

Validation and measurement uncertainty of the determination of 24 elements in drinking water using ICP-MS

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ABSTRACT

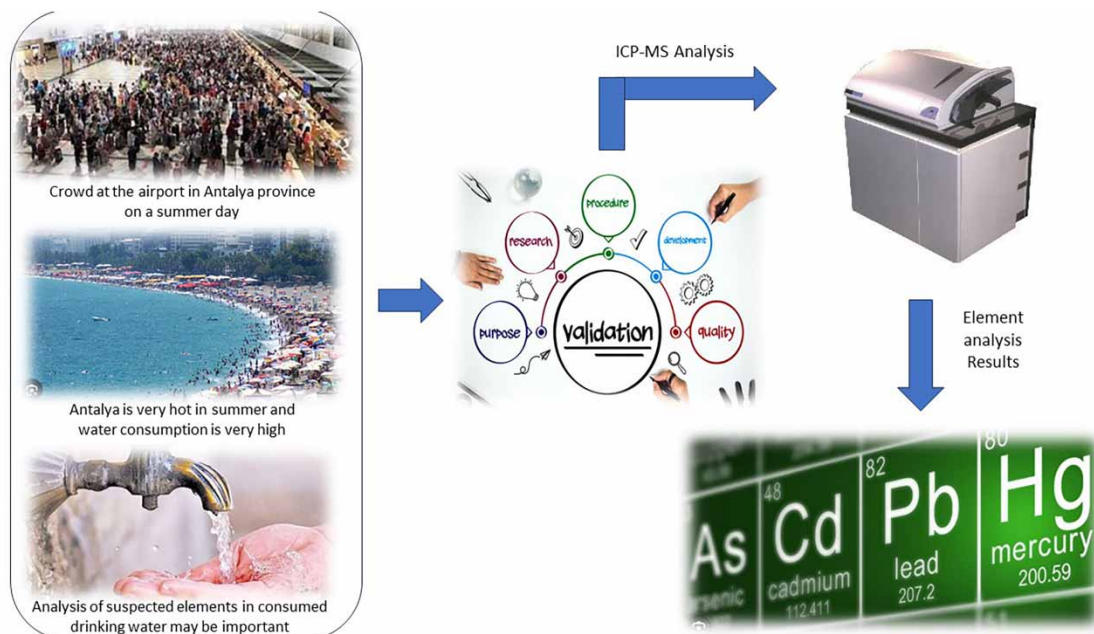
In this study, the concentrations of 24 elements, which are suspicious to be found in drinking and utility waters for the province of Antalya/Turkey, were determined using an inductively coupled plasma-mass spectrometer (ICP-MS). Validated methods with a low limit of detection are required to analyze such waters. The method was validated considering selectivity, limits of detection and quantification, sensitivity, linearity, operating range, accuracy, precision, and measurement uncertainty. All monitored isotope calibration plots had a correlation coefficient of 0.9994 or higher. According to the results of recovery, the expected results of all element isotopes were determined in the range of 94–104%. The average precision quantities for items were calculated as percent relative standard deviation (%RSD) between 0.10 and 2.31%. The analytical method provided here for detecting the concentrations of 24 elements in drinking water samples with demonstrated traceability and estimated uncertainty can yield reliable and internationally comparable results.

Key words: element analysis, ICP-MS method, method validation, quality monitoring

HIGHLIGHTS

- Water-soluble elements can be determined using ICP-MS.
- With the method validation study, reliable results can be obtained in elemental analysis results.

GRAPHICAL ABSTRACT



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INTRODUCTION

According to the World Health Organization (WHO), the term 'drinking water' refers to enough water for human consumption and home use. The safety of city drinking water has long been a contentious societal issue. It has been reported that approximately 2 billion people do not have access to safe drinking water (World Health Statistics 2023). One of the most important of these problems is the problem in drinking water supply. Drinking water quality degrades until it reaches the tap from the drinking water treatment plant (Liu *et al.* 2019), discoloration issues arise (Vreeburg & Boxall 2007; Han *et al.* 2018), heavy metals accumulate in excessive concentrations, and other water quality issues can have serious consequences for human health. Rainwater has been reported to have an impact on drinking and utility water in air mass transportation (Berberler *et al.* 2022). When all of these transports are considered, there are 35 hazardous elements, 23 of which are heavy metals, whose presence in drinking water is questionable. These metals are found in modest concentrations in natural diets and are helpful to human health. Heavy metal concentrations in the environment, on the other hand, can infiltrate the food chain and create harmful and severe effects on the human body if they surpass normal levels (Karaouzas *et al.* 2021). Heavy metals in drinking water are a significant issue for these reasons because they cannot be digested by the body and instead accumulate in adipose tissue, muscles, bones, and joints, producing health complications and diseases (Vatanpour *et al.* 2020). In another study, it has been reported that the accumulation of Pb and Cd in the human body can lead to cancer, kidney disorders, skeletal damage, brain damage, reproductive failure, and poisoning (Shariatifar *et al.* 2022).

Heavy metals deplete and replace other minerals necessary for an organism's health (Liu *et al.* 2020). Heavy metal contamination in drinking water can cause acute and chronic diseases (Zhang *et al.* 2022). The uncontrolled disposal of industrial, agricultural, and domestic waste has contaminated groundwater (Yadav *et al.* 2012). It has been reported that the increasing chemical pollution in surface, groundwater, and coastal sea waters around the world has become an important problem today, and in addition to affecting the health of aquatic animals, especially through the pollution of groundwater and surface water, it also affects human health and the quality of life (Balaram *et al.* 2023). There are many studies in the literature on drinking and utility water. Groundwater pollution has been reported to cause adverse effects on aquatic habitats and human health (Chakrabarty & Sarma 2011; Mahato *et al.* 2016). In another study, it was reported that the main sources of trace elements in plant and animal feeds include irrigation using wastewater, irrigation with groundwater, disposal of municipal and industrial wastes, mining, smelting processes, and atmospheric pollution (Karimi *et al.* 2023). They reported that rapid industrialization and urbanization resulted in trace metal accumulation in water and soil (Kumar *et al.* 2019). Important pollutants such as arsenic (As), chromium (Cr), iron (Fe), pesticides, and other industrial chemicals are causing groundwater pollution. A serious environmental concern is needed, as water pollution leads to the overuse of groundwater (often considered clean water), which is attributed to the declining water level (Kumar *et al.* 2019). As a result, it is everyone's responsibility to find a safe, clean, and consistent source of drinking water to maintain our quality of life. There could be two major sources of elements in fresh and drinkable water that are suspected of being polluted. One of them is due to natural degradation and the other is due to industrial activities, which has been the subject of great concern recently (Vutukuru 2005). Furthermore, the vast range of water pipelines, long transmission and distribution, diverse pipe materials, and water quality conditions generate undulating circumstances in the pipeline's inner wall. With water flow, Fe, Mn, Pb, Zn, and other metal contaminants from raw water, water treatment agents, and pipe materials enter residential use (Tian *et al.* 2021). Particles will pass through the drinking water pipe wall by some physical, chemical, and biological means, adsorption, deposition, and different ways. Decomposition of heavy metals is difficult and accumulation is easy (Zhang *et al.* 2022). It is important to detect heavy metals suspected to be present in drinking water with method validation and good laboratory practice, reliable methods (Ismail & Afify 2022). By following the procedures and recommendations outlined in the validation guide, accurate and reliable results can be obtained. These procedures and recommendations may be adjusted or modified based on the specific type of analytical method being investigated.

