Research Article

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Development of ultrasound-assisted dispersive solid-phase microextraction based on mesoporous carbon coated with silica@iron oxide nanocomposite for preconcentration of Te and Tl in natural water systems<https://doi.org/10.1515/chem-2020-0039>

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Abstract: The main objective of this study was to develop an ultrasound-assisted dispersive solid-phase microextraction (UADSPME) method for separation and preconcentration of tellurium (Te) and thallium (Tl) in environmental samples prior to inductively coupled plasma-optical emission spectrometry determination. The MPC@SiO₂@Fe₃O₄ nanocomposite was used as a nano-adsorbent in the UADSPME method. The nanocomposite was prepared using a coprecipitation and sol-gel method, and it was characterized using scanning electron microscopy/energy-dispersive X-ray spectroscopy, transmission electron microscopy and X-ray powder diffraction techniques. The Box-Behnken design and response surface methodology were used for the optimization of experimental parameters (such as pH, extraction time and mass of adsorbent) affecting the preconcentration procedure. Under optimized conditions, the limits of detection were 0.05 and 0.02 µg L⁻¹ and the limits of quantification were 0.17 and 0.07 µg L⁻¹ for Te and Tl, respectively. The precision expressed as the relative standard deviation (%RSD) was 2.5% and 2.8% for Te and Tl, respectively. Finally, the developed method was applied for the analysis of Tl and Te in real samples.

Keywords: thallium, tellurium, desirability function, response surface methodology, MPC@Fe₃O₄@SiO₂ nanocomposite, environmental matrices

1 Introduction

Trace metals in water may be beneficial or risk to humans as well as other living organisms. For instance, trace metals such as Tl, As, Te, Sb, Hg, Cd and Pb are regarded as toxic inorganic pollutants [1]. These metals exist in trace levels in various matrices such as environmental, biological and water [2]. Toxic metals can cause severe health problems that can even lead to fatalities for animals and human beings; this is due to the fact that unlike organic contaminants, these trace toxic metal ions are non-biodegradable and have a tendency to accumulate in the organs of living organisms, such as liver, lungs, heart and kidneys [2,3]. Trace metals are either essential or toxic; for instance, metals such as tellurium (Te) and thallium (Tl) both are toxic in all their species. Tellurium exists in nature as tellurite(III) and tellurate(IV), which are non-essential toxic metal species widely used in metallurgy in the production of steel, cast iron and bronze and also in catalytic processes, among others [4]. The main sources of Tl are emissions and solid wastes from ferrous/non-ferrous mining and metallurgy, coal combustion, or possibly cement production [5]. Tl is listed among the most toxic heavy metals that are very harmful to human beings owing to its mutagenic, carcinogenic and teratogenic activities [6]. It is widely used in industrial applications such as medicine, nuclear industry, alloys, catalyst and pigments [5], leading to a high risk of occupational poisoning and environmental pollution [6]. Because these toxic metals exist in trace levels, extraction/preconcentration techniques need to be employed [7].

A number of analytical techniques are widely used in the analyses of trace metals in water, food and environmental samples [8,9], such as inductively coupled plasma-optical emission spectrometry (ICP-OES) [10], inductively coupled plasma-mass spectrometry (ICP-MS) [7], flame

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atomic absorption spectrometry (FAAS) [11,12] and electrothermal atomic absorption spectrometry (ETAAS) [13,39]. Even though there are developments in advancing analytical techniques, these techniques cannot handle relatively complex samples directly. Therefore, there is a need for extraction/preconcentration procedures prior to qualitative and/or quantitative analysis of metals [9]. Extraction/preconcentration techniques are preferred because of their ability to eliminate interferences by matrices and increase the detection limit of the analytical technique [14]. In recent years, dispersive liquid-liquid microextraction [15,40,41], cloud point extraction [16], solid-phase extraction [17] and dispersive solid-phase microextraction [18] are among the widely used techniques [9].

