



Tellurium Speciation via Frontal Chromatography ICP-MS: An Innovative and Effective Approach for the Ultratrace Detection in Environmental Matrices

Davide Spanu¹ · Chiara Omodei¹ · Gilberto Binda^{1,2} · Tommaso Grande¹ · Sandro Recchia¹

Received: 21 October 2024 / Accepted: 25 February 2025
© The Author(s) 2025

Abstract

The increasing use of tellurium (Te) in electronics and renewable energy technologies has elevated its environmental concentration, posing ecological and health risks. This study addresses the critical need for effective methods to speciate Te by focusing on its two primary redox states—tellurite (Te(IV)) and tellurate (Te(VI))—which differ in reactivity, mobility, and toxicity. Existing analytical methods for Te speciation are often limited in sensitivity and can't simultaneously determine both species. In response, we present a novel, rapid, practical, and highly sensitive approach for determining Te(IV) and Te(VI) using frontal chromatography coupled with inductively coupled plasma mass spectrometry (FC-ICP-MS). Multivariate optimization of chromatographic conditions, along with the exploitation of the “carbon effect” and careful isotope selection, yield detection limits of 1.0 ng/L for Te(IV) and 1.3 ng/L for Te(VI) with a total analysis time of five minutes. Acidification with nitric acid is the only sample pretreatment required. Applied to natural waters, sediments, and soils, the method demonstrates high accuracy, superior sensitivity, greenness, and practicality, compared to state-of-the-art methodologies, offering an alternative and advantageous solution for routine Te speciation analysis across various environmental compartments.

Keywords Tellurium · Technology critical elements · Chromatography · Speciation · ICP-MS

1 Introduction

The rapid expansion of industrial activities and technological advancements has significantly increased the release of trace element contaminants into the environment. Among these, tellurium (Te) is gaining attention as a technology-critical element due to its widespread use in various industrial applications [1, 2]. While naturally present in the Earth's crust at extremely low concentrations (approximately $1 \times 10^{-7}\%$), human activities have caused a notable rise in Te levels in water, soil, and sediment, making it an emerging pollutant of concern [3–5]. The primary sources of Te pollution stem from its use in electronics, such as the production of optical discs and solar panels [6, 7]. Additionally, metal smelting

and coal combustion contribute to the diffusion of Te species [1, 5]. The increasing demand for Te, driven by the growth of the electronics industry and the transition to renewable energy sources, is expected to further exacerbate its environmental contamination. This may pose serious health risks in the future as Te bioaccumulates in the human body [8, 9], and recent studies have reported a correlation between heightened environmental exposure to Te species and the development of cancers, neurodegenerative conditions, and autoimmune disorders [8].

Hence, it is crucial to understand the behavior and fate of Te in the environment to investigate the potential risks posed to human and environmental health. The redox speciation of Te compounds is mostly overlooked in the current literature, with tellurite Te(IV) and tellurate Te(VI) as predominant species in natural waters and geological samples [1]. These two oxidation states exhibit distinct characteristics in terms of reactivity, mobility, bioavailability, and toxicity, significantly impacting their potential environmental and health risks [10, 11]. Specifically, Te(IV) is considered more mobile and 10 times more toxic than Te(VI). Additionally, Te(IV) is 100–1000 times more toxic than its homologous

✉ Davide Spanu
davide.spanu@uninsubria.it

¹ Department of Science and High Technology, University of Insubria, Via Valleggio 11, 22100 Como, Italy

² Norwegian Institute for Water Research (NIVA), Økernveien 94, 0579 Oslo, Norway

selenite, a well-known toxic substance [5, 12]. The notable toxicity of Te species along with its marked difference between Te(IV) and Te(VI) highlights the need for selective monitoring of these compounds to accurately assess potential environmental and health risks. However, detecting and differentiating Te species is challenging due to the ultralow Te concentrations in all environmental compartments: in open ocean waters, for example, Te concentrations are typically below ~2 ng/L, although levels can increase tenfold in unpolluted freshwater systems [1, 13]. Similarly, in soils and sediments, Te levels generally stay in the low parts-per-billion ($\mu\text{g/L}$) range outside of contamination hotspots [1]. While these concentrations may seem negligible, the bioaccumulation potential of Te species in both fauna and plants raises concerns about significant negative impacts over time [4].

In recent years, various analytical strategies have been developed to address the challenges of detecting ultratrace Te concentrations and differentiating between Te(IV) and Te(VI) species. Hydride generation, combined with sensitive detection systems such as Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and atomic spectroscopy techniques, has emerged as the preferred approach thanks to the low detection limits achieved [14–17]. However, hydride generation is limited to selective Te(IV) determination, with Te(VI) quantified indirectly by subtraction after total Te measurement, which requires pre-reduction of Te(VI), complicating the distinction between the two species. Pre-concentration methods such as solid-phase extraction (SPE) [18–22], hollow fiber liquid phase microextraction (HF-LPME) [23], and dispersive liquid–liquid microextraction (DLLME) [24, 25] with ICP-MS or Electrothermal Atomic Absorption Spectroscopy (ETAAS) have achieved sub-ng/L detection, but, these multistep processes risk analyte loss and rely on Te(IV) selective extraction and/or multiple desorption steps. Catalytic cathodic stripping voltammetry (Cat-CSV) [26] offers detection limits as low as 5 ng/L without preconcentration and at lower cost, but it only detects Te(IV) unless Te(VI) is pre-reduced. Additionally, in all the mentioned strategies the reduction may be hindered by matrix interference (e.g., by nitrate) [26]. These limitations reduce the suitability of these methods for routine environmental monitoring.

Liquid chromatography (LC) hyphenated with ICP-MS for online analysis could present an ideal solution. However, to date, the use of this approach is extremely limited. Reversed-phase high-performance liquid chromatography (RP-HPLC) [27] and ion chromatography (IC) [28] with ICP-MS have been proposed for this purpose: these methods unfortunately demonstrated detection limits which were not applicable to natural waters and geochemical samples (i.e., around 1 $\mu\text{g/L}$ [27, 28]). In the case of RP-HPLC, a further complication is introduced by the Te(IV) and Te(VI)

complexation with chelating agents, which is highly sensitive to experimental conditions (e.g., matrix effect) and can make the accurate differentiation between Te(IV) and Te(VI) challenging [27].

Summing up, a fully practical method for routine streamlined Te speciation remains elusive highlighting how further research is needed to address the scarcity of available data in the literature and to overcome the practical limitations of existing methods. Recently, we have shown that frontal chromatography (FC) coupled with ICP-MS offers a promising solution for the rapid and efficient speciation analysis of ultratrace elements, as demonstrated for As [29], Cr [30], Sb [31, 32] and Hg [33, 34]. This technique significantly reduces both analysis time and complexity while also lowering overall costs. Notably, when the species differ in nature (e.g., ionic vs. non-ionic), the use of HPLC instrumentation is not mandatory, as a simple, low-pressure column with a limited resolving power—fed by a peristaltic pump—can effectively fit to separate them.

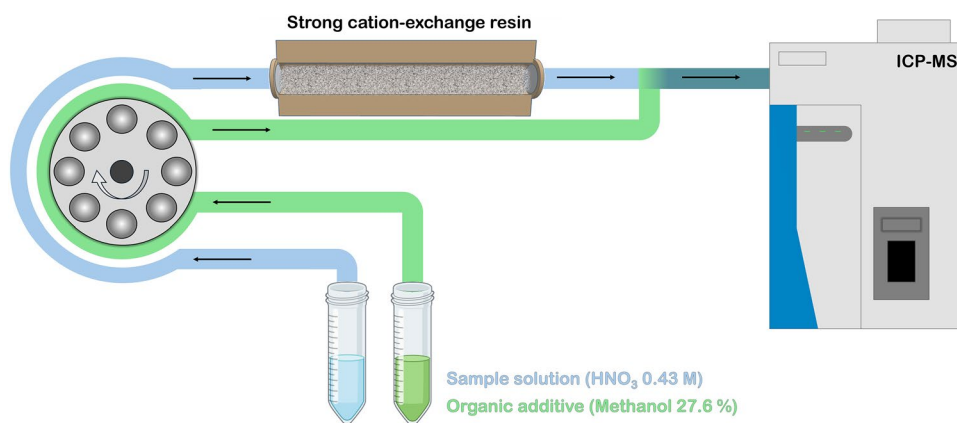
In this study, we adapted the FC-ICP-MS method for the simultaneous determination of Te(IV) and Te(VI) in natural water, sediment, and soil samples. This was achieved by passing acidified samples (with diluted nitric acid) through a custom-built short column packed with a strong cation exchange resin, with the eluate directly analyzed by ICP-MS. The multivariate optimization of chromatographic conditions, along with a thorough investigation of the "carbon effect" and isotopes selection, enabled the simultaneous and accurate detection of both Te species in around five minutes, offering exceptional sensitivity with detection limits for Te(IV) and Te(VI) equal to 1.0 and 1.3 ng/L, respectively.

