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Automated online SPE-ICP-MS for ultra-trace determination of mercury in freshwaters

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Mercury (Hg) contamination in aquatic environments requires analytical methods capable of reliable ultra-trace quantification to support environmental monitoring, regulatory compliance and, ultimately, health risk assessment. Conventional approaches often involve labor-intensive preparation, derivatization steps, or insufficient sensitivity for pristine waters. To overcome these limitations, solid-phase extraction (SPE) has been increasingly employed to preconcentrate Hg prior to detection; however, existing strategies typically rely on complex, customized sorbents, offline procedures, or additional hyphenated techniques for speciation, which increase cost, time, and operational complexity. In this study, we present a fully automated online SPE-inductively coupled plasma mass spectrometry (SPE-ICP-MS) method for total Hg determination in natural waters. The method exploits thiourea-assisted complexation of inorganic and organic Hg species, enabling their simultaneous retention on a cation-exchange resin and species-independent elution with 1 M HCl. Adjustable accumulation times allow tuning between rapid analysis and enhanced sensitivity. Under optimized conditions, the method achieves a detection limit of 0.93 ng L⁻¹, a linear range up to 1600 ng L⁻¹, and accurate recoveries (96–104%) in mineral water samples. Compared with established analytical protocols, the developed system offers competitive sensitivity while enabling high-throughput and simple operation. These features make this method suitable for routine Hg monitoring.

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1. Introduction

Mercury (Hg) contamination in aquatic environments represents one of the most pressing environmental challenges of the 21st century, with severe implications for ecosystem integrity and human health.¹ As a persistent global pollutant, Hg undergoes long-range atmospheric transport, allowing its widespread distribution from anthropogenic emission sources to remote, seemingly pristine environments.² Although Hg is naturally released from the Earth's crust through processes such as volcanic eruptions and rock weathering, human activities (*e.g.*, coal combustion, industrial processes, artisanal gold mining, and waste incineration) have drastically increased its environmental levels.³ Today, anthropogenic emissions far exceed natural geogenic sources.⁴

In aquatic systems, inorganic Hg can be transformed by microbial methylation into methylmercury (MeHg), a potent neurotoxin that biomagnifies through food webs and poses particular risks to top predators and fish-consuming human populations.⁵ This pronounced toxicity and bioaccumulative behavior underpin the stringent regulatory limits established

for Hg in water bodies. For instance, the EU Water Framework Directive sets maximum allowable concentrations for Hg in surface waters at 0.05 µg L⁻¹,⁶ while the WHO drinking water standard is set at 1 µg L⁻¹.⁷ Background Hg levels in unpolluted waters are generally much lower, reaching up to 12 ng L⁻¹ in freshwater systems^{8,9} and up to 20 ng L⁻¹ in marine environments.¹⁰

Current analytical methods for ultra-trace Hg determination are largely based on cold vapor atomic fluorescence spectrometry or atomic absorption spectrometry (CV-AFS, CV-AAS) following oxidative digestion and vapor generation step, *e.g.* the EPA Method 1631E.¹¹ However, these techniques are limited by matrix interferences⁸ and labor-intensive sample preparation. Inductively coupled plasma mass spectrometry (ICP-MS), particularly when coupled with CV generation, provides improved sensitivity¹² but still relies on matrix effects and operational complexity.^{13,14} Direct ICP-MS, on the other hand, generally lacks sufficient sensitivity for the analysis of pristine waters, typically achieving detection limits around 10 ng L⁻¹.¹⁵ Other approaches, including UV-vis spectrophotometry,¹⁶ and electrothermal atomic absorption spectrometry (ETAAS),¹⁷ are either less sensitive or operationally complex.

To overcome these limitations, both solid-^{18–23} and liquid-phase (micro)extraction^{24–26} techniques are widely employed to enhance detection sensitivity. However, common challenges

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include unstable and hazardous derivatizing agents, sensitivity to matrix effects (chloride, dissolved organic matter), and complex multi-step procedures. Online preconcentration strategies could overcome most of these issues, making the entire sample pretreatment process straightforward. Among these, solid-phase extraction (SPE) offers notable advantages for Hg preconcentration, including high enrichment factors, low contamination risk, and compatibility with automation. Yet, most SPE methods reported in the literature are offline,^{18,19} require extensive sample handling and often rely on custom-made sorbents that need synthesis or functionalization. Moreover, many SPE strategies focus on speciation analysis^{19–23} necessitating additional instrumentation (typically high-performance chromatography (HPLC)) and increasing operational complexity. Even when online systems are employed, they frequently involve multiple pumps, auxiliary devices, or manual sample loading. Differently, truly online SPE systems that seamlessly integrate preconcentration with detection can minimize contamination risks and enable fully automated operation. However, the simultaneous accumulation of both inorganic and organic Hg species remains challenging due to their markedly different chemical properties, despite being essential for total Hg determination in water monitoring.

In this study, we aimed to develop an innovative online SPE-ICP-MS method for the fully automated determination of total Hg in pristine natural water samples. The main objective was to establish a sensitive and simple analytical approach suitable for trace-level quantification while minimizing manual handling and sample pretreatment. To this end, a fully automated online SPE system based on a commercial resin was integrated into the ICP-MS instrumentation, providing a streamlined and practical tool for routine Hg monitoring in natural waters.