In this work, the mesoporous carbon coated with iron oxide@silica (MPC@Fe₃O₄@SiO₂) nanocomposites were synthesized and characterized. The synthesized adsorbent was used as the solid material in the ultrasound-assisted dispersive solid-phase microextraction (UADSPME) method for the preconcentration of Te and Tl in environmental samples. The choice of using mesoporous carbon was promoted by the fact that it provides advantages such as high surface area and adsorption capacity [19], and Fe₃O₄, based on its high affinity for metals and its magnetic properties, makes it easy for the adsorbent to be retrieved at the end of the extraction using a magnet [20]. To improve the selectivity and adsorption capacity of MPC, the surface was modified by SiO₂ owing to the functional group it possesses and the fact that it is vital to retain the physical integrity and resistance to heat or pH changes of the nanoparticles [21]. The analytes in the samples were quantified using ICP-OES. The response surface methodology (RSM) based on the Box-Behnken design (BBD) coupled with a desirability function (DF) was used for the optimization of the most influential factors, including sample pH, extraction time and mass of adsorbent. Under optimum conditions, analytical performances of the method were investigated, and the method was applied for the determination of Te and Tl in real samples.

2 Experimental

2.1 Materials and reagents

All chemicals are of analytical reagent grade unless stated otherwise, and double-distilled water is used throughout the experiments. Te and Tl standards (1,000 mg L⁻¹), iron(II) chloride tetrahydrate, iron(III) chloride hexahydrate, silica

gel, starch, tetraethyl orthosilicate (TEOS) (silica precursor), sodium hydroxide solution, ethanol, ammonia (25%) and ultrapure nitric acid (69%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). All the glassware and plastic containers used in this experiment were immersed in a 10% HNO₃ solution overnight and rinsed with deionized water and finally rinsed with ultrapure water.

2.2 Sampling and collection of samples

River water samples were collected from Soweto (Johannesburg, South Africa) and were kept in 1,000 mL polypropylene bottles. All water samples were acidified with nitric acid and stored in a refrigerator at 4°C until analysis. The determination of Te and Tl was performed using the optimum conditions. Before analysis, the samples were filtered through a 0.2 µm PVDF Acrodisc syringe filter.

2.3 Instrumentation

The quantification of the analytes Te and Tl was performed using an ICP-OES spectrometer (iCAP 6500 Duo; Thermo Scientific, UK) equipped with a charge injection device detector. The samples were introduced with a concentric nebulizer and a cyclonic spray chamber. The operating conditions of the instrument are presented in Table 1. ICP-MS was used as the reference method (Agilent 7900 ICP-MS system with the Ultra High Matrix Introduction option and He cell gas option; Agilent Technologies Inc., Tokyo, Japan). The operating parameters for each element were set as recommended by the manufacturer. A Branson 5800 Ultrasonic Cleaner (Danbury, CT, USA) was used for extraction and preconcentration studies. The pH of the samples and model solutions was adjusted using a pH meter with an electronic glass electrode (Mettler-Toledo FE20, Switzerland). An Eppendorf 5702 Centrifuge (Eppendorf Ag, Hamburg, Germany) was used to separate the adsorbent from the sample solution.

A tubular electric furnace was used to perform the pyrolytic process under inert conditions using nitrogen. A digital hot plate (LabTech Africa, South Africa) was used as a heating and stirring source in this study. An oven purchased from Xi'an Unique Electronics, UQ 9053A, was used for drying materials. The morphology of the adsorbent was observed using a scanning electron microscope (SEM, TESCAN VEGA 3 XMU; LMH instrument, Czech Republic) coupled with energy dispersive X-ray spectroscopy (EDS) for elemental composition analysis at an accelerating voltage of 20 kV. Transmission electron microscope (TEM)

Table 1: Operating parameters of ICP-OES

Parameters	Conditions
RF generator power/W	1,150
Frequency of RF generator/MHz	40
Coolant gas flow rate/L min ⁻¹	12
Carrier gas flow rate/L min ⁻¹	0.7
Auxiliary gas/L min ⁻¹	1.0
Maximum integration times/s	15
Pump rate/rpm	50
Viewing configuration/touch mode	Axial
Replicate	3
Flush time (s)	30

(JEM 2100F; JEOL Co., Japan). All the gases to be used for analysis are of instrument grade. The XRD measurements were done on a PANalytical X'Pert X-ray Diffractometer (PANalytical BV, Netherlands) using a Cu K α radiation ($\lambda = 0.15406$ nm) in the 2θ range of 4° – 90° at room temperature.