2 Experimental

2.1 Reagents

To prepare the stock standard solution of Te(IV) (1000 mg/L), a proper amount of sodium tellurite (99.5% pure, Thermo Scientific Chemicals) was dissolved in 30 mL of ultrapure water. The stock standard solution of Te(VI) (1000 mg/L) instead, was prepared by weighing a proper amount of telluric acid dihydrate (> 99% pure, Thermo Scientific Chemicals) and dissolving it in 30 mL of ultrapure water (produced by a Sartorius Arium mini UV Lab Water System). Intermediate standard solutions were prepared by diluting the concentrated solutions and then diluted standard solutions were obtained for calibration. The traceability of the Te concentration of the prepared solutions was determined against a single Te ICP standard (1000 mg/L J.T.Baker®, BAKER INSTRA-ANALYZED®) which

Fig. 1 Schematic representation of the FC-ICP-MS instrumental setup used in this study



contains Te from tellurium dioxide dissolved in 10% hydrochloric acid.

A germanium standard solution (1000 mg/L, Fluka, TraceCERT®) was used as an internal standard by adding an appropriate volume to each sample, achieving a final concentration of 1 µg/L. Ultrapure nitric acid, distilled from reagent-grade HNO₃ (65% purity, Carlo Erba) [35], was used to acidify all samples. The samples were prepared with ultrapure water from a Sartorius Arium mini UV Lab Water System (Varedo) and stored in low-density polyethylene bottles that underwent a decontamination process. This process involved three steps: (i) soaking in a 0.4% *w/w* detergent solution (Nalgene L900, Thermo Scientific) for a week; (ii) soaking in a 2% *w/w* HNO₃ solution for one week; (iii) soaking in a fresh 2% *w/w* HNO₃ solution for another week. The bottles were thoroughly rinsed with ultrapure water between each step and prior to use.

Methanol (Carlo Erba, ACS grade, ≥ 99.9%), ethanol absolute (Supelco, ACS grade), and 2-propanol (Sigma-Aldrich, ACS grade, ≥ 99.8%) were used as organic post-column additives.

2.2 Instrumental Setup and Analytical Protocol

The FC-ICP-MS instrumental setup is depicted in Fig. 1. Separation of tellurium species was achieved with a custom-made Polyether ether ketone (PEEK) column (2–3 mm internal diameter, 25–50 mm length) packed with strong cation exchange resin (Dowex® 50WX8, hydrogen form, 200–400 mesh, Sigma-Aldrich). The packing material was retained by HPLC frits at each end of the column. Large resin particles (55 ± 20 µm) were used to minimize the overpressure, thus eliminating the need for an HPLC pump. As shown in Fig. 1, the short column is positioned between the peristaltic pump (for sample intake) and the ICP-MS nebulizer. As will be discussed below, the instrumental setup was modified to allow the introduction of an organic modifier in the sample flow after the column exit (see Fig. 1). To minimize online dilution, peristaltic pump tubes having different internal

diameters were used to introduce the sample (internal diameter 1.02 mm) and the organic additive (internal diameter 0.38 mm). Optimized analysis conditions involved the acidification of samples to a final concentration of 0.43 M, a sample flow rate of 1.39 mL/min, and a 3 mm × 50 mm column. A 27.6% *V/V* methanol solution in ultrapure water was used as an organic modifier to induce the “carbon effect” (after online dilution, the final concentration is equal to 4%) [36].

Tellurium detection was finally performed using a Thermo Scientific ICAP Q ICP-MS. All measurements were carried out without a collision cell. Additional ICP-MS operational parameters including monitored isotopes are provided in Table S1.

The analysis was automated utilizing an autosampler (CETAC ASX-260 Autosampler, Thermo Scientific), and a standard rinsing/cleaning procedure was applied for automated ICP-MS determinations. After each sample analysis, the uptake tube was transferred to a washout reservoir containing 0.43 M HNO₃, which was then pumped through the column via the peristaltic pump, with the washout time matching that of the sample analysis.

For data processing, analysis time and resolution were determined by calculating the first derivative curve and fitting each peak with a Gaussian function (as shown in Fig. S1). These parameters were computed using the equations in Fig. S1, consistent with standard elution chromatography definitions. Origin 2018 software (version 9.5.1.195, OriginLab) was used for these calculations. Multivariate data analysis, including Design of Experiments (DoE) model computation, was conducted using CAT (Chemometric Agile Tool) software.

2.3 Mineral Water, Sediment, and Soil Samples

Six mineral water samples, each with significantly different mineral salt content (fixed residues ranging from 34.9 to 1300 mg/L), were utilized to evaluate the analytical performance across various matrices. A summary of the collected samples, along with their key chemical compositions and

physicochemical properties, is provided in Table S2. Water sample preparation for FC-ICP-MS analysis followed the procedure outlined in the previous section, involving the addition of HNO_3 and Ge as internal standards.

Concerning the analysis of soil and sediments, a total of five samples (two soils and three glacial sediments) plus the certified reference material GBW07302 (Institute of Geophysical and Geochemical Exploration, stream sediment from Jiangxi, containing $24 \mu\text{g}/\text{kg}$ of Te) were analyzed. The five samples were collected in the Ventina Valley (Central Alps, Northern Italy), a remote area in which atmospheric dry and wet deposition are the only source of anthropic-derived trace elements contamination (as observed in previous work for other trace elements – Ag, Cd, and Zn[37]). Further details on their composition are reported in a previous work (see [37] and refer to V08, V07, and V11 for the sediment samples and to P04 and P05 for the soil samples).

The standardized extraction procedure ISO-17586:2016 [38] was utilized, involving a 2-h extraction with continuous agitation (provided by a Stuart, Vernon Hills, IL, USA, SSL1 lab-scale orbital shaker). During the process, 15 mL of 0.43 M HNO_3 and 300 mg of solid sample were used. After extraction, the solution was filtered through a $0.22 \mu\text{m}$ nylon filter and subsequently analyzed by FC-ICP-MS.

3 Results and Discussion

3.1 From the Idea to the Proof of Concept

To evaluate the applicability of FC-ICP-MS for Te(IV)-Te(VI) speciation, it is crucial to identify chromatographic conditions that fulfill the key requirements of this low-resolution technique, specifically ensuring that the two target species possess completely distinct chemical properties. This characteristic enables the selective retention of one species in the chromatographic column, while the other species remains unretained.

The Pourbaix diagram (obtained using Hydra-Medusa software, Fig. 2) clearly shows that in acidic nonreducing environments (approx. $\text{pH} < 3$, and with an Oxidation–Reduction Potential around 0.75 V) the above discussed requirement is met: Te(IV) exists as a cationic species (TeOOH^+) whereas Te(VI) occurs as a neutral species (H_2TeO_4).

Under these conditions (e.g., in diluted HNO_3), cationic Te(IV) is expected to interact with a strong cation-exchange resin, while Te(VI) should pass through the column without any interaction.