2. Experimental

2.1. Standards, reagents and samples

Ultrapure hydrochloric acid (HCl) and nitric acid (HNO₃) were prepared using a milestone sub-boiling distillation system.²⁷ Ultrapure water (resistivity 18.2 MΩ cm at 25 °C, TOC < 5 ppb), generated by a Sartorius Arium Mini-UV Lab Water System, was employed for the preparation of all standards and solutions. MeHg working solutions were obtained by diluting a certified 1000 ± 20 mg per L MeHg stock solution (Alfa Aesar, expressed as MeHgCl), while a 10 mg L⁻¹ Hg solution (TraceCERT®, Sigma-Aldrich) was used for inorganic Hg standards. Solid thiourea (TU, ≥99% purity, Carlo Erba Reagents), anhydrous CaCl₂ (≥99% purity, Carlo Erba Reagents) and MgCl₂ (≥99% purity, Carlo Erba Reagents) were used. All dilutions were performed gravimetrically using a precision balance with two decimal places.

Three mineral waters (MW1–MW3) with different ionic strengths and compositions were used to assess method performance in representative matrices. Their detailed chemical compositions are reported in Table S1 of the SI.

All samples were stored in low-density polyethylene (LDPE) bottles that had been thoroughly decontaminated to remove trace metal impurities from manufacturing, packaging, or

storage. The cleaning procedure consisted of three consecutive steps:²⁸ (i) immersion in a 0.4% w/w detergent solution (Nalgene L900, Thermo Scientific) for one week; (ii) soaking in 2% w/w HNO₃ for one week; (iii) a second immersion in fresh 2% w/w HNO₃ for another week. Bottles were rinsed extensively with ultrapure water between each step and prior to use.

All calibration standards and sample solutions were prepared and analyzed on the same day, thereby avoiding potentially problematic long-term storage in LDPE containers.^{29–31} The optimized procedure employs an acidic TU solution to preserve the samples and enable their analysis. Under these conditions, Hg is predominantly present as Hg-TU complexes, which are known to stabilize Hg in solution and minimize losses due to adsorption or volatilization.

2.2. Instrumental setup and analytical procedure

The instrumental setup was adapted from our previous work on Hg speciation methods (Fig. 1). Hg accumulation and elution were performed using a custom-made polyether ether ketone (PEEK) column (3 × 50 mm) packed with strong cation-exchange resin (Dowex® 50WX8, hydrogen form, 200–400 mesh, Sigma-Aldrich). The resin was retained at both ends of the column by HPLC frits. Large resin particles (55 ± 20 μm) were selected to minimize backpressure, eliminating the need for an HPLC pump.

As illustrated in Fig. 1, the column is positioned between a peristaltic pump for sample introduction and the ICP-MS nebulizer. An iCAP Q ICP-MS (Thermo Scientific) was used for Hg detection, and detailed instrumental parameters are reported in Table S2. The setup was further modified to allow the addition of TU (190 mM) to the sample flow after the column, effectively suppressing Hg memory effects. The analysis was fully automated using a CETAC ASX-260 autosampler (Thermo Scientific) and followed these sequential steps:

- Uptake of the sample and accumulation of Hg species (Fig. 1a): the sample is spiked with TU (5 mM) and HCl 500 mM under optimized conditions (see Section 3.3). During this phase (2–8 min), Hg species are continuously retained by the resin.
- Complete elution of Hg species with HCl (Fig. 1b): Hg species are simultaneously eluted with an optimized concentration of HCl (1 M) over 3 minutes. This step also functions as a column cleaning procedure, allowing immediate injection of the next sample.

Data processing and calculations were performed using Origin 2018 software (version 9.5.1.195, OriginLab).

3. Results and discussion

3.1. Analytical concept and instrumental setup

The analytical approach developed in this study relies on the on-line preconcentration of Hg species through their selective retention in a cation-exchange column system after complexation with TU. The accumulated Hg-TU species are subsequently subjected to controlled elution using HCl, where H⁺ acts as the competitive ion and Cl⁻ serves as the complexing ligand,