2.4 Preparation of mesoporous carbon

For the preparation of mesoporous carbon, a modified method reported by Li *et al.* [22] was used as follows. Fifteen grams of starch were dissolved in 50 mL of deionized water and heated at 120°C using an oil bath and stirred at 300 rpm to form a homogeneous solution. A 20 g silica solution dissolved in 50 mL of deionized water was added dropwise into the starch solution while stirring. The mixture was then left under vigorous stirring at 700 rpm for 20 min to form a gel-like material. The material was transferred to a Petri dish to cool to room temperature. After cooling down, the material was dried in an oven at 60°C and carbonized in a furnace at 500°C for 3 h under a gentle flow of nitrogen gas. The carbonized material was left to stirring in a 30% NaOH solution overnight. The resulting product was vacuum filtered and washed with a 1:1 ethanol–water solution several times. The residue was then dried in an oven at 60°C .

2.5 Preparation of magnetic Fe₃O₄ nanoparticles

The coprecipitation method reported by Munonde *et al.* [23] was used for the preparation of Fe₃O₄ nanoparticles. To describe the method briefly, 21.20 g of FeCl₃·6H₂O and 10.05 g of FeCl₂·4H₂O were dissolved in 300 mL of deionized water. The mixture was heated at 85°C while stirring at 450 rpm under inert conditions for 1 h. Then, 50 mL of ammonia (25%)

was added dropwise to the solution. After the addition of ammonia, the solution turned from orange to black and it was constantly stirred for another 4 h. The mixture was cooled down and washed several times with deionized water until the pH was 10. The precipitate was then dried at 80°C for 10 h.

2.6 Preparation of MPC@SiO₂@Fe₃O₄ nanocomposite

A modified sol–gel method reported by Nyaba *et al.* [24] was employed for the preparation of the MPC@SiO₂@Fe₃O₄ nanocomposite. To describe the method briefly, 1.5 g of MPC, 0.75 g of Fe₃O₄ and 1.24 mL of TEOS (in the ratio of 2:1:1 w/w/v) were added into 100 mL of ethanol while stirring. Ammonia (25%) was added dropwise to the mixture until it formed a sol–gel material. The material was left to mature at room temperature for 24 h prior to being dried in the oven at 60°C for 24 h. The dried material was calcined at 500°C for 4 h producing a dark brown powder.

2.7 UADSPME procedure

A synthetic sample of 10 mg L^{-1} was prepared from single-element standards of Tl and Te at a concentration of $1,000\text{ mg L}^{-1}$. From the 10 mg L^{-1} stock solution, three more synthetic sample solutions of $50\text{ }\mu\text{g L}^{-1}$ with a pH of 3, 6 and 9 were prepared. A 20 mL aliquot of these samples was transferred into pre-cleaned centrifuge tubes. Appropriate masses of adsorbents (50, 100 and 150 mg) were added to the respective pH-specific solution samples. The samples were then sonicated in an ultrasound water bath specific to their appropriate times of 5, 12.5 and 20 min. Complete separation of the adsorbent and supernatant was achieved by the use of an external magnet. The supernatant was discarded, and the retained analyte was eluted using dilute nitric acid solution (2 mL). The elution was assisted by ultrasonication for 5 min and followed by separation by an external magnet. The supernatant was then analyzed on the ICP-OES for the determination of Te and Tl concentration.

