia variant were not of a quality as consistent as those obtained by H_2SO_4 or $HClO_4$ digestions and the procedure was much longer (more than 4 h).

The aqua regia digestion according to the ISO 11466 protocol gave acceptable recoveries (slightly high) for OREAS 603, 600, 135, whereas it produced anomalously low and high values for OREAS 522 (~60 %) and OREAS 903 (140 %) respectively. Again, this aqua regia digestion procedure appeared to be less reliable than other acid digestion procedures, and was considerably longer (16 + 2 h).

The lithium metaborate fusion digestions produced acceptable, although slightly low, recoveries for the highly concentrated samples OREAS 603 and 600. Digestion was complete in both instances and we hypothesised that losses may have occurred through alloying of Te with platinum crucibles at high temperatures, a problem explicitly cautioned against in the literature (Heinrichs and Herrmann 1990).

The digestion with molten sodium hydroxide was incomplete (a black insoluble residue remained after leaching) and returned a highly unsatisfactory recovery of only ~40 % for OREAS 603.

Fusion or sintering with sodium peroxide performed adequately over the whole range of concentrations for the five OREAS samples, which yielded recoveries slightly in excess of 100 % in all cases. Digestions were invariably complete, so that no doubt ever remained whether some important Te bearing phase may have eluded determination, and any organic matter was reliably destroyed. The digestion was done at a lower temperature than the lithium metaborate fusion (480 °C versus 800 °C) and thus could be done quicker and did not require platinum crucibles. The difficulty in finding the reagent in acceptable purity was a possible drawback. We are currently investigating the possibility to synthesise sufficiently pure sodium peroxide from sodium amalgam (commercial sodium metal proved too highly contaminated).

The use of the pyrosulfate flux provided acceptable recoveries for the more concentrated samples OREAS 603 and 600 and also the least concentrated sample OREAS 903, and gave low recoveries for OREAS 522 and 135. Digestions were not complete and we suspected this may be the main reason for the variable performance. This is a quick and simple method.

Among the acid digestion techniques, we give preference to H_2SO_4 and $HClO_4$ digestions. The latter would probably be favoured by most analysts, as H_2SO_4 is not routinely used, whereas the performance of $HClO_4$ for other elements is very well studied. This digestion is probably the best option if Te is to be determined as part of a suite of other analyte elements. Our results do not indicate obvious losses by aqua regia digestions, as there is no general trend for low recoveries when compared with the complete, peroxide sintering digestion. Moreover, where certified values by aqua regia and another techniques (4-acid digestion) are available, as is the case for OREAS 603, 600 and 522, the aqua regia values are higher in one case (OREAS 603) and lower in the other two, with the difference not always being significant. Several authors claim that HCl never leads to Te losses when combined with some other acid (Chen et al. 2016 and references cited therein). Yet, our results show that there is considerable variation between samples, with the added difficulty that aqua regia digestions can give divergent results depending on the precise protocol chosen, particularly at low concentrations, a point well illustrated by the samples OREAS 522, 135 and 903.

Among the fusion techniques, we favour sintering with Na_2O_2 as it was the only technique that yielded equally good recoveries for all samples with concentrations spanning three orders of magnitude. The technique is reasonably quick, inexpensive and can be automated at least in part; unfortunately, reagent blanks can be an issue. Its unquestionable advantage lies in the reliable digestion of organic matter, which is why we adopted this technique in the analysis of sediment CRM (Table 2). No certified values for these materials exist; but values of several tens of ppb are most frequently reported for ocean sediment (Filella et al. 2019). The higher value found for BCR-701, fresh water sediment from Lake Orta in northern Italy, seems plausible, given the fact that this lake has a history of severe industrial pollution, mainly by Cu (from artificial silk manufacturing industry). Overall, H_2SO_4 and $HClO_4$ digestions and sintering with Na_2O_2 in glassy carbon can be recommended as universally applicable on the basis of our results, while the popular aqua regia digestion protocols may be adequate, depending on the nature of the sample.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

This research did not receive any specific funding.

References

Bezerra de Oliveira AL, Afonso JC, Da Silva L, Alcover Neto A, Castro Carneiro M, Dias da Silva LI, Couto Monteiro I (2019). Hydrofluoric acid-free digestion of geological samples for the quantification of rare earth elements by inductively coupled plasma-optical emission spectrometry. *Geostandards and Geoanalytical Research*. doi:10.1111/GGR.12286

Biver M, Filella M (2018*a*). Germanium and solid sample digestion with *aqua regia*: the nescience of chemistry basics and its sequels. *Monatshefte für Chemie – Chemical Monthly* **149**, 461–465. doi:10.1007/S00706-017-2131-5

Biver M, Filella M (2018*b*). Selective determination of niobium in natural waters at the low ng L^{-1} level by differential pulse cathodic stripping voltammetry in the presence of pyrogallol red. *The Science of the Total Environment* **615**, 1406–1410. doi:10.1016/J.SCITOTENV.2017.09.040

Biver M, Quentel F, Filella M (2015). Direct determination of tellurium and its redox speciation at the low nanogram level in natural waters by catalytic cathodic stripping voltammetry. *Talanta* **144**, 1007–1013. doi:10.1016/J.TALANTA.2015.07.010