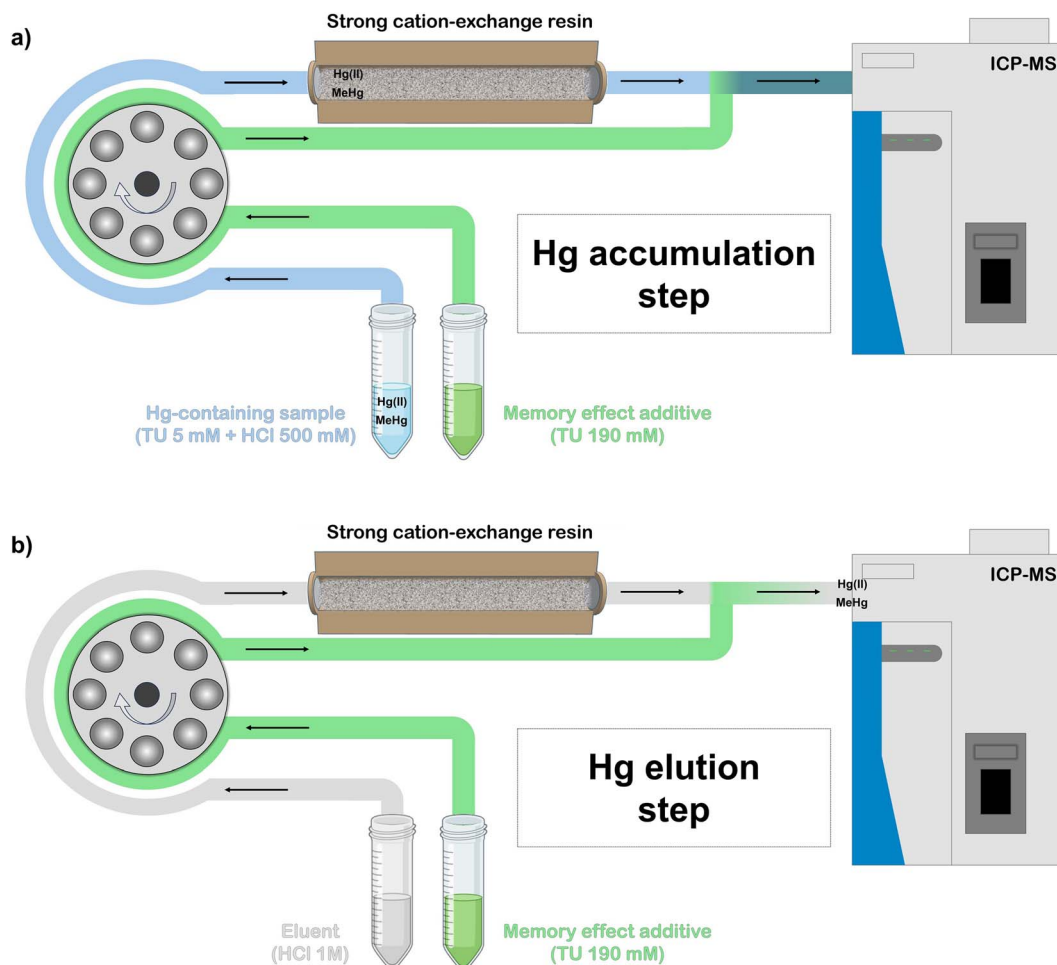


Fig. 1 Schematic representation of the online preconcentration system coupled with ICP-MS used for the determination of Hg species. The analytical procedure involves two sequential steps: (a) Hg accumulation step and (b) Hg elution step, achieved by switching the solution fed through the column.

forming neutral and anionic complexes (with Hg(II) and MeHg, respectively), that enable efficient desorption from the resin.

The rationale behind this strategy lies in the well-known ability of TU to act as a soft Lewis base by strongly coordinating Hg(II) and MeHg, forming the cationic complexes $[\text{Hg}(\text{TU})_x]^{2+}$ and $[\text{MeHgTU}]^+$, respectively.³² These species exhibit high affinity for cation-exchange resins, enabling their simultaneous retention. Unlike methods in which TU is immobilized on the stationary phase *via* lab-made functionalization,³³ using TU as a complexing agent allows greater flexibility and prevents excessively strong Hg binding: indeed, TU-based resins are widely used for Hg removal due to the high stability of Hg-TU complexes.^{33,34} Finally, the use of a commercially available strong cation-exchange resin, instead of a custom-made sorbent, enhances method reproducibility and transferability, allowing straightforward implementation in routine analytical laboratories equipped with commonly available instruments and consumables.

The overall instrumental apparatus and analytical protocol are depicted in Fig. 1. During the accumulation step (Fig. 1a), the sample (previously spiked with TU) is passed through the

cation-exchange column, where the cationic complexes are retained on the stationary phase. In the elution step (Fig. 1b), a HCl solution is employed to release the trapped species for measurement. To suppress Hg memory effects and ensure reproducibility, the sample is spiked with a 190 mM TU solution *via* a Y-fitting before entering the nebulizer,^{35,36} without interfering with the Hg-resin interactions. The sample flow rate (1.7 mL min^{-1}) was not systematically optimized, as we selected the highest flow rate compatible with stable signals aiming at reducing the analysis time.

As illustrated in Fig. S1, both inorganic and organic Hg species are efficiently retained during the accumulation step upon complexation with 5 mM TU: no analytical signal is observable for Hg when a solution containing $1 \mu\text{g L}^{-1}$ of both Hg(II) and MeHg is passed through the column. This evidence confirms that TU complexation induces the effective accumulation of Hg(II) and MeHg on the cation-exchange resin. The same behavior was observed using TU in the concentration range of 0.5–10 mM, confirming the robustness of the process.

These findings provide the basis for a systematic study of the elution conditions, which is discussed in the following section.

3.2. Optimization of elution conditions

Co-elution of all Hg species is mandatory if total Hg is to be targeted in accordance with regulatory requirements. Inorganic and methylmercury standards were preconcentrated for 2 minutes and eluted by HCl solutions to explore their elution profiles. This acid was chosen for its ability to form $[\text{HgCl}_4]^{2-}$ with Hg(II) and MeHgCl with MeHg facilitating efficient desorption from the cation-exchange resin and ideally yielding well-defined peaks. Notably, the elution step also rinses and regenerates the column, preparing the system for subsequent analyses.

At the lowest tested HCl concentration (HCl 0.3 M, see Fig. 2a), the peaks of Hg(II) and MeHg are markedly separated, with Hg(II) eluted at longer times. This elution order is reasonably explained by the stronger affinity of the Hg(II) -TU complex with the cation exchange column, which leads to greater retention.