2.8 Optimization of the extraction procedure

The procedure that was selected for the optimization of extraction of this experiment was a multivariate optimization approach based on the full-factorial design. This approach was chosen as it saves time and cost because three parameters are being investigated simultaneously. The parameters investigated were pH, the mass of

Table 2: Factors and levels used in the 2^3 -factorial design for extraction and preconcentration

Factors	Low level (−1)	Central point (0)	High level (+1)
pH	3	6	9
Mass of adsorbent (MA) (mg)	50	100	150
Extraction time (ET) (min)	5	12.5	20

adsorbent and extraction time. Table 2 presents the levels and factors of the parameters affecting the preconcentration and extraction of the experiment.

Ethical approval: This study is not related to either human or animal use and hence does not need approval.

3 Results and discussions

3.1 Characterization of mesoporous carbon

Scanning electron microscopy analysis shows a smooth surface with ordered cubic mesostructure characteristic

of mesoporous carbon [25]. An in-depth analysis using TEM was used to further confirm the mesostructures that were observed in SEM (Figure 1). Honeycomb pores on the prepared mesoporous carbon are well defined being a particular property described in the literature [26]. The presence of carbon and oxygen as major components is shown by chemical composition determined by EDS. It should be noted that the presence of a small amount of Si and Na was due to the impurities from the template and solution used to remove the template (Figure 1).

The wide-angle X-ray diffraction patterns of raw mesoporous carbon are shown in Figure 2. The mesoporous materials exhibited a broad peak at 20° – 30° θ , which can be attributed to the graphitic carbon-based plane diffraction [27,28]. The crystalline structures observed can be attributed to a silica template. These results are in line with those observed when using EDS.

3.2 Characterization of ferro-ferric oxide

Scanning electron microscopy shows the cubic structures of ferro-ferric oxide nanoparticles (Figure 3). The particles display the cubic structure that existed in different sizes. Morphology of the Fe_3O_4 nanoparticles was further

Figure 1: SEM (left), TEM (right) and EDS (bottom) images for mesoporous carbon.

Figure 2: XRD patterns for mesoporous carbon.

investigated using TEM (Figure 3). Figure 3 shows the TEM images of Fe_3O_4 with a uniform pattern of Fe_3O_4 nanoparticles without any agglomeration. In this pattern, cubic structures of the synthesized Fe_3O_4 nanoparticles were observed. The EDS determined iron and oxygen as the major components. The XRD pattern (Figure 3) for the Fe_3O_4 nanoparticles shows six major characteristic peaks of Fe_3O_4 at 30.3° , 35.7° , 43.3° , 53.7° , 57.3° and 62.9° , respectively,

which are in agreement with the patterns obtained in the literature [29]. These characteristic peaks were indexed as 220, 311, 222, 400, 422 and 511 from the peak list obtained from the XRD report data.

3.3 Characterization of nanocomposite

The surface morphology of the $\text{MPC@Fe}_3\text{O}_4\text{/SiO}_2$ nanocomposite is shown in Figure 4. As can be seen in Figure 4, the TEM and SEM images show that their nanoparticles are present on the surface of MPC. Figure 4 illustrates the XRD pattern of the $\text{MPC@Fe}_3\text{O}_4\text{/SiO}_2$ and SiO_2 . It can also be seen that the diffraction peaks of the nanocomposite at about $2\theta = 30.3^\circ$, 35.7° , 43.6° , 54.1° , 57.1° and 63.01° can be attributed to the incorporation of Fe_3O_4 onto the surface of MPC [17]. In addition, the XRD pattern for SiO_2 displayed a broad peak at $2\theta = 23^\circ$, which was attributed to the amorphous nature of SiO_2 . It was observed that there was no characteristic peak for SiO_2 and MPC in the nanocomposite. For this reason, it was concluded that the XRD patterns of Fe_3O_4 had strong intensities such that the diffraction peaks of SiO_2 and MPC were suppressed. These observations proved that $\text{MPC@Fe}_3\text{O}_4\text{/SiO}_2$ was successfully prepared (Figure 4).

Figure 3: SEM (left), TEM (right), EDS (bottom) and XRD pattern of Fe_3O_4 nanoparticles.

Figure 4: SEM (left), TEM (right) and XRD pattern of MPC@Fe₃O₄@SiO₂.