Bokhari SNH, Meisel TC (2017). Method development and optimisation of sodium peroxide sintering for geological samples. *Geostandards and Geoanalytical Research* **41**, 181–195. doi:10.1111/GGR.12149

Chen M, Ma LQ (2001). Comparison of three aqua regia digestion methods for twenty Florida soils. *Soil Science Society of America Journal* **65**, 491–499. doi:10.2136/SSSAJ2001.652491X

Chen Y-W, Alzahrani A, Deng T-L, Belzile N (2016). Valence properties of tellurium in different chemical systems and its determination in refractory environmental samples using hydride generation-atomic fluorescence spectroscopy. *Analytica Chimica Acta* **905**, 42–50. doi:10.1016/J.ACA.2015.11.035

Cotta AJB, Enzweiler J (2012). Classical and new procedures of whole rock dissolution for trace element determination by ICP-MS. *Geostandards and Geoanalytical Research* **36**, 27–50. doi:10.1111/J.1751-908X.2011.00115.X

Ehrlich G, Danzer K (2006). 'Nachweisvermögen von Analysenverfahren. Objektive Bewertung und Ergebnisinterpretation.' (Springer: Berlin) [in German]

Filella M, Rodushkin I (2018). A concise guide for the determination of less-studied technology-critical elements (Nb, Ta, Ga, In, Ge, Te) by ICP-MS in environmental samples. *Spectrochimica Acta. Part B, Atomic Spectroscopy* **141**, 80–84. doi:10.1016/J.SAB.2018.01.004

Filella M, Reimann C, Biver M, Rodushkin I, Rodushkina K (2019). Tellurium in the environment: current knowledge and identification of the gaps. *Environmental Chemistry* **16**, 215–228. doi:10.1071/EN18229

Fujii T, Obata K, Kubota T, Kamiya M, Yamana H (2004). Volatility of tellurium and various fission products in heated nitric acid solutions. *Journal of Radioanalytical and Nuclear Chemistry* **262**, 551–554. doi:10.1007/S10967-004-0474-Y

Hannaker P, Hou Q.-L. (1984). Dissolution of geological material with orthophosphoric acid for major-element determination by flame atomic-absorption spectroscopy and inductively-coupled plasma atomic-emission spectroscopy. *Talanta* **31**, 1153–1157. doi:10.1016/0039-9140(84)80267-2

Healy TC (1958). The reaction of nitric acid with formaldehyde and with formic acid and its application to the removal of nitric acid from mixtures. *Journal of Applied Chemistry* **8**, 553–561. doi:10.1002/JCTB.5010080903

Heinrichs H, Herrmann AG (1990). 'Praktikum der analytischen Geochemie.' (Springer: Berlin) [in German]

Hoffman JI, Lundell GEF (1939). Volatilization of metallic compounds from solutions in perchloric or sulfuric acid. *Journal of Research of the National Bureau of Standards* **22**, 465–470. doi:10.6028/JRES.022.030

Hoyle WC, Diehl H (1971). Rapid dissolution of sulphide ore for the determination of copper. *Talanta* **18**, 1072–1074. doi:10.1016/0039-9140(71)80184-4

ISO (1995). ISO 11466: Soil quality – extraction of trace elements soluble in aqua regia. Available at https://www.iso.org/standard/19418.html [verified 26 October 2019]

IUPAC (1978). Nomenclature, symbols, units and their usage in spectrochemical analysis—II. Data interpretation Analytical chemistry division. *Spectrochimica Acta. Part B, Atomic Spectroscopy* **33**, 241–245. doi:10.1016/0584-8547(78)80044-5

Jankovsky J, Kšir O (1960). Photometric determination of tellurium with Bismuthiol II. *Talanta* **5**, 238–249. doi:10.1016/0039-9140(60)80179-8

Jefferey PG, Hutchinson D (1981). 'Chemical methods of rock analysis.' Pergamon series in analytical chemistry, vol. 4. (Pergamon Press: Oxford)

Johnson WM, Maxwell JA (1989). 'Rock and mineral analysis, 2nd edn.' (Krieger: Malabar, FL)

Luke CL (1959). Photometric determination of traces of selenium or tellurium in lead or copper. *Analytical Chemistry* **31**, 572–574. doi:10.1021/AC50164A035

Meisel T, Schöner N, Paliulionyte V, Kahr E (2002). Determination of rare earth elements, Y, Th, Zr, Hf, Nb and Ta in geological reference materials G-2, G-3, SCo-1 and WGB-1 by sodium peroxide sintering and inductively coupled plasma-mass spectrometry. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis* **26**, 53–61. doi:10.1111/J.1751-908X.2002.TB00623.X

Potts PJ (1992). 'A handbook of silicate rock analysis.' (Springer Science+Business Media: New York, NY)

Ure AM, Davidson CM (2002). 'Chemical speciation in the environment, 2nd edn.' (Blackwell Science: Oxford)

Watterson JR, Neuerburg GJ (1975). Analysis for tellurium in rocks to 5 parts per billion. *Journal of Research of the U.S. Geological Survey* **3**, 191–195.

Handling Editor: Kevin Francesconi