For the first preliminary experiment, all chromatographic parameters were selected arbitrarily, leveraging our expertise in the field. The chosen parameters included: HNO_3 concentration (0.25 M), column length (50 mm), column width

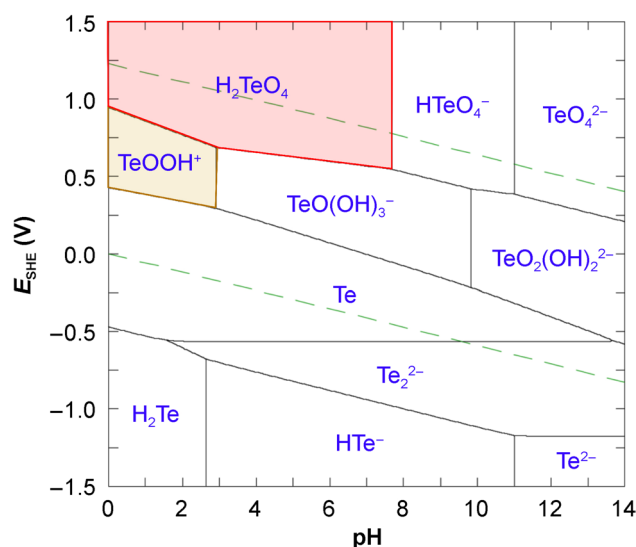


Fig. 2 Pourbaix diagram of tellurium species constructed using Hydra-Medusa software [39] ($T=25 \text{ }^\circ\text{C}$, Te total concentration = $1 \times 10^{-9} \text{ M}$)

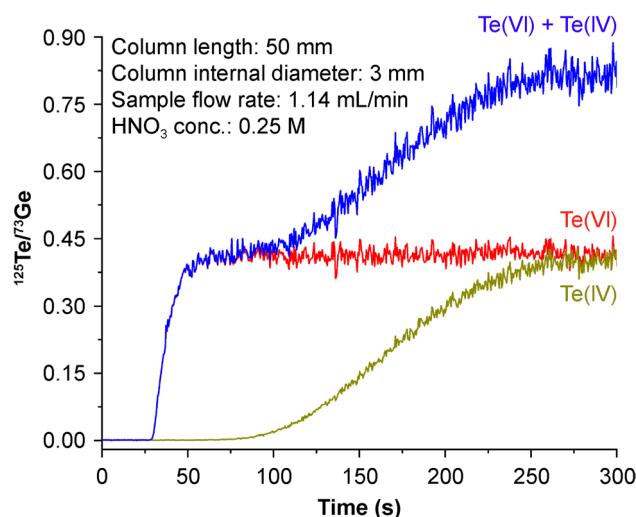


Fig. 3 Frontal chromatogram of a 0.25 M HNO_3 solution containing $1 \mu\text{g}/\text{kg}$ of Te(VI) (red line), Te(IV) (gold line), and both Te(VI) and Te(IV) species (blue line). Experimental conditions are detailed in the figure

(3 mm), and sample flow rate (1.14 mL/min). The results of this experiment are presented in Fig. 3.

As can be seen, when a mixture of Te(IV) and Te(VI) is introduced into the FC system, two distinct sigmoidal curves are observed. At this stage, we recorded the frontal chromatograms by monitoring the interference-free ^{125}Te isotope, which is the default and preferred option for Te determination using ICP-MS. The first curve corresponds to unretained neutral Te(VI), while the second, broader curve is

related to cationic Te(IV), which is partially retained by the stationary phase. Notably, two well-defined plateaus can be distinguished, for Te(VI) between 60–100 s and for Te(IV) between 250–300 s, allowing for the quantification of both species by measuring the height of their respective fronts. As a final remark, the chromatogram is reported as corrected by internal standard ^{73}Ge which occurs as a neutral species (H_2GeO_3) under these conditions, thus it is not retained by the cation-exchange resin. This choice was made to compensate for any fluctuation of the ^{125}Te signal (see Fig. S2 for a comparison with ^{125}Te and ^{73}Ge raw data).

In addition to the effective separation of Te(IV) and Te(VI), the elution time is relatively short, around 5 min. However, there is space to further shorten this time to make it suitable for routine analysis, while still maintaining comparable separation efficiency. A Design of Experiments (DoE) approach was therefore employed to optimize the chromatographic parameters (see next paragraph). Furthermore, the exploitation of the so-called “carbon effect” and the careful selection of isotopes were also investigated to further enhance the method's sensitivity. These steps are essential to meet the analytical requirements for detecting ultratrace levels of Te in environmental samples. All these optimizations will be detailed in the following paragraphs.

3.2 Design of Experiment: Optimizing Chromatographic Parameters

Optimal conditions were sought using a full factorial 2^4 design, which systematically evaluated the effects of (i) column length (25 and 50 mm), (ii) column width (2 and 3 mm), (iii) sample flow rate (1.39 and 1.14 mL/min), and (iv) HNO_3 concentration (0.25 and 0.50 M) on two responses: analysis time and chromatographic resolution. The aim is to find analysis conditions that maintain sufficient resolution to effectively separate the two species while keeping minimum analysis time. The specific conditions tested in each experiment are outlined in Table 1 and Table S3.

The resulting 16 conditions (full-factorial DoE) were applied to the analysis of Te(IV)-Te(VI) mixture solutions (concentrations = 1 $\mu\text{g}/\text{kg}$). The effect of each single parameter can be immediately observed in Fig. 4.

The chromatograms show that all the parameters influence the elution profile. Since Te(VI) does not interact with the cation-exchange resin, its elution time is very slightly influenced by sample flow rate and column geometry whereas the chemistry of the mobile phase does not play any role. Contrarily, the elution time and width of the front of cationic Te(IV) are significantly affected by all investigated parameters. Generally, increasing the sample flow rate and decreasing column size speed up the elution of Te species as expected. Moreover, higher HNO_3 concentrations notably

Table 1 Chromatographic conditions and corresponding levels used in the Design of Experiments (DoE) model for data standardization and centering, selected for all experiments within the explored domain

Parameter	Low level (– 1)	High level (+ 1)
Column length (mm)	25	50
Column internal diameter (i.d., mm)	2	3
HNO_3 concentration (M)	0.25	0.50
Sample flow rate (mL/min)	1.14	1.39

reduce analysis time at the expense of the resolution, as H^+ ions enhance the rapid elution of Te(IV).

Multivariate regression analysis was conducted to quantitatively assess the effects and optimize the chromatographic conditions that were initially observed qualitatively. Once the resolution and the analysis time were rigorously determined (see details in Fig. S1), their responses were modeled by second-order equations including interaction terms. Figure 5 shows the obtained coefficients, while the surface responses are depicted in Fig. S3.

The goodness of the regression model is demonstrated by the high explained variance (94.4% for the resolution model and 99.1% for the analysis time model) and the low, randomly scattered residuals, as illustrated in Fig. S4.

As shown in Figs. 5a-b, all main effects have a statistically significant impact ($p\text{-value} \leq 0.05$) on both resolution and analysis time, except for the sample flow rate, which does not significantly affect resolution. This is consistent with the data in Fig. 4, where column geometry (length and internal diameter, i.d.) and acid concentration are identified as the primary factors influencing responses. Furthermore, interaction terms involving column geometry and HNO_3 concentration significantly affect both resolution and analysis time, while other interaction terms are negligible. The surface response plots in Fig. S3 provide further illustration of these findings. As expected, regions within the experimental domain that exhibit high resolution are also associated with longer analysis times. This underscores the need to find a compromise in chromatographic parameters. As summarized in Table S1, resolutions varied from 0.38 to 1.77, and analysis times ranged from 59 to 290 s. Given the low separation capacity of the FC system, a resolution greater than 1 is considered satisfactory. Among the tested conditions, the chromatographic run with all parameters set to high levels (see experiment No. 9 in Table S1) proved to be optimal, achieving a resolution of 1.05 and a very short analysis time (147.9 s). The chromatogram in Fig. S5 shows effective separation between Te(IV) and Te(VI), allowing for their speciation analysis in around 2.5 min. Anyway, we opted to slightly enhance the resolution by decreasing the HNO_3 concentration from 0.5 M to 0.43 M: this straightforward adjustment is expected to enhance chromatographic separation while