The observed behavior may, in principle, be favorable for applying this procedure to speciation analysis, though the resolution remains insufficient for accurate species-specific quantification, and speciation analysis should be avoided. At intermediate HCl concentration (0.5 M, Fig. 2b), elution times are shorter, but the Hg(II) and MeHg peaks are still separated: using 1 M HCl (Fig. 2c) produces rapid elution of both species (~ 3 minutes) with analogous peak shapes for both Hg species, which is ideal for total Hg analysis through co-elution. Under these conditions, all Hg species are quantitatively recovered in a single measurement, providing a robust, fast, and reproducible method for total Hg determination.

These observations highlight that HCl concentration is a critical parameter controlling both the efficiency of elution and the selectivity between species. The method was further studied and optimized for total Hg determination using 1 M HCl as the eluent.

3.3. Preconcentration time and analytical performances

Different accumulation times between 2 and 8 minutes were investigated to evaluate the increase in the enrichment factor. The analytical signal of both Hg(II) and MeHg was found to be directly proportional to the accumulation time, as shown in Fig. 3 and S2.

From here, an accumulation time of 4 minutes was selected as the default experimental protocol to ensure a balance between analytical throughput (total analysis time ~ 7 minutes) and preconcentration efficiency. However, the accumulation time can be extended in case very low Hg concentration samples are analyzed.

The linearity of the analytical signal with respect to Hg species concentration was verified in the range $0\text{--}1600\text{ ng L}^{-1}$ (Fig. S3). The slopes of the calibration curves obtained for MeHg and Hg(II) ($(1.060 \pm 0.007) \times 10^5$ and $(1.063 \pm 0.010) \times 10^5$, respectively) were not statistically different, indicating that the two species exhibit equivalent analytical responses under the selected experimental conditions. Therefore, for the sake of practicality, Hg(II) standard only was used for calibration in total Hg determination.

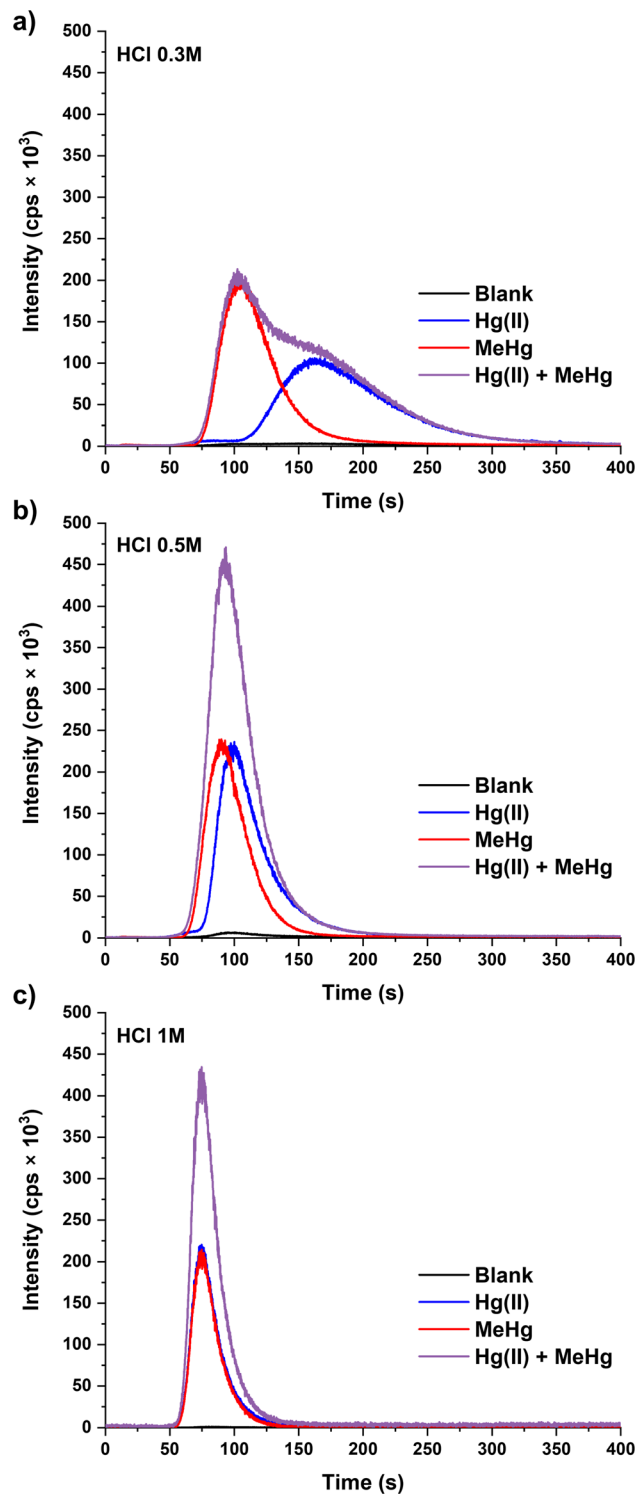


Fig. 2 Elution profiles obtained for Hg(II) (blue line), MeHg (red line), and their mixture (purple line) at different HCl concentrations: (a) 0.3 M, (b) 0.5 M, and (c) 1 M. The black line represents the blank. Signal intensity is expressed in counts per second (cps). The accumulation time was 2 minutes and the concentration of Hg(II) and MeHg was $1\text{ }\mu\text{g L}^{-1}$.