The process of identifying an analytical need and validating that the method under consideration is compatible with what the application demands is referred to as method validation (Kılıç *et al.* 2015). Selectivity, limit of detection (LOD) and limit of quantitation (LOQ), working range, analytical sensitivity, accuracy, precision, and measurement uncertainty are all performance parameters that are generally evaluated during method validation (Kargarghomsheh *et al.* 2023; Kılıç *et al.* 2015). However, for quantitative analysis, the uncertainty for

analytical measurements must be estimated by quality control principles and ISO/IEC 17025:2017 (Loizou *et al.* 2010). There are numerous analytical techniques available for detecting and quantifying elements in drinking water. However, inductively coupled plasma-mass spectrometry (ICP-MS) is regarded as a critical, dependable, and widely used analytical technique for this purpose (Komorowicz & Baralkiewicz 2016).

Heavy metals and metalloid arsenic (^{75}As) can be found in water and everywhere (Sahu & Saha 2020). Natural (stripping of ore deposits and bedrock) and anthropogenic (industrial and agricultural wastewater) sources of arsenic and heavy metal pollutants in water contamination have been reported in over 70 countries, threatening over 100 million people worldwide (Rasool *et al.* 2016). As and heavy metal contamination in drinking water increases the risk of chronic disease and cancer in humans (Ravenscroft *et al.* 2009; Khan *et al.* 2019). Therefore, elemental analysis, especially the determination of ^{75}As concentrations in drinking and utility water, should be based on reliable results. The combination of chlorine (^{35}Cl) in drinking water and argon gas (^{40}Ar) used to act like ^{75}As is the most likely interference. As a result of entering the mass detector with a molecular weight of ($^{40}\text{Ar} + ^{35}\text{Cl} \rightarrow ^{75}\text{As}$), it causes an increase in the amount of arsenic in the sample results and adverse effects in terms of reliability during concentration determinations. Some interferences are shown in Table 1 (Soriano *et al.* 2018). We discovered that the procedure we used on the samples reduced the amount of chlorine in the study we conducted with our team. Although there is no significant salt content in drinking and utility water, there may be some overloading with the high number of sample readings. These issues can have an impact on concentration. As a result, it is intended to minimize the chlorine contamination that may occur during the preliminary preparation technique used on the samples (Kilic *et al.* 2023).

Table 1 | Elements' isotopes and interferences in drinking water were studied (Leonhard *et al.* 2002; Soriano *et al.* 2018)

Isotope	Interferences
^{75}As	$^{40}\text{Ar}^{35}\text{Cl}$, $^{40}\text{Ca}^{35}\text{Cl}$
^{111}Cd	$^{79}\text{Br}^{32}\text{S}$
^{59}Co	$^{40}\text{Ar}^{23}\text{Na}$, $^{24}\text{Mg}^{35}\text{Cl}$, $^{40}\text{Ca}^{16}\text{OH}$, $^{23}\text{Na}^{35}\text{ClH}$
^{52}Cr	$^{40}\text{Ar}^{16}\text{O}$, $^{40}\text{Ar}^{12}\text{C}$, $^{35}\text{Cl}^{16}\text{OH}$, $^{37}\text{Cl}^{14}\text{NH}$
^{63}Cu	$^{40}\text{Ar}^{23}\text{Na}$, $^{40}\text{Ca}^{23}\text{Na}$
^{55}Mn	$^{23}\text{Na}^{16}\text{O}_2$, $^{39}\text{K}^{16}\text{O}$, $^{40}\text{Ar}^{14}\text{NH}$
^{60}Ni	$^{23}\text{Na}^{35}\text{Cl}$, $^{25}\text{Mg}^{35}\text{Cl}$
^{51}V	$^{35}\text{Cl}^{16}\text{O}$
^{66}Zn	$^{40}\text{Ar}^{26}\text{Mg}$

Salt deposits on the extraction or skimmer cones, or both, reduce the efficient cone hole diameter and thus ion conduction, potentially preventing the entire sample from reaching the detector (Brenner 2010). Elements such as Na, K, Li, Ca, and Mg disrupt the normal distribution of excited ion and atom species in multi-element analysis plasma. Interference effects also occur at the interface between the ICP and the sampling cone and skimmer cone of the mass spectrometer (Brenner 2010). Although salt ions are present at low concentrations in drinking and utility water, the ICP-MS device was kept under control with the QC and approved reference material standards throughout the operation, taking into account the contaminations it may cause (Ismail & Afify 2022). About 50 samples of drinking utility water were collected from various locations around Antalya/Konyaalti in the spring and summer of 2023. The amounts of water-soluble elements were measured using an ICP-MS. The study's main goal is to support them with method validation studies, and it aims to ascertain the concentrations of 24 elements with the isotopes of (^{75}As , ^{208}Pb , ^{111}Cd , ^{59}Co , ^{52}Cr , ^{51}V , ^{57}Fe , ^{63}Cu , ^{55}Mn , ^{60}Ni , ^{27}Al , ^{138}Ba , ^{24}Mg , ^{107}Ag , ^{205}Tl , ^9Be , ^{209}Bi , ^{133}Cs , ^7Li , ^{121}Sb , ^{88}Sr , ^{66}Zn , ^{11}B , and ^{202}Hg) suspected to be present in drinking and utility water utilized in Antalya/Konyaalti.

MATERIAL AND METHOD

Sample collection

In the spring and summer of 2023, drinking water samples were collected from about 50 different locations within the Antalya/Konyaalti sampling area. Using a polyethylene bottle that had been acid-washed, 500 mL of drink water was collected and brought to the lab for elemental analysis. Three replicates of each sample

were examined, and mean concentrations were determined. The ICP-MS device, a Perkin Elmer Elan DRC-e model, was utilized to acquire prompt and dependable results because the elements to be detected in drinking and utility water samples have concentrations that fall within the low-high dynamic range. The element concentrations in the samples were measured using the analysis method (EPA METHOD 6020 A; Kilic *et al.* 2023).

Reagents, standards, and apparatus

Perkin Elmer Inc. (Boston, USA) provided the ICP-MS (mix-3) multi-element calibration standard 3 solutions (10 mg L^{-1} , Perkin Elmer N9300233). Nitric acid (Suprapur grade, 65%), hydrochloric acid (Suprapur grade, 35%), and HF (40%) were supplied from Merck (Darmstadt, Germany). The solutions were diluted with ($18.2 \text{ M}\Omega \text{ cm}$ at 25°C) deionized water from a Millipore[®] ultra-pure water purification system (Bedford, USA). For the examination of the trueness, the matrix reference material (Certified Reference Material (CRM); Enviro MAT-Drinking Water-Low SCP SCIENCE, Quebec, Canada) was employed. A Thermomac TM 19-D (Biotech GmbH, Germany) hot plate was utilized to perform open acid digestion (Kilic *et al.* 2015).

Sample preparation method for elemental analysis

Around 100 mL of aliquot of 500 mL samples were taken and transferred to a 250 mL beaker. The acid digestion was applied to the whole drinking water sample without any pretreatment to obtain the total concentration (not only dissolved) of elements. The acid mixture of 4 mL of HNO_3 , 0.5 mL of HCl, and 0.5 mL of HF (HF was added to dissolve silicates in particles that may be present in water samples) was added to a 100 mL drink water matrix to dissolve all particulates and to remove Cl^- ions as gaseous HCl on the hot plate at 60°C under the hood. The sample evaporation was continued to 10–15 mL without boiling. The evaporation processes were repeated two times on the heater. After the evaporation process was completed, the volume was completed to 25 mL with deionized water. With this preliminary method, the elements found in low concentrations in the samples were easier to detect by concentrating them (Kilic *et al.* 2015).