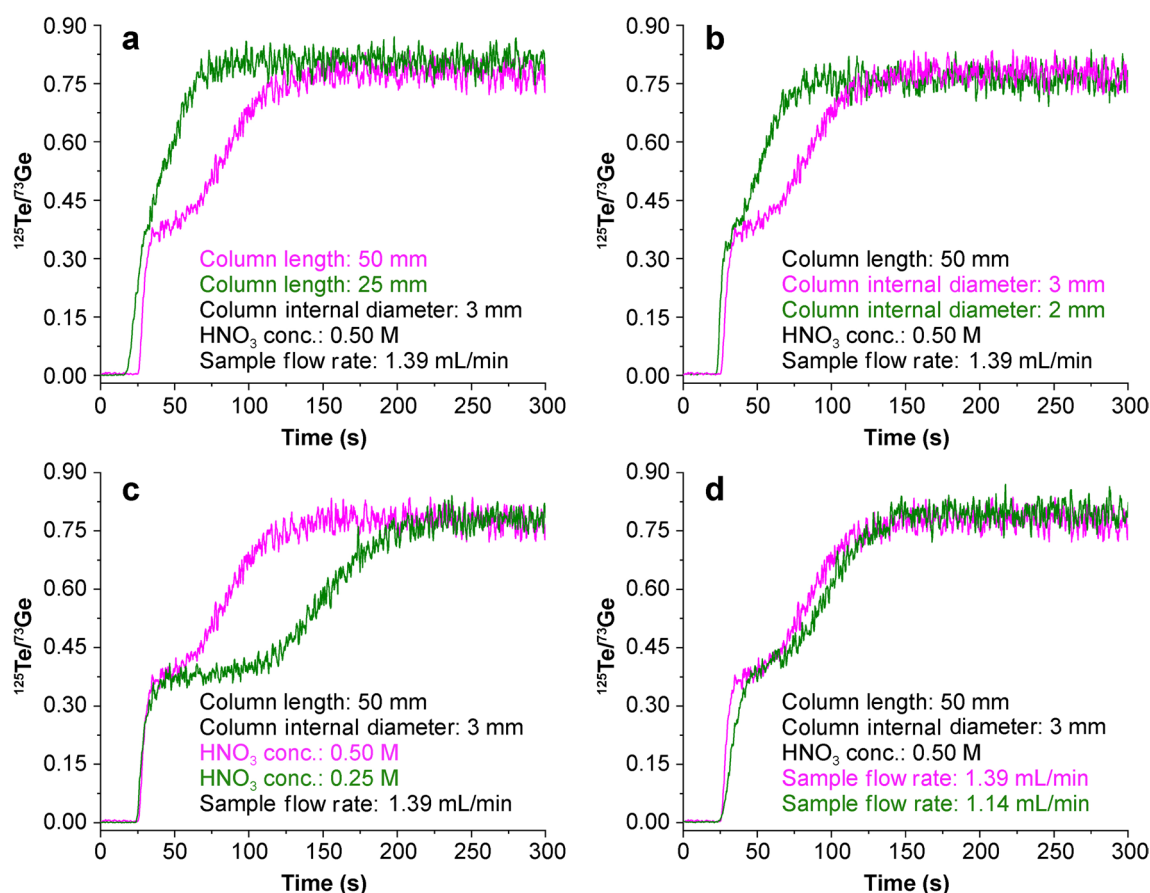


Fig. 4 Effects of chromatographic parameters on the elution profile of Te species: **a** column length; **b** column internal diameter; **c** HNO_3 concentration, and **d** sample flow rate. The chromatographic conditions for each test are reported in the corresponding panel

also unlocking the direct analysis of soil and sediment extraction solutions for geochemically reactive elements, utilizing the standardized method with 0.43 M HNO_3 [38]. With this modification, we finally achieved a resolution of 1.12 and an analysis time of 152.6 s (Fig. 6).

The front height of Te(IV) can be reliably estimated as the average signal within the range of 50–55 s, while Te(VI) can be quantified within the range of 150–155 s. Given that these conditions were satisfactory, further optimizations were performed using the following chromatographic parameters: column length = 50 mm, column width = 3 mm, HNO_3 concentration = 0.43 M, sample flow rate = 1.39 mL/min.

As a final remark, we verified that Te species do not undergo interconversion and that their concentrations remain stable for at least 72 h in 0.43 M HNO_3 .

3.3 Increasing the Sensitivity: Carbon Effect and Isotope Selection

Once optimized the rapid elution of Te species, we assessed the possibility of enhancing the sensitivity of the method by the so-called “carbon effect” [36], i.e., the

matrix effect induced by simple organic compounds that can significantly enhance the limit of detection (LOD) for elements with high ionization potential, including Te. Although the exact mechanism behind this signal enhancement remains unclear, it seems primarily ascribable to improved ionization efficiency through charge transfer between C^+ ions and analyte atoms in the plasma, increasing signal intensity [36].

Organic modifiers were introduced post-column in the FC-ICP-MS to prevent any alteration of the chromatographic system (refer to the configuration in Fig. 1). The flow rate of the additive was adjusted to minimize the online dilution of the samples (dilution factor of approximately 1.18). As shown in Fig. 7, we tested three different alcohols, namely ethanol (EtOH), methanol (MeOH), and 2-propanol (iPrOH) at three different concentrations for the analysis of a Te(IV)-Te(VI) mixture solution (1 $\mu\text{g}/\text{kg}$). For comparison purposes, an experiment was conducted using ultrapure water as the additive to simulate the same dilution.

Regardless of the organic modifiers used, sensitivity significantly increases. The best result was achieved with 4% V/V MeOH, which increased the ^{125}Te signal by a factor of

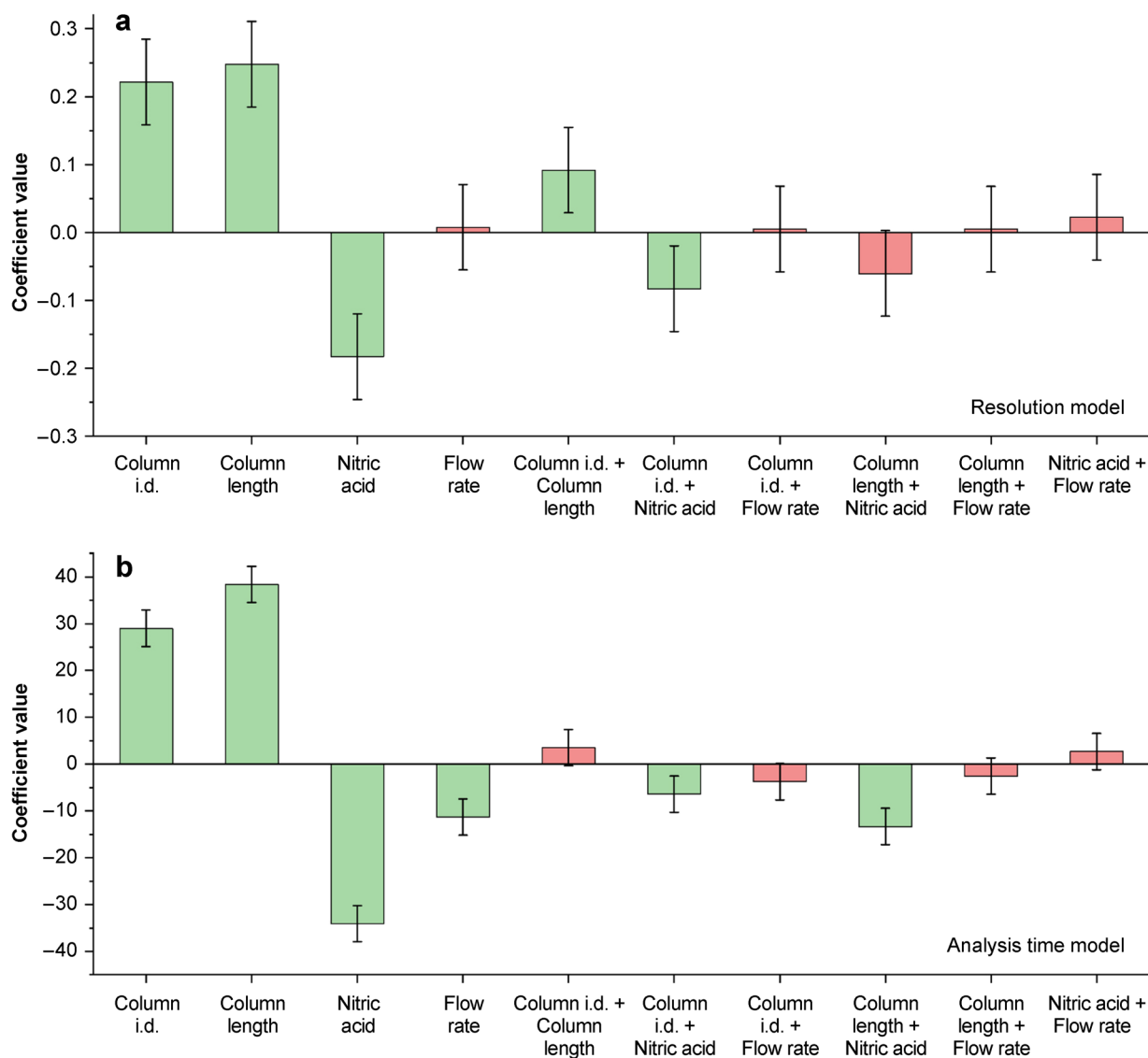


Fig. 5 Coefficients resulting from multivariate regression analysis on the data presented in Table S3 to model **a** chromatographic resolution and **b** analysis time. Green bars mean statistically significant parameters with a p-value of ≤ 0.05 and red bars mean not statistically significant factors