The limit of detection (LOD) was then determined following European guidelines³⁷ for two different accumulation times, 4 and 8 minutes. Ten replicates of a 5 ng per L Hg(II) solution were

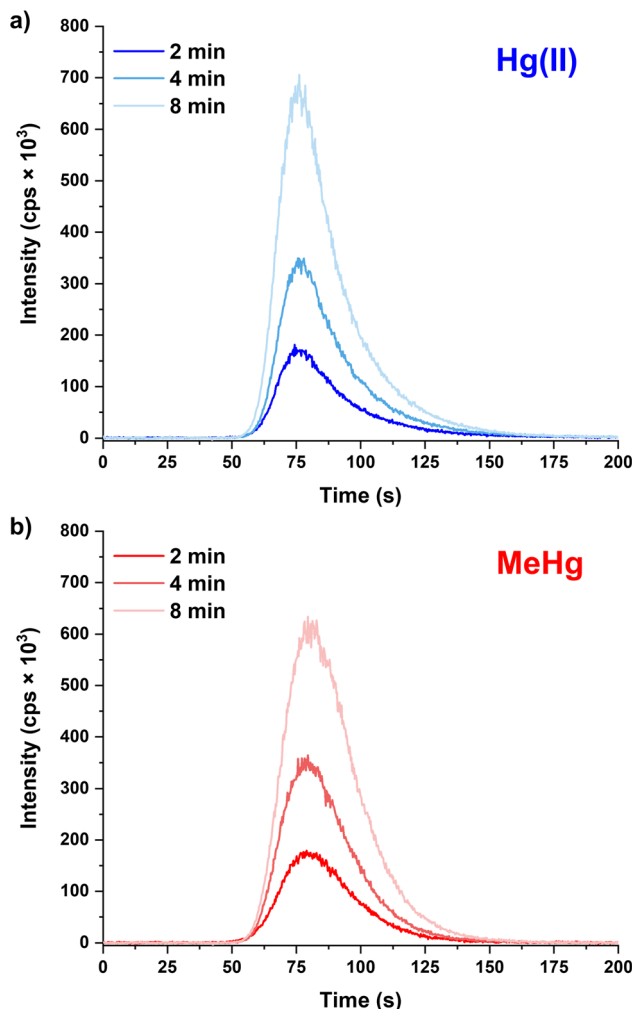


Fig. 3 Effect of the accumulation time on Hg(II) (a) and MeHg (b) analytical signal. (a) and (b) Show the transient intensity profiles for different accumulation times (2, 4, and 8 min). The corresponding integrated peak areas *versus* accumulation time with linear regression are depicted in Fig. S2. The concentration of Hg(II) and MeHg was $1 \mu\text{g L}^{-1}$.

analyzed, yielding LODs of 1.3 ng L^{-1} and 0.93 ng L^{-1} , respectively (signals shown in Fig. S4).

The accuracy was evaluated by spiking ultrapure water, and subsequently mineral water with different compositions, with Hg(II) and MeHg at various concentrations and ratios. It is important to emphasize that we adopted a spike-and-recovery validation strategy, a widely accepted approach in trace analysis, as the available certified reference materials (CRMs) were not fully suitable for our specific purpose. Available CRMs either contain Hg at concentrations well above environmentally relevant levels (*e.g.*, NIST SRM 1641, 0.1013 mg L^{-1}) or consist of spiked ultrapure water (*e.g.*, NRCC ORMS-6, 26.18 ng L ; GBW08603, $9.7 \mu\text{g L}^{-1}$), thus not fully representative of natural freshwater matrices. Accordingly, spike-and-recovery experiments enabled accuracy to be assessed at environmentally relevant concentrations and in the presence of representative matrix components. Spiking solutions were prepared from

certified standards to ensure appropriate metrological traceability. Moreover, both inorganic and organic Hg species were added to ultrapure and mineral water, providing a more rigorous validation framework that accounts for Hg speciation, unlike the aforementioned CRMs, which typically contain a single mercury form.

The measured total Hg concentrations and recoveries are summarized in Table S3. The recoveries ranged from 96% to 108%, and all values were found to be not significantly different from 100% within the 95% confidence intervals. These results demonstrate that the method provides accurate quantification of total Hg across different spiking levels and Hg(II)/MeHg ratios.

To evaluate matrix effects in real samples, three mineral waters (MW1–MW3) with different ionic strengths were investigated (see Table S1, SI). MW2 is a very low-mineralized water, MW1 a moderately mineralized one, and MW3 a highly mineralized matrix, with fixed residues of 14.4, 34.9, and 123.6 mg L^{-1} , respectively. Overall, these samples cover a representative range of salinity and ionic composition, allowing the assessment of potential matrix effects. Recoveries of Hg in these samples were considerably below 100% and highly variable (mean recovery for 10, 25 and 50 ng per L spikes: $11 \pm 12\%$), indicating pronounced matrix effects in the presence of interfering ions.

This matrix effect was addressed by acidifying the mineral water samples with HCl. Mild acidification is expected to minimize interferences from naturally occurring ligands capable of binding Hg species.³⁸ Importantly, the introduction of HCl should not interfere with TU coordination as the stability of Hg-TU complexes far exceeds that of Hg-Cl species, preventing chloride from competing for binding or affecting the analytical response. Based on these considerations, HCl (500 mM) was added to the sample solution containing TU (5 mM) for the preconcentration of Hg species. These revised conditions were applied to both calibration standards and mineral water samples. The results reported in Table 1 demonstrate excellent recoveries across the investigated concentration range ($10\text{--}50 \text{ ng L}^{-1}$), demonstrating the accuracy and robustness of the method for trace-level Hg determination in complex matrices.