Preparation of matrix for the calibration and validation

A matrix was created by combining three drinking water samples in order to validate the procedure. The necessary additions from the stock calibration standard and CRM solutions were made on the drink water matrix for the recovery, precision, and trueness studies. Following these preparations, the calibration standards were applied after the blank was examined, the matrix blank analysis, and the blank analysis. An analysis of recovery standards was done at the end. QC monitoring (5 and $25 \mu\text{g L}^{-1}$) was carried out, while the ICP-MS device was used to determine the sample concentrations (Kilic *et al.* 2015). Deviations in tune values in device performance were considered very important in terms of monitoring device performance (Berberler *et al.* 2022). The CRM was preferred as another QC solution and ran every 10 samples. According to the results obtained, it was used to detect problems such as poor performance, interference, and deterioration of calibration (Kilic *et al.* 2023). It has been emphasized that the use of CRM is very important in validating different analytical methods, analytical measurement procedures, and protocols (Balaram & Satyanarayanan 2022).

Calibration method

Calibration curves were obtained by adding standards to the matrix. For Hg calibration, calibration standards were prepared with final volumes of 0.2, 0.5, 1.5, 2.5, and $5 \mu\text{g L}^{-1}$ in 2% HNO_3 (v/v) and 1% HCl solutions using an intermediate stock standard ($1,000 \mu\text{g mL}^{-1}$). For this reason, low concentrations of calibration points were preferred for the determination of mercury element, which has a legal limit of $1 \mu\text{g L}^{-1}$ in drinking water. Calibration standards ($2, 5, 10, 25, 50, 100,$ and $200 \mu\text{g L}^{-1}$) were prepared for boron using 2% HNO_3 (v/v) by preparing intermediate stock solutions from a certified standard ($1,000 \mu\text{g mL}^{-1}$) solution (Ismail & Afify 2022). Calibration standards were prepared using 2% HNO_3 (v/v) and 1% HCl ($2, 5, 10, 25, 50, 100,$ and $200 \mu\text{g L}^{-1}$) from a certified $1,000 \mu\text{g mL}^{-1}$ antimony standard. Calibration standards ($2, 5, 10, 25, 50, 100,$ and $200 \mu\text{g L}^{-1}$) from a standard stock solution from a certified standard (mix-3 $10 \mu\text{g mL}^{-1}$) for As, Pb, Cd, Co, Cr, V, Fe, Cu, Mn, Ni, Al, Ba, Mg, Ag, Tl, Be, Bi, Cs, Li, Sr, and Zn. All samples, blanks, and standards were prepared in polypropylene bottles (Kilic *et al.* 2015). Three drinking and utility water samples were mixed to obtain a matrix to validate the method. Required additions from the stock calibration standard for recovery, precision, and accuracy studies and CRM solutions were made on the matrix (Yenisoy-Karakaş 2012). A two-step digestion procedure was performed, and the final volume was made up to 25 mL with deionized water. Table 2 lists the chemicals and devices used.

Table 2 | Chemicals and devices

Chemical name	Chemical Information	Brand/Model
Nitric acid	65% HNO ₃ (v/v), Suprapure [®] grade	Merck (Darmstadt, Germany)
Hydrofluoric acid	40% HF (v/v) Suprapure [®] grade	Merck (Darmstadt, Germany)
Hydrochloric acid	35% HCl (v/v) Suprapure [®] grade	Merck (Darmstadt, Germany)
Mix-3 element standard (10 µg mL ⁻¹)	As, Pb, Cd, Co, Cr, V, Fe, Cu, Mn, Ni, Al, Ba, Mg, Ag, Tl, Be, Bi, Cs, Li, Zn and Sr	Perkin Elmer, USA
Single element standard (10 µg mL ⁻¹)	(Hg), 5% HNO ₃	Perkin Elmer, USA
Single element standard (1,000 µg mL ⁻¹)	(B), H ₂ O	Perkin Elmer, USA
Single element standard (1,000 µg mL ⁻¹)	(Sb)	Perkin Elmer, USA
Multi-element internal standard (10 µg mL ⁻¹)	Bi, In, Li, Sc, Tb, Y	Perkin Elmer, USA
Argon flow	High Purity 99.999%	Habaş (İstanbul, Turkey)
Certified reference material (CRM)	Enviro MAT-drinking water-low (CRM)	(SCP SCIENCE, Quebec, Canada)
Device Name	Working area	Brand/Model
ICP-MS	Element analysis	Perkin Elmer Elan DRC-e
Microwave system	Sample digestion	Milestone ETHOS One Microwave Digestion
Oven	In the drying process	Nüve NC500 (Ankara, Turkey)
Ultra-pure water device	Solution preparation	Millipore Milli-Q (Bedford, MA, USA)
Precision balance	Sample weighing	Mettler Toledo

Inductively coupled plasma-mass spectroscopy analysis method

All measurements were done by using the Perkin Elmer ELAN DRC-e model ICP-MS instrument to determine the concentrations of elements (As, Pb, Cd, Co, Cr, V, Fe, Cu, Mn, Ni, Al, Ba, Mg, Ag, Tl, Be, Bi, Cs, Li, Sb, Sr, B, Zn, and Hg). Table 3 lists the instrument method parameters for ICP-MS. Before beginning analysis with the ICP-MS instrument, performance calibration tests were configured according to the instrument manufacturer's instructions. Running the particular tuning solution through the instrument confirmed its stability, the relative standard deviation of the absolute readings for all analytes is less than 5% (Environmental Protection Agency Method 2008). Calibration tests in the ICP-MS device software were renewed using their solutions (detector voltage, mass calibration, dual detector, lens voltage, auto lens, nebulizer gas flow, ICP RF Power, X-Y calibration, and daily performance) (Brenner 2010). The tune parameter values applied were determined in the desired ranges and concluded successfully. The data obtained are shown in Table 4.

RESULTS AND DISCUSSION

Method validation

The performance of the applied method was assessed in terms of linearity, LOD and LOQ, recovery, accuracy, and precision. The CRM includes 20 elements (As, Pb, Cd, Co, Cr, V, Fe, Cu, Mn, Ni, Al, Ba, Mg, Tl, Be, Li, Sb, Sr, Zn, and B). Because CRM lacks Ag, Bi, and Cs, the calibration standard containing Ag, Bi, and Cs was preferred for recovery and precision calculations at three levels of support (Balaram *et al.* 2023). Spiking was performed on the sample matrix at three fortification levels, representing the early (2 µg L⁻¹), middle (25 µg L⁻¹), and last (50 µg L⁻¹) parts of the linear range of the calculations plot. Recovery values, mean recovery, and percent relative standard deviation (%RSD) results were calculated from the data obtained (Yenisoy-Karakaş 2012). The data obtained are shown in Table 5. Since the concentration of mercury in drinking and utility waters is monitored at low concentrations within the legal limits, recovery studies were prepared using a certified standard substance on the matrix, with final volumes of 0.5 and 2 µg L⁻¹. The standard addition method on the matrix was made to