2.9 for both Te(IV) and Te(VI) species. No specific effects instead were found for the internal standard ^{73}Ge .

The step forward involved the choice of the best Te isotope to be used to improve sensitivity without incurring significant interference. Tellurium presents challenges for ICP-MS determination due to the numerous isotopes suffering from isobaric interference from xenon (Xe) isotopes originating from plasma gas impurities. Additionally, the most abundant isotope, ^{130}Te , is affected by isobaric interference from ^{130}Ba and ^{130}Xe . This Te isotope was not therefore considered in this study. We considered the following isotopes:

^{125}Te : 7.14% abundant, with no known interferents, the default isotope in ICP-MS analysis [1].

^{126}Te : 18.95% abundant, interfered with by ^{126}Xe (0.09% abundant).

^{128}Te : 31.69% abundant, interfered with by ^{128}Xe (1.91% abundant).

Signal corrections were applied based on the equations reported in Table S4. Sensitivities were determined from the slopes of the calibration curves within the range 0.01–1 $\mu\text{g}/\text{kg}$. Excellent linearity was observed for all studied isotopes, with $R^2 > 0.9998$ (Fig. S6). Enhanced analytical signals compared to ^{125}Te were observed for ^{126}Te (2.7-fold increase) and ^{128}Te (4.7-fold increase). Despite the higher sensitivity offered by ^{128}Te , the best compromise between sensitivity and signal-to-noise ratio was achieved using the ^{126}Te isotope. This is primarily due to the more significant corrections required for Xe interference, which greatly increases signal noise. Consequently, the LODs were achieved on the ^{126}Te channel: 1.0 ng/kg for Te(IV) and 1.3 ng/kg for Te(VI).

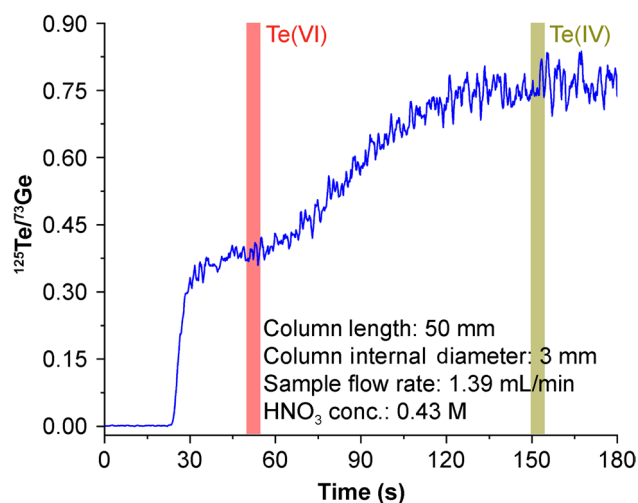


Fig. 6 Frontal chromatogram obtained for a Te(IV)-Te(VI) mixture solution (both species at a concentration equal to 1 $\mu\text{g}/\text{kg}$) under optimized conditions (column internal diameter=3 mm, column length=50 mm, HNO_3 concentration=0.43 M, and sample flow rate=1.39 mL/min). Red and gold regions denote the time intervals utilized to determine the height of the fronts

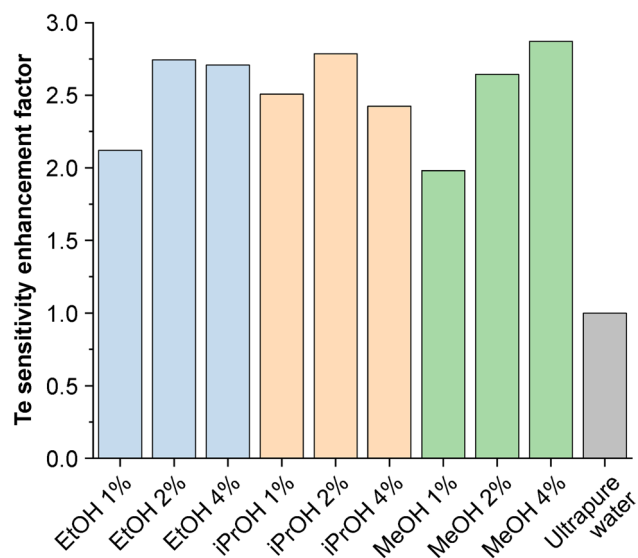


Fig. 7 Evaluation of the carbon effect using three different organic modifiers at three concentration levels. The sensitivity enhancement factor was calculated by normalization against ultrapure water sensitivity. Te(IV)-Te(VI) mixture solutions (1 $\mu\text{g}/\text{kg}$) were analyzed for this purpose

For comparison, ^{128}Te under the same conditions provided LODs of 2.8 ng/kg for Te(IV) and 2.7 ng/kg for Te(VI), while uncorrected ^{125}Te produced LODs of 2.7 ng/kg for Te(IV) and 2.5 ng/kg for Te(VI). This difference can be attributed to the higher variance induced by the much more marked interference correction needed for ^{128}Te , supporting

the greater reliability of the ^{126}Te isotope which was chosen as the optimal channel to be monitored. All LOD values were estimated by analyzing ten replicates of 5 ng/kg standard solutions of Te(IV) and Te(VI) (see Fig. S7 for ^{126}Te signals): this concentration is approximately five times the standard deviation of the background signal, in line with European guidelines for estimating LOD [40].

The notably low LOD values warrant careful consideration, as the simultaneous presence of both species might introduce errors, particularly at ultratrace levels when one species is significantly orders of magnitude more prevalent [31, 32]. To address this, the method's predictive accuracy was tested by analyzing nine different Te(IV)-Te(VI) mixture solutions with various concentrations (10, 100, and 1000 ng/kg). The findings are summarized in Table 2.

The recoveries are close to 100% in most cases, validating that the method performs well for Te(VI) with minimal loss or enhancement. As expected, significant overestimation occurred only under extreme conditions, specifically when the Te species ratio was 1:100, where a relative recovery of 200% was observed for both Te(IV) and Te(VI). It is important to note that these high relative recoveries are associated with very low absolute errors, around 10 ng/kg (1% of the interferent species signal), which is approximately three times the limit of quantification. Furthermore, the presence of an interferent Te species in concentrations two orders of magnitude higher (1 $\mu\text{g}/\text{kg}$) does not represent a realistic scenario. As demonstrated, we can safely state that concentrations below 100 ng/kg do not present any cross-interference issue given that the absolute error of 1 ng/kg lies close to the LOD.

The repeatability was assessed through three replicates of the nine standard solutions detailed in Table 1. The relative standard deviations (RSDs) observed were 4.2% for Te(IV) and 2.8% for Te(VI), aligning well with the expected RSD values for conventional ICP-MS measurements. Inter-day precision was assessed by analyzing both single standard solutions and Te(IV)-Te(VI) mixture solutions over three consecutive days. The results showed inter-day precision below 5% for both Te species, further demonstrating the robustness of the method.