To further assess matrix robustness under controlled conditions, a synthetic water was prepared by spiking ultrapure water with CaCl_2 and MgCl_2 ($14.4 \text{ mg L}^{-1} \text{ Ca}^{2+}$, $10.2 \text{ mg L}^{-1} \text{ Mg}^{2+}$, and $55.4 \text{ mg L}^{-1} \text{ Cl}^{-}$, $206 \mu\text{S cm}^{-1}$). Recovery tests were performed for Hg at concentrations of 10 and 25 ng L^{-1} , yielding recoveries of 95% in both cases, confirming that the presence of these ions does not significantly affect the preconcentration of Hg-TU complexes. These results complement the MW1–MW3 dataset by isolating the effect of divalent cations and chloride, the latter being present at comparatively low levels in the mineral waters. Overall, this synthetic matrix extends the investigated compositional range beyond that of the mineral water samples.

Finally, both filtered ($0.45 \mu\text{m}$ nylon filter) and unfiltered samples were analyzed and no statistically significant difference in Hg concentrations were observed. This indicates that Hg was

Table 1 Recovery of Hg from mineral water samples (MW1–MW3) spiked at different Hg concentrations. Reported concentrations correspond to the mean of three replicates ($n = 3$), with uncertainties expressed as 95% confidence intervals calculated using the coverage factor $t(0.95, 2 \text{ df}) = 4.303$

	MW1		MW2		MW3	
Hg spiked (ng L^{-1})	Hg measured (ng L^{-1})	Recovery (%)	Hg measured (ng L^{-1})	Recovery (%)	Hg measured (ng L^{-1})	Recovery (%)
0	<LOD	n.a.	1.0 ± 0.7	n.a.	1.7 ± 0.8	n.a.
10	9.9 ± 0.6	99 ± 6	11.4 ± 0.9	104 ± 9	11.5 ± 0.7	98 ± 7
25	24 ± 2	96 ± 8	27 ± 2	104 ± 8	27 ± 1	104 ± 4
50	50 ± 3	100 ± 6	51 ± 2	100 ± 4	52 ± 3	101 ± 6

predominantly present in a readily mobilizable form, with no substantial contribution from fine particulate- or colloidal-bound fractions under the investigated conditions. We acknowledge that samples rich in organic matter and characterized by a high fraction of particulate-bound Hg may require additional treatment to release Hg species, which could be addressed in future studies. Nevertheless, the combined use of TU and HCl is well documented in the literature as an effective strategy for mitigating matrix effects in humic acid-rich waters.³⁸

3.4. Comparison with existing methods

The developed online SPE-ICP-MS method demonstrates competitive analytical performance when compared to established techniques for total Hg determination in water samples. The dual-mode approach offers flexibility between rapid screening (down to 5 min of analysis time) and enhanced sensitivity (11 min, LOD = 0.93 ng L^{-1}), with both modes maintaining an adequate linear range extending to 1600 ng L^{-1} . This linear range is sufficient for most environmental water monitoring applications where Hg concentrations typically vary from ultratrace to low $\mu\text{g L}^{-1}$ levels. Table S4 provides a comparison of the detection capabilities and linearity range between the proposed method and existing approaches in literature. Cold vapor ICP-MS (CV-ICP-MS) represents a highly sensitive approach for seawater analysis, achieving an LOD of 0.8 ng L^{-1} and LOQ of 2.7 ng L^{-1} .³⁹ However, this method exhibits a narrow linear range ($1.9\text{--}50 \text{ ng L}^{-1}$), limiting its applicability for samples with variable Hg content. Importantly, CV techniques require Hg chemical reduction using reagents such as stannous chloride (SnCl_2) or sodium borohydride (NaBH_4), which introduce additional reagent costs, preparation steps, and potential sources of contamination in contrast with green analytical chemistry principles. Flow injection CV-AAS coupled with ionic liquid extraction⁴⁰ shows comparable detection capabilities (LOD 2.3 ng L^{-1}) but requires extensive offline sample preparation, specialized solvents, and longer total analysis time (19 min for extraction and back-extraction plus the detection time, approximately 2 min).

Direct ICP-MS analysis without preconcentration provides moderate sensitivity, with a limit of detection (LOD) of 7.9 ng L^{-1} reported in the literature,¹⁵ which is very close to the LOD of 7.8 ng L^{-1} obtained with our instrumentation. The

approximately 8-fold higher LOD compared to the developed SPE-ICP-MS method limits its application for compliance monitoring at stringent regulatory levels.

Thermal decomposition amalgamation AAS (TDA-AAS) with direct sampling offers the advantage of eliminating wet chemistry preparation. However, its LOD (350 ng L^{-1}) is more than 300-fold higher than the developed online SPE-ICP-MS method, restricting its use to heavily contaminated samples rather than trace-level water analysis.