Table 3 | ICP-MS operation method parameters

Instrument	Elan DRC-e (PerkinElmer SCIEX, Norwalk, CT, USA)
Spectrometer	Elan DRC-e
Sample introduction	Scott Spray Chamber
RF power (W)	1,000
Skimmer cone	Nickel
Sample cone	Nickel
Gaz flow rate (L min ⁻¹)	Nebulizer gas flow: 0.90, auxiliary gas flow:1.21, plasma gas flow:18
Nebulizer	Meinhard TQ plus Quartz 0.5 mL
Scanning mode	Peak hopping
Analytical masses (amu)	Standard mode (⁷⁵ As, ²⁰⁸ Pb, ¹¹¹ Cd, ⁵⁹ Co, ⁵² Cr, ⁵¹ V, ⁵⁷ Fe, ⁶³ Cu, ⁵⁵ Mn, ⁶⁰ Ni, ²⁷ Al, ¹³⁸ Ba, ²⁴ Mg, ¹⁰⁷ Ag, ²⁰⁵ Tl, ⁹ Be, ²⁰⁹ Bi, ¹³³ Cs, ⁷ Li, ¹²¹ Sb, ⁸⁸ Sr, ⁶⁶ Zn, ¹¹ B, and ²⁰² Hg)
Number of weeps/ readings	20
Number of readings/ replicates	3
Number of replicates	3
Autosampler	CETAX ASX-520
Dwell time per amu (ms)	50
Sample flush	Time (50), speed (+/- rpm)-48
Read delay	Time (15), speed (+/- rpm)-20

Table 4 | ICP-MS performance test results

Analyte	¹² C	²⁴ Mg	⁷⁸ Ar ₂	¹¹⁵ In	¹⁴⁰ Ce	²⁰⁸ Pb	²³⁸ U
Mass (amu)	12.00	23.985	75.93	114.904	139.905	207.997	238.050
Measured (amu)	12.025	24.025	75.975	114.875	139.925	207.975	238.025
Oxides and doubly charged ions	Parameter	Specification	Result				
	CeO/Ce	<3%	2%				
	Ba ⁺⁺ / Ba	<3%	2.4%				
Sensitivity and background							
Element		Specification	Result				
²⁴ Mg		>50.000 cps/10 ppb	64,512				
¹¹⁵ In		>250.000 cps/10 ppb	298,518				
²³⁸ U		>200.000 cps/10 ppb	400,345				
Detection limits/element		Specification	Result				
⁹ Be		<9.0 ppt	3.83				
⁵⁹ Co		<1.0 ppt	1.13				
¹¹⁵ In		<0.5 ppt	0.49				
²³⁸ U		<0.5 ppt	0.54				
Mean count rate – mass 220 (std. mode)		≤2 cps	0.83				

obtain the calibration curves (Kılıç *et al.* 2015). All monitored isotope calibration plots had a correlation coefficient of 0.9994 or higher. The obtained data are shown in Supplementary Table S1.

Interferences can cause negative or positive errors in the analyses, so it must be identified and corrected. The phrase 'lowest concentration at which method performance has been tested and data quality is acceptable for its

Table 5 | Data on recovery and repeatability at three fortification levels are compared

Elements	Recovery values spiking of 2 µg L ⁻¹ (N = 10)			Recovery values spiking of 25 µg L ⁻¹ (N = 10)			Recovery values spiking of 50 µg L ⁻¹ (N = 10)		
	Mean recovery	RSD %		Mean recovery	RSD %		Mean recovery	RSD %	
As	1.99	99.7	1.14	25.3	101	1.36	50.8	102	0.27
Pb	2.06	103	2.12	25.2	101	2.49	50.5	101	1.56
Cd	1.95	97.0	1.08	23.6	94.6	0.88	48.8	97.5	1.21
Co	2.01	100	2.17	25.2	101	3.36	50.8	102	1.34
Cr	1.99	99.0	2.40	25.2	101	0.55	50.8	102	0.21
V	2.05	102	2.10	24.1	96.3	1.29	49.4	99.0	1.41
Fe	-	-	-	23.5	94.1	2.16	49.8	99.6	2.31
Cu	2.09	105	1.90	25.6	103	2.36	50.3	101	0.10
Mn	2.00	100	1.35	24.6	98.6	0.20	48.3	99.7	0.51
Ni	1.95	97.7	2.86	24.9	99.5	0.48	50.0	99.9	2.00
Al	-	-	-	25.6	102	0.98	50.5	101	0.13
Ba	1.95	97.3	2.17	24.1	96.4	1.94	50.9	102	0.35
Mg	-	-	-	24.5	98.2	1.43	49.3	98.6	0.80
Ag	1.98	99.0	1.86	25.2	101	2.10	50.3	101	2.10
Tl	2.06	103	2.40	24.8	99.3	0.54	49.3	98.6	0.67
Be	1.98	99.2	1.97	26.1	104	2.05	51.4	103	1.22
Bi	2.02	101	0.83	24.8	99.1	0.54	50.2	100	1.09
Cs	2.05	103	2.41	24.3	97.1	0.48	50.9	102	1.07
Li	1.97	98.3	1.44	25.8	103	1.22	49.5	98.9	0.34
Sb	2.04	102	3.88	25.5	102	1.67	50.2	100	1.42
Sr	2.08	104	2.99	25.7	103	1.75	49.1	982	0.43
Zn	1.96	98.0	1.43	25.1	100	1.77	50.4	101	0.64
B	1.98	99.2	1.62	25.2	101	0.62	51.0	102	1.01
Hg*	0.49	97.6	3.02	2.01	100	1.44			

Note: Hg* matrix was spiked (0.5 -1 and 2 µg L⁻¹).

intended use' means 'lowest concentration at which method performance has been tested and data quality is acceptable for its intended use.' The slope of the calibration curve and the standard deviation of instrument response were then used to calculate LOD and LOQ for each run using the equations below (Szymczycha-Madeja *et al.* 2014; Kılıç *et al.* 2015; Ismail & Afify 2022; Kargarghomshah *et al.* 2023). The results of the LOD and LOQ calculations are shown in Supplementary Table S1. All elements investigated had detection limits ranging from 0.04 to 1.53 µg L⁻¹.

$$\text{LOD} = (3 \times \sigma)/S \text{ and } \text{LOQ} = (10 \times \sigma)/S$$

LOD is the limit of detection, LOQ is the limit of quantitation (both measured in µg L⁻¹), σ is the standard deviation of 10 blank solutions (or the lowest level standard), and S is the slope (µg L⁻¹).

When calculating the recovery values, the reagent blanks were subtracted from the sample values. The obtained values are shown in Supplementary Table S2. The calculated percent relative error values vary between 0.04 and 1.94%. The method's specificity/selectivity, precision, and recoveries of the standards within the described calibration range are all determined in Table 5. It shows the mean recovery and precision (%RSD) data. Studies on recovery that used CRM had acceptable ranges (98.8 and 101%) in Supplementary Table S2. Spiking was performed as low (2 µg L⁻¹), medium (25 µg L⁻¹), and the end of the linear range (50 µg L⁻¹). As a result, the method's specificity/selectivity was deemed acceptable for all elements between 98.8 and 101% (Millour *et al.* 2011). The average %RSD values obtained with a three-level spike for elements ranged between 0.13 and 2.31.

Linearity, LOD, LOQ, and recovery

The (matrix) spike approach was used for recovery experiments using CRM. The analytical methods used in this investigation were created following the recommendations of Eurachem. Supplementary Table S1 summarizes the linearity and LOD–LOQ values. Studies using the spike method in drinking water were conducted for elemental analysis to represent low, medium, and high concentrations. Compared with previously published data, the LOD and LOQ values of the analytical method are close (Alrimawi *et al.* 2008; Kiliç 2019; Ismail & Afify 2022).