3.4 Application to Mineral Water, Sediment, and Soil Samples

Six natural water samples were analyzed to validate the applicability of the FC-ICP-MS method across various mineral compositions. The physicochemical parameters and major ion concentrations are provided in Table S2. All samples contained extremely low levels of Te species, with Te(IV) consistently below the LOD, while Te(VI) was detected at concentrations up to 7.4 ng/kg (Table 3). No clear correlations between Te speciation and the specific

Table 2 Quantification of Te(IV) and Te(VI) in spiked ultrapure water solutions. The FC-ICP-MS analysis was carried out under optimized conditions. Uncertainties are expressed as two times the standard deviation ($n = 3$)

Sample	Spiked Te(VI) concentration (ng/kg)	Spiked Te(IV) concentration (ng/kg)	Experimental Te(VI) concentration (ng/kg)	Experimental Te(IV) concentration (ng/kg)	Recovery Te(VI) (%)	Recovery Te(IV) (%)
Mix-1	1000	10	997 ± 15	23 ± 13	99.7 ± 1.5	230 ± 130
Mix-2	1000	100	1012 ± 16	113 ± 18	101.2 ± 1.6	113 ± 18
Mix-3	1000	1000	1000 ± 14	999 ± 40	100.0 ± 1.4	99.9 ± 4.0
Mix-4	100	10	99 ± 3	10.3 ± 1.8	99 ± 3	103 ± 18
Mix-5	100	100	103 ± 3	93 ± 7	103 ± 3	93 ± 7
Mix-6	100	1000	109 ± 10	992 ± 18	109 ± 10	99.2 ± 1.8
Mix-7	10	10	9.4 ± 0.8	10.2 ± 1.7	94 ± 8	102 ± 17
Mix-8	10	100	11 ± 2	101 ± 2	110 ± 20	101 ± 2
Mix-9	10	1000	20 ± 1	959 ± 19	200 ± 10	95.9 ± 1.9

characteristics of the water samples were observed, suggesting that the geochemical setting and geographical origin of the water source may influence Te distribution.

Furthermore, mineral waters spiked with very low concentrations of Te(IV) and Te(VI) (5 ng/kg) were analyzed for validation. This choice was made because that no certified reference materials are available for Te speciation. As shown in Table 3, recoveries were (97 ± 5)% for Te(VI) and (115 ± 16)% for Te(IV). This demonstrates the reliability of the method for detecting ultratrace levels of Te species under challenging conditions, with the spike concentration approaching the limit of quantification.

Similarly, we applied the developed method to determine the weakly bound, geochemically reactive fraction of Te species in sediments and soils. The standardized extraction procedure ISO-17586:2016 [38] was employed. As this protocol involves an extraction using 0.43 M HNO₃, it is fully compatible with the direct analysis of the filtered samples without requiring dilution. This feature significantly enhances analytical sensitivity, enabling the detection of ultratraces even in solid samples. The analyses (Table 4) show, as expected, extremely low concentrations of Te species (with concentrations in solid samples in the range 0.34–3.5 µg/kg and 0.13–0.56 µg/kg for Te(VI) and Te(IV), respectively). These results are consistent with the uncontaminated setting in which the samples were collected, i.e., a remote area presenting negligible local sources of contamination. The ability to detect such ultratrace levels highlights the method's capability to accurately measure Te even in samples that should be regarded as background references. Concerning Te species distribution, Te(VI) is largely the predominant species in sediment samples, with Te(IV) in some cases falling below the LOD. This consideration applies also to the certified reference material (total Te concentration equal to 24 µg/kg), where the weakly bound Te fraction is made of Te(VI), only.

Regardless of the extraction capabilities of the standardized ISO-17586:2016 procedure (and hence what “geochemical reactive species” clearly refers to), we spiked the post-extraction solutions to verify whether the co-extracted substances interfere with the Te species concentrations and distributions. As can be seen in Table 4, Te(IV) and Te(VI) remain stable in the extraction media even after 72 h, with recoveries not statistically different from 100%, thus confirming the consistency and accuracy of the obtained data. These results strongly highlight also the robustness of this protocol: the analyzed samples present significant geochemical anomalies, including elevated levels of potential interferents (i.e., Sn and W for GBW07302, as well as Ni and Cr in the samples from the Ventina Valley [41]). This demonstrates the method's reliability, even when applied to challenging matrices.

3.5 Comparison with Existing Methods

Table 5 presents a comparison of representative analytical features between the developed method and recent protocols reported in the literature for Te speciation analysis in water and soil samples. Both chromatographic and non-chromatographic methods were considered in this evaluation. No focus will be given to extraction techniques from soil or sediment samples since a standardized extraction protocol was used here (and therefore this aspect was neither optimized nor developed in the present study). Differently, any other relevant pretreatment (e.g., pre-concentration, derivatization) steps will be discussed.

Currently, only a limited number of chromatographic methods are available for the simultaneous determination of Te species [27, 28]. However, these methods fall short compared to the proposed approach, particularly in terms of LOD. Most existing strategies are inadequate for quantifying Te in uncontaminated natural matrices, as their LODs typically exceed 1 µg/kg, restricting their practical application.

Table 3 Te(IV) and Te(VI) quantifications in mineral water samples and mineral water samples added with 5 ng/kg of both Te species. Quantifications were performed by external calibration. Uncertainties are expressed as two times the standard deviation ($n=3$)

Sample	Te(VI) (ng/kg)	Te(IV) (ng/kg)	Te(VI) in spiked solution (ng/kg)	Te(IV) in spiked solution (ng/kg)	Te(VI) spike recovery (%)	Te(IV) spike recovery (%)
Wat-1	<LOD	<LOD	4.6±0.43	6±1.0	92±9	117±16
Wat-2	7.3±0.7	<LOD	11.8±0.70	6±1.0	89±6	127±16
Wat-3	7.4±0.8	<LOD	12.4±0.90	6±1.1	99±7	115±18
Wat-4	3.1±0.5	<LOD	7.9±0.61	7±1.0	96±8	136±14
Wat-5	<LOD	<LOD	5.3±0.44	5.2±0.68	105±8	105±13
Wat-6	4.8±0.5	<LOD	9.7±0.91	4.5±0.73	99±9	91±16

Table 4 Te(IV) and Te(VI) quantifications in soil and sediment samples, as well as the samples spiked with 50 ng/kg of both Te species (100 ng/kg for the certified reference material GBW07302). Spiked solutions were analyzed 72 h after the spiking. Quantifications were performed by external calibration. Uncertainties are expressed as two times the standard deviation ($n=3$)

Sample	Te(VI) in solution (ng/kg)	Te(IV) in solution (ng/kg)	Te(VI) in solid sample (µg/kg)	Te(IV) in solid sample (µg/kg)	Te(VI) in spiked solution (ng/kg)	Te(IV) in spiked solution (ng/kg)	Te(VI) spike recovery (%)	Te(IV) spike recovery (%)
V08	22±1	4±2	1.11±0.07	0.18±0.04	73±3	54±3	102±2	100±6
V07	32±2	3.5±0.2	1.6±0.1	0.18±0.01	82±3	57.8±0.9	103±4	99±2
V11	28.7±0.6	3±2	1.43±0.06	0.13±0.09	80±6	53±4	103±7	100±8
P04	6.7±0.1	2.5±0.1 ^(*)	0.34±0.01	0.134±0.004	58±5	52±8	100±9	109±15
P05	16.9±0.4	11.1±0.6	0.85±0.04	0.56±0.03	69±4	62±5	104±5	102±8
GBW07302	70±5	<LOD	3.5±0.3	<LOD	175±15	99±3	105±8	99±3

^(*) concentration below the limit of quantitation (LOQ)

While some methods offer analysis times comparable to the FC-ICP-MS (around 300 s for the fastest HPLC-based strategies in the literature [28]), they do not match the sensitivity of the proposed method.

The lowest LODs (down to sub-ng/L levels) have been achieved using hydride generation systems coupled with ICP-MS/MS [14]. Despite their sensitivity, vapor generation-based methods do not support the simultaneous determination of both Te species [14, 43]. Typically, they quantify either Te(IV) or total Te, with the latter requiring the pre-reduction of Te(VI) using agents like Ti(III) in combination with strong acids at high temperatures. However, the reduction with TiCl₃ can be problematic since nitrates in water samples may interfere [26]. This additional step complicates the process, extends the analysis time, and reduces environmental sustainability.