Concerning other SPE-based strategies, most articles focused on speciation analysis,^{19–23} which is not the primary objective when addressing Hg water monitoring. HPLC is mostly used^{20–23} in combination with complex stationary phases (e.g., functionalized silica,^{19,22} carbon nanotubes,²⁰ zwitterion polymers,²¹ magnetic functionalized particles⁴¹) that require either synthesis or functionalization of commercial resins. These strategies may also involve multiple HPLC pumps, columns, or auxiliary devices, and in some cases manual sample loading,^{22,23} increasing operational complexity. Additionally, some SPE-based strategies are offline.^{19,41} Reported LODs range from 0.001 to 0.78 ng L^{-1} , and the linear response interval is often narrow, which may be limiting for environmental samples with variable Hg levels. Finally, analysis times range from 5 to more than 10 minutes, comparable to our method that requires 7 minutes per sample. In contrast to other SPE-based approaches, our method employs a column packed with a commercially available strong cation-exchange resin and uses TU in HCl as the sole reagents, requiring no resin functionalization or additional complex chemicals. It achieves a LOD of 0.93 ng L^{-1} and offers a wide linear range up to 1600 ng L^{-1} . Moreover, the entire procedure is fully automated using the ICP-MS autosampler and peristaltic pump, offering a simple and high-throughput approach for total Hg determination in low-salinity natural waters.

4. Conclusions

In this work, we developed and validated a fully automated online SPE-ICP-MS method for trace-level determination of total Hg in freshwaters. The approach relies on the quantitative retention of inorganic and organic Hg after TU complexation in a low-pressure cation exchange column, followed by simultaneous elution and ICP-MS detection. The method offers excellent sensitivity (LOD 0.93 ng L^{-1}), a wide linear range, and

accurate recoveries in mineral water, enabling reliable compliance monitoring of total Hg in line with regulatory limits, while minimizing sample preparation and environmental impact. The method was specifically developed and validated for low-salinity freshwater samples and has not been tested for higher salinity samples like seawater; nevertheless, the approach might in principle be adaptable to higher-salinity matrices in future investigations. Key advantages include the use of a commercially available cation-exchange resin, full automation without the need for hyphenated systems, and adjustable accumulation times for rapid screening or enhanced sensitivity. These features make the workflow flexible and readily transferable to routine laboratory settings for high-throughput environmental monitoring. Finally, although validated for total Hg determination, the selective retention of both inorganic and organic species suggests potential applicability to Hg speciation studies under controlled conditions, paving the way for future investigations into Hg(II) and MeHg distribution in natural waters.

Author contributions

Davide Spanu: conceptualization; methodology; validation; resources; data curation; writing—original draft preparation; visualization; supervision. Sandro Recchia: conceptualization; resources; writing—review and editing. Damiano Monticelli: conceptualization; methodology; resources; writing—review and editing; supervision. Alejandro R. López: validation; formal analysis; investigation; data curation; writing—original draft preparation. Simone Mason: validation; formal analysis; investigation; data curation.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting the findings in this study are available within the article. Additional raw data that supports the findings in this study are available from the corresponding author upon reasonable request.

Supplementary information (SI) is available. See DOI: <https://doi.org/10.1039/d6ja00046k>.

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References

- 1 R. Pant, N. Mathpal, R. Chauhan, A. Singh and A. Gupta, in *Mercury Toxicity Mitigation: Sustainable Nexus Approach*, ed. N. Kumar, Springer Nature Switzerland, 1st edn, 2024, pp. 93–115.
- 2 W. F. Fitzgerald, D. R. Engstrom, R. P. Mason and E. A. Nater, *Environ. Sci. Technol.*, 1998, **32**, 1–7.
- 3 C. T. Driscoll, R. P. Mason, H. M. Chan, D. J. Jacob and N. Pirrone, *Environ. Sci. Technol.*, 2013, **47**, 4967–4983.
- 4 B. M. Geyman, D. G. Streets, C. I. Olson, C. P. Thackray, C. L. Olson, K. Schaefer, D. P. Krabbenhoft and E. M. Sunderland, *Environ. Sci. Technol.*, 2025, **59**, 8578–8590.
- 5 R. A. Lavoie, T. D. Jardine, M. M. Chumchal, K. A. Kidd and L. M. Campbell, *Environ. Sci. Technol.*, 2013, **47**, 13385–13394.
- 6 European Parliament and Council, *Directive 2008/105/EC of 16 December 2008 on Environmental Quality Standards in the Field of Water Policy*, 2008.
- 7 World Health Organization, *Mercury in Drinking-Water: Background Document for Development of WHO Guidelines for Drinking-Water Quality*, WHO, Geneva, Switzerland, 2005.
- 8 I. F. Dennis, T. A. Clair, C. T. Driscoll, N. Kamman, A. Chalmers, J. Shanley, S. A. Norton and S. Kahl, *Ecotoxicology*, 2005, **14**, 113–123.
- 9 P. S. Ramlal, F. W. B. Bugenyi, G. W. Kling, J. O. Nriagu, J. W. M. Rudd and L. M. Campbell, *J. Great Lake. Res.*, 2003, **29**, 283–291.
- 10 J. M. Neff, in *Bioaccumulation in Marine Organisms*, Elsevier, 2002, pp. 103–130.
- 11 U.S. Environmental Protection Agency, *Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*, Office of Water, U.S. EPA: Washington, DC, USA, August 2002.
- 12 E. Kenduzler, M. Ates, Z. Arslan, M. McHenry and P. B. Tchounwou, *Talanta*, 2012, **93**, 404–410.
- 13 W. Chen, P. Wee and I. D. Brindle, *J. Anal. At. Spectrom.*, 2000, **15**, 409–413.
- 14 J. Allibone, E. Fatemian and P. J. Walker, *J. Anal. At. Spectrom.*, 1999, **14**, 235–239.
- 15 C. S. Provete, B. M. Dalfior, R. Mantovaneli, M. T. W. D. Carneiro and G. P. Brandão, *ACS Omega*, 2024, **9**, 49229–49238.
- 16 D. C. Simião, F. P. de Andrade, W. G. Lima, M. L. de Jesus, P. H. G. Dorim and M. C. Paiva, *Water Supply*, 2022, **22**, 5535–5548.
- 17 A. Thongsaw, Y. Udnan, G. M. Ross and W. C. Chaiyasith, *Talanta*, 2019, **197**, 310–318.
- 18 D. SÁnchez, *Talanta*, 2000, **52**, 671–679.
- 19 S. Kulomäki, E. Lahtinen, S. Perämäki and A. Väisänen, *Talanta*, 2022, **240**, 123163.
- 20 A. Londonio, P. E. Hasuoka, P. Pacheco, R. A. Gil and P. Smichowski, *J. Anal. At. Spectrom.*, 2018, **33**, 1737–1744.
- 21 X. Jia, J. Zhao, H. Ren, J. Wang, Z. Hong and X. Zhang, *Talanta*, 2019, **196**, 592–599.