Uncertainty estimation

In this investigation, we employed the same formulas that we had previously used successfully for uncertainty studies (Kiliç *et al.* 2015). Using Equation (1), the element concentrations in the samples were calculated as $\mu\text{g L}^{-1}$. The concentrations of the samples, which began with 100 mL of drinking water sample and whose final volume was completed to 25 mL after the device reading, were calculated as follows.

$$C = (CA \times V_{\text{diluted}}) / V_{\text{original}} \quad (1)$$

C is the concentration of element in a water sample ($\mu\text{g L}^{-1}$); CA is the element concentration in the sample obtained from the calibration ($\mu\text{g L}^{-1}$); V_{diluted} is the final diluted volume after digestion (0.025 L); and V_{original} is the filtered sample volume (0.1 L).

The device reading of the element arsenic, whose actual amount is $2.5 \mu\text{g L}^{-1}$ in the samples, was measured as $10 \mu\text{g L}^{-1}$ with this method (Berberler *et al.* 2022) due to preconcentration step in the digestion. It can be said that the main parameters affecting the element concentration results are the concentrations obtained from the calibration curve, dilution factor, recovery, and reproducibility. As a result, element concentrations in water samples are calculated using the following parameters. Supplementary Tables S3 and S4 show arsenic results as an example of data derived from the computations (Kiliç *et al.* 2015). The main parameters affecting element concentration are concentrations obtained from the calibration curve, dilution factor, recovery, and reproducibility. Consequently, the combined uncertainty of the elemental concentrations in water samples are calculated using Equation (2) (Yenisoy-Karakaş 2012; Kiliç *et al.* 2015).

$$u_{\text{rel}}(C) = \sqrt{u_{\text{rel}}^2(CA) + u_{\text{rel}}^2(\text{rep}) + u_{\text{rel}}^2(\text{DF}) + u_{\text{rel}}^2(R)} \quad (2)$$

The uncertainties arising from the calibration curve and the standard stock solution were calculated using Equation (3), separately. The elemental concentrations given in the manufacturer's certificate, u_{element} , and the volumetric flasks and pipettes used for dilution, u_v , contribute to the uncertainty in the preparation of stock solutions (1 mg L^{-1}). The uncertainties of calibration standards are certified as 10 mg L^{-1} , with $\pm 0.5\%$ for each element (Yenisoy-Karakaş 2012; Kiliç *et al.* 2015).

$$U_{\text{std}} = \sqrt{(u_v/V)^2 + (u_{\text{element}}/C_{\text{element}})^2} \times C_{\text{std}} \quad (3)$$

U_{std} is the intermediate stock solution standard uncertainty (1 mg L^{-1}); C_{std} is the intermediate stock solution concentration (1 mg L^{-1}); V is the remaining stock solution volume (10 mL); u_v is the 10 mL volumetric flask standard uncertainty; C_{element} is the concentration of element in Mix-3 stock solution (10 mg L^{-1}); and U_{element} is the standard uncertainty of its concentration in 10 mg L^{-1} stock solution

Using Equation (4) from the Eurachem/Citac guide (2000), the calibration curve's uncertainty is computed. (Ellison *et al.* 2012).

$$U(C_o) = \frac{S}{B_1} \sqrt{\frac{1}{p} + \frac{1}{n} + \frac{(c_o - \bar{c})^2}{S_{xx}}} \quad S_{xx} = \sum_{i=1}^n (c_i - \bar{c})^2 \quad (4)$$

S stands for the residual standard deviation; B_1 represents the slope; p is the number of measurements to be determined; n is the number of calibration measurements; C_o is the determined analyte concentration in

water; \bar{c} is the mean value of the several calibration standards (n measurements); i is the number of measurements required to obtain the calibration curve; and c_i is the calibration equation's specific calibration standard value.

In this case ($p = 3$ and $n = 21$), a seven-point calibration standard was prepared, and each calibration point was read on the ICP-MS device to obtain three replicate measurement results. The calibration curve's standard preparation is a major source of uncertainty. In total, 1 mg L^{-1} was diluted to 10 mL from a 10 mg L^{-1} standard solution to make 100 mL of an intermediate stock solution, and a 1 mg L^{-1} intermediate stock mix standard was prepared. The uncertainty of the calibration standard in the certificate (10 mg L^{-1}) is given as 0.5% for each element. Using these data, the standard uncertainty was calculated as $0.005/2$ ($k = 2$). Mercury, antimony, and boron standards were prepared with the help of a single certified stock standard. The volumetric calibration standard uncertainty for the 5 mL automatic pipette used was calculated considering the coefficient of variation (CV) value of 0.14 reported by the manufacturer (i.e. $u_{\text{pipcal}} = (0.14/100) * 2 = 0.028 \text{ mL}$). The uncertainty for the 10 mL capacity volumetric flask was $\pm 0.025 \text{ mL}$. The standard uncertainty of the flask was calculated $u(\text{flask}) = 0.025/\sqrt{3}$ considering the rectangular distribution. For the calculation of u , Equations (5)–(7) were used (int.stock) (Yenisoy-Karakaş 2012; Kılıç *et al.* 2015).

$$\frac{u(\text{int.stock})}{C_{\text{int.stock}}} \sqrt{\left(\frac{u(\text{flask})}{V_{\text{flask}}}\right)^2 + \left(\frac{u(\text{pipette})}{V_{\text{pipette}}}\right)^2 + \left(\frac{u(\text{stock})}{C_{\text{stock}}}\right)^2} \quad (5)$$

$$u(\text{pipette}) = \sqrt{(u(\text{pipcal}))^2 + (u(\text{temp}))^2} \quad (6)$$

The standard uncertainty from temperature change was estimated using the rectangular distribution and is shown in Equation (7) (Kılıç *et al.* 2015).

$$u(\text{temp}) = 3 \times V \times Q/1.73 \quad (7)$$

where $u(\text{temp})$ is the standard uncertainty of the temperature effect; V is the measured volume (e.g. 1 mL for pipette); and Q is the coefficient of volume expansion of the water ($Q_{\text{water}} = 0.000124 \text{ }^\circ\text{C}^{-1}$).

The standard uncertainty from the volumetric flask ($u(\text{flask})$) was calculated using formulas 6 and 7.

Acid purity, digesting procedure losses, glassware and pipette calibration precision, instrument stability, and other factors contribute to repeatability uncertainty. The complete method was applied to 30 subsamples that were prepared and analyzed on the same day at three fortification levels. The repeatability standard uncertainty determined by averaging the RSD values of all three levels. The standard uncertainty was determined by dividing the mean RSD of these samples by the sample's square root, $n = 50$, (RSD/\sqrt{n}) (Kılıç *et al.* 2015). The errors coming from temperature change and the calibration of volumetric flasks determine the dilution's uncertainty. Using Equation (7), where u_{temp} represents the standard uncertainty of the temperature effect, V is the measured volume (e.g. 2 mL), and Q is the coefficient of volume expansion of the water ($Q_{\text{water}} = 0.000124 \text{ }^\circ\text{C}^{-1}$). The volumetric calibration standard uncertainty, u_{pipcal} , for a 5 mL automatic pipette is computed based on the manufacturer's reported CV value of 0.14 (i.e. $u_{\text{pipcal}} = (0.14/100) \times 2 = 0.028 \text{ mL}$). In Equation (6), these numbers are added together to calculate the uncertainty associated with ingesting 100 mL of water. Using the same procedures, the standard uncertainty of a 25 mL capacity volumetric flask was computed. The uncertainty stated in the certificate of the volumetric flask with a capacity of 25 mL was $\pm 0.040 \text{ mL}$ (Kılıç *et al.* 2015). The standard uncertainty of repeatability is not provided here since the repeatability for all conceivable sources is collected separately under the repeatability term.