The limited LODs have also driven the adoption of pre-concentration techniques to enhance sensitivity. However, these methods often suffer from analyte loss and discrepancies in the pre-concentration behavior of Te(IV) and Te(VI). This issue frequently necessitates the pre-reduction of Te(VI) to Te(IV), further complicating the procedure and

preventing the simultaneous determination of both species [21, 22]. Nevertheless, the LODs achieved through these techniques are comparable or, in some cases, superior to those of the present work.

Electrochemical methods also face similar challenges, as they are selective for Te(IV) and do not detect Te(VI), which is non-electroactive [26]. Although preconcentration is not required, these methods are limited to Te(IV) and, while they can achieve LODs as low as 5 ng/kg, they are unsuitable for comprehensive speciation analysis [26].

By comparison, the proposed method offers notable LODs similar to or better than most of the state-of-the-art techniques for Te analysis, with the great advantage of allowing a direct and fast speciation analysis, having minimal or no sample workup. As a potential drawback, this method may appear to require a much larger sample volume compared to other techniques (e.g., HPLC) due to the high flow rate at which the sample solution is continuously fed to the ICP-MS. However, the actual sample volume needed is still relatively small, with just 5 mL sufficient for a single analysis: this volume should not pose a critical limitation for the analysis of environmental

Table 5 Comparison of the analytical features between existing procedures for the determination of Te species in natural water or soil samples and the proposed method

Matrix sample	Pretreatment	Detection technique	Te(VI) LOD (ng/L)	Te(IV) LOD (ng/L)	References
Water and soils	For soils: extraction of water-soluble fraction of Te species in de-ionized water for 2 h	CE-UV	346,000	509,000	[42]
Water	–	LC-ICP-MS	500	1400	[27]
Soil	Ultrasound-assisted extraction of Te species from soils with 100 mM citric acid (4 h)	IC-ICP-MS	2000	4000	[28]
Water	i) reduction of Te(VI) species with TiCl_3 for the determination of total Te ii) H_2Te generation by HCl/ NaBH_4 reaction	HG-ICP-MS/MS	Not selectively detected, determined by subtraction	0.07	[14]
Water	i) reduction of Te(VI) with HCl and KBr at 90–100 °C for 45 min ii) magnetic solid phase extraction (MSPE)	MSPE-ICP-MS	Not selectively detected, determined by subtraction	1.2	[21]
Water	i) reduction of Te(VI) with L-cysteine and HCl for the determination of total Te (~ 100 °C for 1 h) ii) capillary microextraction (CME)	CME-ICP-MS	Not selectively detected, determined by subtraction	5.9	[22]
Water	i) reduction of Te(VI) with 6 M HCl (95 °C) ii) photochemical vapor generation in a mixture of acetic acid-formic acid with the addition of Mn^{2+} and Fe^{2+} ions	FI-PVG-ICP-MS/MS	Not selectively detected, determined by subtraction	1.3	[43]
Water	reduction of Te(VI) species with TiCl_3 for the determination of total Te	DP-Cat-CSV	Not selectively detected, determined by subtraction	5.0	[26]
Water, sediments, and soils	For soils and sediments: extraction of geochemically reactive species (ISO-17586:2016), 2 h in 0.43 M HNO_3	FC-ICP-MS	1.3	1.0	This work

CE capillary electrophoresis, HG hydride generation, FI flow injection, PVG photochemical vapor generation, DP-Cat-CSV differential pulse catalytic cathodic stripping voltammetry.

samples. Finally, we successfully addressed potential limitations arising from common matrix effects that could impact chromatographic separation through the validation of environmental samples. The traceability of the investigated interferents is ensured by data reported on the composition of all analyzed water samples (Table S2) and soils and sediments (standard GBW07302 and reference [37]).

In summary, the simplicity and strong analytical performance of this approach make it highly suitable for high-throughput routine Te speciation analysis, while also offering an environmentally friendly option.

4 Conclusions

This study presents a significant advancement in Te speciation analysis through developing an innovative FC-ICP-MS method. This approach effectively addresses the limitations of existing techniques by offering simultaneous determination of tellurite (Te(IV)) and tellurate (Te(VI)) with exceptional sensitivity, achieving detection limits of 1.0 ng/L for Te(IV) and 1.3 ng/L for Te(VI) within a rapid five-minute analysis.

Application of this method to natural mineral water, sediment, and soil samples demonstrated its effectiveness

across various mineral compositions with recovery rates close to 100% for spiked samples, validating the method's accuracy and reliability. Analysis of water, sediments, and soils revealed extremely low levels of Te species, consistent with uncontaminated samples and demonstrated the method's capability to detect ultratrace concentrations even in samples that could be proposed as background references.

The FC-ICP-MS method outperforms existing techniques by providing superior (or comparable) detection limits, reducing analysis time, and extremely simplifying sample preparation. This makes it a highly effective tool for routine environmental monitoring of tellurium, offering a more practical and environmentally sustainable solution for assessing the distribution and risks of this emerging pollutant.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s41664-025-00366-x>.

Acknowledgements Scientific support from CRIETT centre of University of Insubria (instrument code: MAC10) is greatly acknowledged.

Author contributions Davide Spanu: Conceptualization, Data curation, Investigation, Methodology, Supervision, Validation, Visualization, Writing—original draft. Chiara Omodei: Data curation, Formal analysis, Investigation, Validation. Gilberto Binda: Methodology, Visualization, Writing—review and editing. Tommaso Grande: Investigation, Writing—review and editing. Sandro Recchia: Conceptualization, Methodology, Supervision, Writing—original draft.

Funding Open access funding provided by Università degli Studi dell'Insubria within the CRUI-CARE Agreement.

Data availability The data supporting the findings of this study are available from the corresponding author upon request.

Declarations

Conflict of interest The authors have no competing interests to declare that are relevant to the content of this article.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Filella M, Reimann C, Biver M, Rodushkin I, Rodushkina K. Tellurium in the environment: current knowledge and identification of gaps. *Environ Chem*. 2019;16:215–28.
- McNulty BA, Jowitt SM. Barriers to and uncertainties in understanding and quantifying global critical mineral and element supply. *IScience*. 2021;24:102809.
- Wiklund JA, Kirk JL, Muir DCG, Carrier J, Gleason A, Yang F, Evans M, Keating J. Widespread atmospheric tellurium contamination in industrial and remote regions of Canada. *Environ Sci Technol*. 2018;52:6137–45.
- Missen OP, Ram R, Mills SJ, Etschmann B, Reith F, Shuster J, Smith DJ, Brugger J. Love is in the Earth: A review of tellurium (bio)geochemistry in surface environments. *Earth-Sci Rev*. 2020;204:103150.
- Belzile N, Chen YW. Tellurium in the environment: a critical review focused on natural waters, soils, sediments and airborne particles. *Appl Geochemistry*. 2015;63:83–92.
- Zha J, Dong D, Huang H, Xia Y, Tong J, Liu H, Chan HP, Ho JC, Zhao C, Chai Y, Tan C. Electronics and optoelectronics based on tellurium. *Adv Mater*. 2024. <https://doi.org/10.1002/adma.202408969>.
- Willner J, Fornalczyk A, Jablonska-Czapla M, Grygoc K, Rachwal M. Studies on the content of selected technology critical elements (germanium, tellurium and thallium) in electronic waste. *Materials (Basel)*. 2021;14:3722.
- Ashraf MW, Haider SI, Solangi AR, Memon AF. Toxicity of tellurium and its compounds. *Phys Sci Rev*. 2023;8:4375–90.
- L. Gerhardsson, Tellurium, in: *Handb. Toxicol. Met.*, Elsevier, 2022: pp. 783–794. <https://doi.org/10.1016/B978-0-12-822946-0.00027-1>.
- Ogra Y. Biology and toxicology of tellurium explored by speciation analysis. *Metallomics*. 2017;9:435–41.
- Qin H-B, Takeichi Y, Nitani H, Terada Y, Takahashi Y. Tellurium Distribution and speciation in contaminated soils from abandoned mine tailings: comparison with selenium. *Environ Sci Technol*. 2017;51:6027–35.
- Chasteen TG, Bentley R. Biomethylation of selenium and tellurium: Microorganisms and plants. *Chem Rev*. 2003;103:1–25.
- Romero-Freire A, Santos-Echeandía J, Neira P, Cobelo-García A. Less-studied technology-critical elements (Nb Ta Ga In Ge Te) in the marine environment: review on their concentrations in water and organisms. *Front Mar Sci*. 2019. <https://doi.org/10.3389/fmars.2019.00532>.
- García-Figueroa A, Musil S, Matoušek T. Non-chromatographic speciation analysis of tellurium by HG-ICP-MS/MS at Sub ng L⁻¹ Concentration in natural waters using Ti^{III} as a pre-reducing agent. *Anal Chem*. 2022;94:13995–4003.
- Chen M, Wu L, Yi X, Yang K, Xie H. Tellurium speciation in a bioleaching solution by hydride generation atomic fluorescence spectrometry. *Anal Methods*. 2017;9:3061–6.
- Körez A, Eroglu AE, Volkan M, Yavuz Ataman O. Speciation and preconcentration of inorganic tellurium from waters using a mercaptosilica microcolumn and determination by hydride generation atomic absorption spectrometry. *J Anal At Spectrom*. 2000. <https://doi.org/10.1039/b004696p>.
- Viñas P, López-García I, Merino-Meroño B, Hernández-Córdoba M. Ion chromatography-hydride generation-atomic fluorescence spectrometry speciation of tellurium. *Appl Organomet Chem*. 2005;19:930–4.
- Yu C, Cai Q, Guo ZX, Yang Z, Khoo SB. Simultaneous speciation of inorganic selenium and tellurium by inductively coupled plasma mass spectrometry following selective solid-phase extraction separation. *J Anal At Spectrom*. 2004;19:410–3.
- Yu C, Cai Q, Guo ZX, Yang Z, Khoo SB. Speciation analysis of tellurium by solid-phase extraction in the presence of ammonium pyrrolidine dithiocarbamate and inductively coupled plasma mass spectrometry. *Anal Bioanal Chem*. 2003;376:236–42.