- 22 S. Yang, D. Zhang, H. Cheng, Y. Wang and J. Liu, *Anal. Chim. Acta*, 2019, **1074**, 54–61.
- 23 Y. Song, Q. Ma, H. Cheng, J. Liu and Y. Wang, *Anal. Chim. Acta*, 2021, **1157**, 338388.
- 24 A. Afkhami, T. Madrakian and H. Siampour, *Int. J. Environ. Anal. Chem.*, 2006, **86**, 1165–1173.
- 25 M. Sadeghi, Z. Nematifar, M. Irandoust, N. Fattahi, P. Hamzei, A. Barati, M. Ramezani and M. Shamsipur, *RSC Adv.*, 2015, **5**, 100511–100521.
- 26 L. R. Bravo-Sánchez, J. Ruiz Encinar, J. I. Fidalgo Martínez and A. Sanz-Medel, *Spectrochim. Acta, Part B*, 2004, **59**, 59–66.
- 27 D. Monticelli, A. Castelletti, D. Civati, S. Recchia and C. Dossi, *Int. J. Anal. Chem.*, 2019, **2019**, 1–5.
- 28 D. Spanu, L. Butti, G. Boldrocchi, R. Bettinetti and D. Monticelli, *Anal. Sci.*, 2020, **36**, 889–892.
- 29 J. L. Parker and N. S. Bloom, *Sci. Total Environ.*, 2005, **337**, 253–263.
- 30 H. Louie, C. Wong, Y. J. Huang and S. Fredrickson, *Anal. Methods*, 2012, **4**, 522–529.
- 31 C. R. Hammerschmidt, K. L. Bowman, M. D. Tabatchnick and C. H. Lamborg, *Limnol Oceanogr. Methods*, 2011, **9**, 426–431.
- 32 T. A. Olsen, T. H. Huang, R. Kaniserry and R. J. M. Hudson, in *Trace Materials in Air, Soil, and Water*, ed. K. R. Evans, E. S. Roberts-Kirchhoff, M. A. Benvenuto, K. C. Lanigan, A. Rihana-Abdallah, American Chemical Society, 2015, ch. 6, pp. 115–151.
- 33 Z.-X. Jin, H.-J. Lu, X.-W. Chen, Y.-H. Li, S.-C. Zhu, X.-L. Li, Z.-Q. Jia, Y. Guo, Y. Yang and L.-A. Hou, *Desalination*, 2025, **603**, 118696.
- 34 C. El Khoueiry, F. Giusti, E. Lelong, G. Arrachart, B. Nsouli, I. Karame and S. Pellet-Rostaing, *ChemistrySelect*, 2023, **8**(44), e202303015.
- 35 D. Spanu, L. Butti, S. Recchia, C. Dossi and D. Monticelli, *Talanta*, 2024, **270**, 125612.
- 36 D. Spanu, L. Butti, G. Boldrocchi, R. Bettinetti, S. Recchia and D. Monticelli, *Anal. Chim. Acta*, 2022, **1206**, 339553.
- 37 T. Wenzl, J. Haedrich, A. Schaechtele, P. Robouch and J. Stroka, *Guidance Document on the Estimation of LOD and LOQ for Measurements in the Field of Contaminants in Feed and Food*, 2016.
- 38 S. Kulomäki, S. Perämäki and A. Väisänen, *Talanta*, 2020, **218**, 121125.
- 39 R. Sánchez, J. Snell, A. Held and H. Emons, *Anal. Bioanal. Chem.*, 2015, **407**, 6569–6574.
- 40 E. M. Martinis, P. Bertón, R. A. Olsina, J. C. Altamirano and R. G. Wuilloud, *J. Hazard. Mater.*, 2009, **167**, 475–481.
- 41 C. Peng, M. He, B. Chen, L. Huang and B. Hu, *Analyst*, 2017, **142**, 4570–4579.