Recovery

Method recovery (R_m) can be calculated for a given sample as $C_{\text{observed}}/C_{\text{spike}}$. R_m is an estimate of the method's overall recovery, including digestion and analysis. R_m is measured (ideally) with a matrix-approved reference sample. As a matrix-compatible CRM, we used samples with Enviro MAT-Drinking Water added to the matrix in this study (Froes *et al.* 2009). Because of the variability of the reference value used and the specific measure of recovery in that material, this value is subject to uncertainty. R_m 's standard uncertainty was calculated using

Equation (8) (Millour *et al.* 2011; Kılıç *et al.* 2015).

$$u(\bar{R}_m) = \bar{R}_m \sqrt{\frac{s_{\text{obs}}^2}{n \times \bar{C}_{\text{obs}}^2} + \frac{u(C_{\text{spike}})^2}{C_{\text{spike}}^2}} \quad (8)$$

\bar{R}_m represents spiked samples, the average recovery value obtained ($C_{\text{obs.}}/C_{\text{spike}}$); n is the number of spiked samples ($n = 14$); C_{obs} is the spiked samples' average concentration value; S_{obs} is the standard deviation of spiked sample concentration; C_{spike} is the theoretical value of the spiked concentration; and $u(C_{\text{spike}})$ is the standard uncertainty of spiked concentration ($s_{\text{obs}}^2/\bar{C}_{\text{obs}})/\sqrt{n}$.

This calculation was used for As, Pb, Cd, Co, Cr, V, Fe, Cu, Mn, Ni, Al, Ba, Mg, Tl, Be, Li, Sb, Sr, B, Zn, and Hg. For the elements Ag, Bi, and Cs, the recovery values obtained from the reference material spiking experiments were used. Enviro MAT-Drinking Water-Low lacks a certified concentration of Ag, Bi, or Cs. A significance test was used to determine whether the R -value was significantly different from 1.0. If the resulting R -value differs from one by a statistically significant amount, the recovery correction factor should almost certainly be included in the model equation. The test statistic t was calculated using Equation (9) to perform the significance test (Millour *et al.* 2011; Kılıç *et al.* 2015; Ismail & Afify 2022).

$$t = \frac{|1 - R|}{u(R)} \quad (9)$$

At a 95% confidence level, the value from this equation was compared to two-tailed critical values. According to the test, the R_m value for Bi and Cs was statistically significantly different from 1. The R_m values were taken as 1 for As, Pb, Cd, Co, Cr, V, Fe, Cu, Mn, Ni, Al, Ba, Mg, Ag, Tl, Be, Li, Sb, Sr, Zn, B, and Hg. It is convenient to include the recovery correction factor for Cs in the model equation. However, the difference is not considered to be of practical significance in the routine application of the method, and no correction to the final result is applied to account for the uncorrected bias, the uncertainty associated with method recovery must be increased using Equation (10). The coverage factor, k , was used in the expanded uncertainty calculation (Millour *et al.* 2011; Kılıç *et al.* 2015).

$$u(\bar{R}) = \sqrt{\left(\frac{1 - \bar{R}}{k}\right)^2 + u(\bar{R})^2} \quad (10)$$

Supplementary Table S5 shows the calculation of relative uncertainty for the element arsenic as an example. Pb, Cd, Co, Cr, V, Fe, Cu, Mn, Ni, Al, Ba, Mg, Ag, Tl, Be, Bi, Cs, Li, Sb, Sr, Zn, B, and Hg had the relatively expanded uncertainties (%) of 18, 19, 4, 15, 15, 32, 11, 13, 20, 29, 16, 25, 15, 14, 15, 17, 17, 23, 13, 21, 21, 9, and 7, respectively. The contribution of each source to the relative combined uncertainties is presented in Supplementary Table S6. Figure 1 depicts the contribution of each source to the relative combined uncertainty. Without a doubt, the calibration curve and recovery were the most essential components. The uncertainties generated by samples' initial and final volumes and stock solution preparation, which contribute to calibration curve concentration (CA) and repeatability, did not affect the combined relative uncertainties seriously (Yenisoy-Karakaş 2012; Kılıç *et al.* 2015).

Drinking utility water sample analysis

Prolonged transport of water between water and pipes during transport from production facilities to consumers can often cause some elements to accumulate in corrosion scales (Peng *et al.* 2012). These deposited metals can be re-released into the water from sediments as a result of changes in water quality, stagnation time, and other factors (Sun *et al.* 2017). It even causes water discoloration. Although the use of metal pipes has decreased, they are largely used as indoor water supply pipes in old buildings, especially in many areas (e.g. Poland: 53%; USA: 56.6%) (Veschetti *et al.* 2010). In addition, due to the high costs of replacing the existing infrastructure, this situation is not expected to be replaced with new pipe structures for a long time (Li *et al.* 2016). As a result, existing galvanized steel pipes with extensive deposits of deposits may potentially release significant amounts of accumulated Fe, Mn, Zn, Pb, and other metal elements. According to various reports, high metal

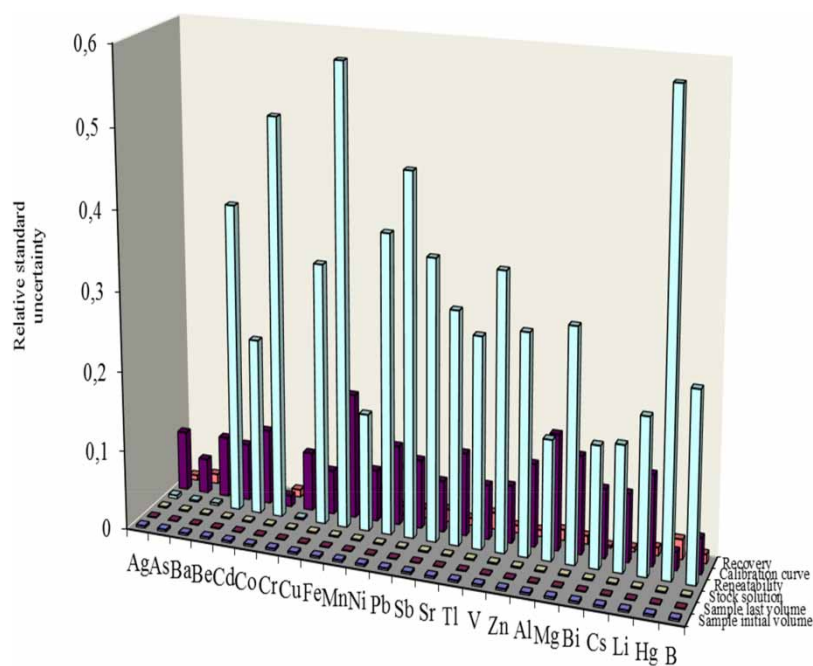


Figure 1 | Each factor's contribution to the total uncertainty for a drinking utility water sample.