20. Huang C, Hu B. Speciation of inorganic tellurium from seawater by ICP-MS following magnetic SPE separation and preconcentration. *J Sep Sci.* 2008;31:760–7.
21. He M, Su S, Chen B, Hu B. Simultaneous speciation of inorganic selenium and tellurium in environmental water samples by poly-aniline functionalized magnetic solid phase extraction coupled with ICP-MS detection. *Talanta.* 2020;207:120314.
22. Ou X, Wang C, He M, Chen B, Hu B. Online simultaneous speciation of ultra-trace inorganic antimony and tellurium in environmental water by polymer monolithic capillary microextraction combined with inductively coupled plasma mass spectrometry. *Spectrochim Acta Part B At Spectrosc.* 2020;168:105854.
23. Ghasemi E, Najafi NM, Raofie F, Ghassempour A. Simultaneous speciation and preconcentration of ultra traces of inorganic tellurium and selenium in environmental samples by hollow fiber liquid phase microextraction prior to electrothermal atomic absorption spectroscopy determination. *J Hazard Mater.* 2010;181:491–6.
24. Najafi NM, Tavakoli H, Alizadeh R, Seidi S. Speciation and determination of ultra trace amounts of inorganic tellurium in environmental water samples by dispersive liquid-liquid microextraction and electrothermal atomic absorption spectrometry. *Anal Chim Acta.* 2010;670:18–23.
25. Liu Y, He M, Chen B, Hu B. Simultaneous speciation of inorganic arsenic, selenium and tellurium in environmental water samples by dispersive liquid liquid microextraction combined with electrothermal vaporization inductively coupled plasma mass spectrometry. *Talanta.* 2015;142:213–20.
26. Biver M, Quentel F, Filella M. Direct determination of tellurium and its redox speciation at the low nanogram level in natural waters by catalytic cathodic stripping voltammetry. *Talanta.* 2015;144:1007–13.
27. Narukawa T, Wada A, Cheong C, Chiba K. Separation and determination of tellurium(IV) and tellurium(VI) using reversed-phase high-performance liquid chromatography-inductively coupled plasma mass spectrometry. *Anal Sci.* 2024. <https://doi.org/10.1007/s44211-024-00663-y>.
28. Grygoyć K, Jabłońska-Czapla M. Development of a tellurium speciation study using ic-icp-ms on soil samples taken from an area associated with the storage, processing, and recovery of electrowaste. *Molecules.* 2021. <https://doi.org/10.3390/molecules26092651>.
29. Spanu D, Monticelli D, Rampazzi L, Dossi C, Recchia S. Introducing frontal chromatography-inductively coupled plasma-mass spectrometry as a fast method for speciation analysis: the case of inorganic arsenic. *Anal Chem.* 2019;91:13810–7.
30. Spanu D, Monticelli D, Binda G, Dossi C, Rampazzi L, Recchia S. One-minute highly selective Cr(VI) determination at ultra-trace levels: An ICP-MS method based on the on-line trapping of Cr(III). *J Hazard Mater.* 2021. <https://doi.org/10.1016/j.jhazmat.2021.125280>.
31. Spanu D, Fantinuoli S, Binda G, Rampazzi L, Monticelli D, Recchia S. Streamlining antimony speciation analysis in natural waters with frontal chromatography-ICP-MS. *Spectrochim Acta Part B At Spectrosc.* 2023;207:106762.
32. López AR, Binda G, Roncoroni G, Recchia S, Monticelli D, Spanu D. Optimizing antimony speciation analysis via frontal chromatography-ICP-MS to explore the release of PET additives. *Molecules.* 2024;29:2870.
33. Spanu D, Butti L, Boldrocchi G, Bettinetti R, Recchia S, Monticelli D. Selective organomercury determination by ICP-MS made easy. *Anal Chim Acta.* 2022;1206:339553.
34. Spanu D, Butti L, Recchia S, Dossi C, Monticelli D. A high-throughput, straightforward procedure for biomonitoring organo-mercury species in human hair. *Talanta.* 2024;270:125612.
35. Monticelli D, Castelletti A, Civati D, Recchia S, Dossi C. How to efficiently produce ultrapure acids. *Int J Anal Chem.* 2019;2019:1–5.
36. Grindlay G, Mora J, De Loos-Vollebregt M, Vanhaecke F. A systematic study on the influence of carbon on the behavior of hard-to-ionize elements in inductively coupled plasma-mass spectrometry. *Spectrochim. Acta - Part B At Spectrosc.* 2013;86:42–9.
37. Binda G, Pozzi A, Livio F. An integrated interdisciplinary approach to evaluate potentially toxic element sources in a mountainous watershed. *Environ Geochem Health.* 2020;42:1255–72.
38. Groenenberg JE, Römkens PFAM, Van Zomeren A, Rodrigues SM, Comans RNJ. Evaluation of the single dilute (0.43 M) nitric acid extraction to determine geochemically reactive elements in soil. *Environ Sci Technol.* 2017. <https://doi.org/10.1021/acs.est.6b05151>.
39. I. Puigdomenech, Hydra/Medusa chemical equilibrium database and plotting software (2004).
40. Wenzl T, Haedrich J, Schaechtele A, Robouch P, Stroka J. Guidance document on the estimation of LOD and LOQ for measurements in the field of contaminants in feed and food. Tech Rep. 2016. <https://doi.org/10.2787/8931>.
41. Binda G, Pozzi A, Livio F, Piasini P, Zhang C. Anomalously high concentration of Ni as sulphide phase in sediment and in water of a mountain catchment with serpentinite bedrock. *J Geochemical Explor.* 2018;190:58–68.
42. Casiot C, Alonso MCB, Boisson J, Donard OFX, Potin-Gautier M. Simultaneous speciation of arsenic, selenium, antimony and tellurium species in waters and soil extracts by capillary electrophoresis and UV detection. *Analyst.* 1998;123:2887–93.
43. Jeníková E, Nováková E, Hraníček J, Musil S. Ultra-sensitive speciation analysis of tellurium by manganese and iron assisted photochemical vapor generation coupled to ICP-MS/MS. *Anal Chim Acta.* 2022. <https://doi.org/10.1016/j.aca.2022.339634>.