element contents in drinking water can affect turbidity and harm the human body. Large amounts of Fe and Mn elements, for example, will cause noticeable changes in turbidity, causing consumers to complain about water quality (Husband *et al.* 2008). In this sense, the method applied for the preliminary study to determine the concentrations of the elements suspected to be present in drinking utility water has been successful. Acceptance criteria for the recovery percentage should be between 80 and 120%. However, because permissible recovery is determined by concentration and analysis purpose, less rigorous recovery limits can be applied during recovery trials. For example, an acceptable recovery limit is recommended between 60 and 120% for concentrations ≥ 1 and $< 10 \mu\text{g kg}^{-1}$, and 80–110% for concentrations $\geq 100 \mu\text{g kg}^{-1}$. In this context, the preliminary preparation process, which is acidified twice on the magnetic heater and exposed to evaporation, can prevent the problem of undesired contamination to be seen in the samples because of the chlorination process applied to the drinking water by the local authorities. For this reason, the above-mentioned method was applied in the sample studies, since it was found to be particularly successful in contaminations affecting the arsenic concentration. After the evaporation process of the samples in the magnetic heater was completed, the final volume was completed with distilled water to be 25 mL. $\text{pH} < 2$ was verified before processing.

With this method, it is shown in Table 6 that the effects of undesirable contamination in the samples are reduced. Successful results have been obtained with this preliminary preparation method. It has been observed that it is more successful for elements that are difficult to detect due to their low concentration value. The concentration value of an element with a concentration value of $0.5 \mu\text{g L}^{-1}$ in the sample was increased fourfold, making its detection easier. All samples were repeated three times and mean values were calculated. ^{59}Co , ^{51}V , ^{55}Mn , ^{60}Ni , ^{107}Ag , ^{205}Tl , ^9Be , ^{209}Bi , ^{133}Cs , ^7Li , ^{111}B , ^{121}Sb , and ^{202}Hg elements could not be detected in the samples ($< \text{LOD}$).

CONCLUSIONS

A quick, easy, and concurrent analytical technique has been developed and validated for the quantitative determination of 24 elements in drinking water in terms of selectivity, sensitivity, LOD and LOQ, linearity, working range, trueness, precision, and measurement uncertainty. The removal of chlorine from the samples was realized by adding acid solutions on the hot plate at 60°C . Such a preliminary study was performed to minimize salt deposition in matrix-derived interface cones and to reduce or eliminate interference with the matrix. For recovery, precision, and accuracy studies, necessary additions from stock mix-3 calibration standard and CRM solutions were made on the drinking water matrix by the spiking method. The concentrations of 24 elements in drinking

Table 6 | Composition of samples obtained by ICP-MS ($\mu\text{g L}^{-1} \pm \text{U}$, $k=2$) ($N=3$)

Samples	As	Ba	Cd	Cr	Cu	Fe	Pb	Sr	Zn	Al	Mg
1	5.08 ± 0.91	<LOD	2.18 ± 0.03	3.53 ± 0.01	1.69 ± 0.02	77.75 ± 0.21	0.65 ± 0.01	3.06 ± 0.01	6.13 ± 0.01	3.86 ± 0.03	15.31 ± 0.21
2	2.77 ± 0.15	0.40 ± 0.04	1.49 ± 0.04	3.76 ± 0.02	1.80 ± 0.01	86.38 ± 0.89	0.92 ± 0.01	3.61 ± 0.05	6.09 ± 0.03	4.45 ± 0.01	21.83 ± 0.02
3	2.98 ± 0.08	1.19 ± 0.01	1.55 ± 0.06	4.30 ± 0.05	2.78 ± 0.01	79.15 ± 0.28	1.47 ± 0.01	4.41 ± 0.03	7.38 ± 0.07	5.82 ± 0.02	22.51 ± 0.06
4	1.56 ± 0.13	<LOD	1.77 ± 0.01	3.91 ± 0.02	2.40 ± 0.01	55.45 ± 0.63	1.00 ± 0.02	5.64 ± 0.02	3.15 ± 0.19	4.96 ± 0.02	27.42 ± 0.07
5	2.15 ± 0.11	<LOD	1.33 ± 0.01	3.63 ± 0.01	2.51 ± 0.01	51.02 ± 0.33	0.60 ± 0.02	8.62 ± 0.04	0.23 ± 0.08	4.09 ± 0.17	28.71 ± 0.49
6	0.81 ± 0.13	<LOD	1.37 ± 0.01	3.76 ± 0.01	<LOD	32.89 ± 0.88	0.23 ± 0.01	8.90 ± 0.06	<LOD	4.46 ± 0.01	30.71 ± 0.44
7	0.20 ± 0.09	<LOD	1.61 ± 0.01	3.39 ± 0.02	0.24 ± 0.01	24.20 ± 0.80	0.25 ± 0.01	<LOD	<LOD	<LOD	35.49 ± 0.53
8	<LOD	<LOD	1.06 ± 0.01	4.07 ± 0.01	0.42 ± 0.01	28.63 ± 0.68	0.56 ± 0.01	<LOD	<LOD	4.27 ± 0.02	28.99 ± 0.26
9	<LOD	<LOD	<LOD	6.77 ± 0.08	1.17 ± 0.03	41.85 ± 0.73	0.57 ± 0.01	<LOD	<LOD	<LOD	<LOD
10	<LOD	<LOD	<LOD	6.50 ± 0.03	2.01 ± 0.16	55.97 ± 1.53	<LOD	3.07 ± 0.04	<LOD	<LOD	<LOD
11	<LOD	<LOD	<LOD	<LOD	1.74 ± 0.01	69.95 ± 0.66	<LOD	2.67 ± 0.03	<LOD	<LOD	15.03 ± 0.33
12	<LOD	<LOD	0.63 ± 0.01	<LOD	<LOD	68.05 ± 1.11	<LOD	<LOD	<LOD	<LOD	12.37 ± 0.28
13	<LOD	<LOD	<LOD	3.89 ± 0.02	<LOD	36.15 ± 0.37	<LOD	1.79 ± 0.02	<LOD	<LOD	<LOD
14	0.39 ± 0.05	<LOD	<LOD	<LOD	2.07 ± 0.02	54.65 ± 0.08	<LOD	<LOD	<LOD	7.71 ± 0.03	11.97 ± 0.24
15	2.65 ± 0.08	<LOD	<LOD	<LOD	<LOD	72.84 ± 0.62	<LOD	<LOD	<LOD	<LOD	<LOD
16	5.76 ± 0.51	<LOD	<LOD	<LOD	<LOD	80.54 ± 0.39	<LOD	<LOD	<LOD	<LOD	10.97 ± 0.17
17	7.39 ± 0.32	<LOD	1.75 ± 0.03	3.06 ± 0.03	1.47 ± 0.01	11.33 ± 0.26	0.50 ± 0.02	<LOD	<LOD	10.61 ± 0.05	9.61 ± 0.11
18	<LOD	<LOD	<LOD	<LOD	<LOD	50.05 ± 0.87	0.56 ± 0.01	<LOD	2.71 ± 0.03	8.91 ± 0.02	<LOD
19	<LOD	<LOD	<LOD	<LOD	<LOD	67.71 ± 0.16	0.67 ± 0.02	<LOD	<LOD	7.61 ± 0.02	13.59 ± 0.03
20	<LOD	<LOD	<LOD	<LOD	<LOD	51.00 ± 0.41	<LOD	<LOD	<LOD	6.45 ± 0.03	1.83 ± 0.01
21	3.37 ± 0.24	0.61 ± 0.01	<LOD	3.82 ± 0.22	2.14 ± 0.02	14.02 ± 0.47	0.92 ± 0.01	1.07 ± 0.01	3.79 ± 0.02	7.03 ± 0.03	3.35 ± 0.02
22	2.99 ± 0.73	1.09 ± 0.03	0.81 ± 0.02	<LOD	3.16 ± 0.06	44.60 ± 1.12	<LOD	<LOD	6.19 ± 0.02	9.07 ± 0.02	3.04 ± 0.03
23	3.76 ± 0.09	0.99 ± 0.01	1.51 ± 0.10	4.46 ± 0.01	2.95 ± 0.01	38.36 ± 0.19	1.27 ± 0.01	<LOD	8.30 ± 0.13	<LOD	4.06 ± 0.04
24	4.80 ± 0.26	1.31 ± 0.01	<LOD	2.37 ± 0.01	3.64 ± 0.01	59.00 ± 0.33	1.83 ± 0.01	<LOD	13.49 ± 0.17	4.90 ± 0.02	3.84 ± 0.05
25	3.91 ± 0.12	1.24 ± 0.01	1.78 ± 0.02	4.83 ± 0.01	3.49 ± 0.01	54.40 ± 0.15	<LOD	<LOD	17.38 ± 0.15	4.50 ± 0.01	<LOD
26	<LOD	<LOD	<LOD	<LOD	<LOD	63.05 ± 0.51	<LOD	<LOD	<LOD	<LOD	13.34 ± 0.17
27	<LOD	<LOD	1.54 ± 0.04	1.35 ± 0.01	<LOD	69.47 ± 0.11	0.63 ± 0.01	<LOD	<LOD	8.94 ± 0.02	<LOD
28	<LOD	<LOD	<LOD	<LOD	<LOD	33.51 ± 0.36	<LOD	<LOD	4.63 ± 0.02	9.49 ± 0.02	12.31 ± 0.11
29	<LOD	<LOD	<LOD	<LOD	<LOD	10.55 ± 0.50	<LOD	<LOD	2.80 ± 0.03	6.33 ± 0.03	14.27 ± 0.10

(Continued.)

Table 6 | Continued

Samples	As	Ba	Cd	Cr	Cu	Fe	Pb	Sr	Zn	Al	Mg
30	<LOD	<LOD	<LOD	<LOD	<LOD	10.41 ± 0.11	<LOD	<LOD	3.10 ± 0.02	10.49 ± 0.04	12.98 ± 0.08
31	4.17 ± 0.08	<LOD	1.11 ± 0.01	0.86 ± 0.02	3.56 ± 0.09	26.14 ± 0.18	0.96 ± 0.02	<LOD	14.25 ± 0.04	11.17 ± 0.04	12.90 ± 0.09
32	2.86 ± 0.10	<LOD	<LOD	<LOD	<LOD	33.12 ± 0.34	<LOD	<LOD	8.76 ± 0.04	4.75 ± 0.02	11.08 ± 0.07
33	1.37 ± 0.09	<LOD	0.93 ± 0.01	2.22 ± 0.02	5.15 ± 0.08	23.37 ± 0.21	1.13 ± 0.01	2.17 ± 0.03	23.17 ± 0.38	21.22 ± 0.01	13.17 ± 0.10
34	3.34 ± 0.10	<LOD	<LOD	<LOD	4.66 ± 0.07	42.54 ± 0.89	<LOD	<LOD	8.05 ± 0.27	23.56 ± 0.03	14.06 ± 0.09
35	5.87 ± 0.04	<LOD	<LOD	<LOD	6.18 ± 0.07	38.75 ± 0.22	<LOD	<LOD	7.76 ± 0.19	10.84 ± 0.02	15.84 ± 0.08
36	<LOD	<LOD	<LOD	<LOD	<LOD	44.67 ± 1.08	<LOD	<LOD	12.09 ± 0.21	9.44 ± 0.02	11.24 ± 0.11
37	<LOD	<LOD	<LOD	<LOD	<LOD	35.66 ± 0.23	<LOD	<LOD	<LOD	12.11 ± 0.02	10.86 ± 0.12
38	<LOD	<LOD	<LOD	<LOD	<LOD	57.84 ± 0.35	<LOD	<LOD	<LOD	8.56 ± 0.02	13.17 ± 0.11
39	<LOD	<LOD	1.08 ± 0.01	<LOD	<LOD	49.35 ± 0.56	<LOD	<LOD	<LOD	7.75 ± 0.02	14.21 ± 0.21
40	4.73 ± 0.09	<LOD	<LOD	1.18 ± 0.01	2.27 ± 0.02	37.13 ± 0.44	<LOD	3.36 ± 0.03	21.17 ± 0.33	11.14 ± 0.02	10.89 ± 0.13
41	3.98 ± 0.07	<LOD	<LOD	2.08 ± 0.06	1.36 ± 0.02	26.33 ± 0.18	<LOD	4.17 ± 0.02	14.75 ± 0.15	<LOD	13.36 ± 0.14
42	6.45 ± 0.05	<LOD	<LOD	3.11 ± 0.02	3.55 ± 0.01	27.85 ± 0.22	<LOD	2.86 ± 0.04	11.36 ± 0.08	<LOD	12.56 ± 0.09
43	5.67 ± 0.06	<LOD	<LOD	4.17 ± 0.03	4.78 ± 0.03	36.54 ± 0.66	<LOD	2.11 ± 0.02	9.84 ± 0.09	8.99 ± 0.03	12.24 ± 0.09
44	<LOD	<LOD	<LOD	<LOD	<LOD	29.44 ± 0.51	<LOD	<LOD	<LOD	<LOD	10.83 ± 0.06
45	<LOD	<LOD	<LOD	<LOD	<LOD	29.12 ± 0.26	<LOD	<LOD	<LOD	<LOD	17.11 ± 0.05
46	<LOD	<LOD	<LOD	<LOD	<LOD	27.08 ± 0.32	<LOD	<LOD	<LOD	12.09 ± 0.03	9.85 ± 0.08
47	<LOD	<LOD	<LOD	<LOD	<LOD	13.17 ± 0.13	<LOD	<LOD	<LOD	10.11 ± 0.03	8.54 ± 0.07
48	<LOD	<LOD	<LOD	<LOD	<LOD	12.25 ± 0.24	<LOD	<LOD	13.22 ± 0.12	11.27 ± 0.03	13.27 ± 0.06
49	<LOD	<LOD	<LOD	<LOD	<LOD	17.86 ± 0.18	<LOD	<LOD	12.85 ± 0.11	<LOD	5.66 ± 0.05
50	<LOD	<LOD	<LOD	<LOD	<LOD	21.13 ± 0.27	<LOD	<LOD	9.56 ± 0.09	7.56 ± 0.02	6.47 ± 0.07

Note: Co, V, Mn, Ni, Ag, Ti, Be, Bi, Cs, Li, B, Sb, and Hg elements could not be detected in the samples.

water samples were reported with traceability and estimated uncertainty. Therefore, the method was shown to be reliable and internationally comparable. After this validation, the selected performance criteria (linearity, LOD, LOQ, specificity, accuracy, repeatability) showed that both open-vessel digestion and the use of ICP-MS for detection allowed an accurate determination. Since the quality of drinking water and sources of pollution may vary from year to year, it is recommended that ongoing monitoring be maintained.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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