3.4 Selection of eluent type and concentration

The selection of the eluent type was carried out using HCl and HNO₃ at different concentrations, and the eluent volume was fixed to be 2.0 mL. These eluents were evaluated for elution of the adsorbed Te and Tl ions from the nanoadsorbent. The results obtained are illustrated in Figure 5. As can be seen, the desorption of the analytes increased with increasing concentration of the investigated acids. Nitric acid proved to be the better eluent than HCl such that quantitative recoveries were obtained at 2.0 mol L⁻¹ HNO₃ and above. Therefore, 2 mL of 2 mol L⁻¹ HNO₃ was used for further studies.

3.5 Multivariate optimization

The optimization of the most influential parameters for the preconcentration of Te and Tl was conducted using RSM based on BBD combined with a DF. The sample pH, mass of adsorbent and extraction time were found to play a significant role in the preconcentration of target analytes.

Figure 5: Selection of the eluent type and concentration.

The design matrix (15 standard experimental runs carried out in triplicates) with their respective analytical responses expressed as a percentage of recoveries (%R) is presented in Table 3.

3.5.1 BBD statistical analysis

Analysis of variance was used to analyze the experimental data and are expressed as Pareto charts (Figure 6). The Pareto charts were used to evaluate the significant influence of the investigated variables and their interactions on the analytical response. It should be noted that in the Pareto charts, an independent variable or the interactions are only significant if they have passed a 95% confidence level which is indicated as the red line [24]. It can be seen that, for Te, only the sample pH had an effect on the extraction and

preconcentration, while all the other parameters and their interactions were not significant at the 95% confidence level. The main effect sign for the sample pH was negative, indicating that the sample pH must decrease from the maximum value towards the minimum for a quantitative preconcentration of Te. For the preconcentration of Tl, sample pH and mass of adsorbent were found to be statistically significant at the 95% confidence level. The bar length and the main effect sign for the sample pH suggested that this variable had a significant effect on the analytical response. The positive sign shows that the analytical response increases with increasing pH or mass of the adsorbent.

Generally, it is important to check the adequacy of the fitted response surface models because they can produce poor or misrepresentative results. Therefore, diagnostic plots such as predicted versus obtained values are used to assess

Tellurium

Figure 6: Pareto charts for standardized effects and observed vs. predicted values for the preconcentration of Te and Tl.

Table 3: Design matrix with a percentage of recoveries

Std. run	pH	ET (min)	MA (mg)	%Recovery	
				Te	Tl
1	3	5	100	87.1	70.0
2	9	5	100	46.3	98.3
3	3	20	100	96.2	71.15
4	9	20	100	51.4	99.3
5	3	13	50	95.4	67.5
6	9	13	50	48.9	95.3
7	3	13	150	99.7	72.8
8	9	13	150	62.3	98.7
9	6	5	50	83.2	83.2
10	6	20	50	88.3	85.3
11	6	5	150	86.7	91.3
12	6	20	150	81.3	94.2
13	6	13	100	89.2	93.9
14	6	13	100	89.3	94.4
15	6	13	100	89.6	93.6

the model suitability and the relationship between experimental data and predicted data. From Figure 6, it can be observed that the data points for both predicted and obtained data were very close to the straight line, meaning that there was a high correlation between the experimental data and predicted data. The square of the correlation coefficient values (R^2) for Te and Tl were 0.9812 and 0.9940, indicating that about 1.88% and 0.6% of the total dissimilarities could not be explained based on the predicted model [30]. In addition, the adjusted R^2 values were 0.9482 and 0.9832, which are closer to unity, suggesting that the model was reliable for predicting the equivalent experimental data.

3.5.2 RSM

The RSM was plotted using a quadratic equation [31]. From the experimental runs conducted, the acquired results

Figure 7: Three-dimensional response surface plots for the preconcentration of Te as a function of experimental parameters.

Figure 8: Three-dimensional response surface plots for the preconcentration of Tl as a function of experimental parameters.

generated three-dimensional (3D) response surface plots (Figures 7 and 8). The 3D response surface plots were used to examine the individual effects and combined interactions of the variables on the preconcentration of Te and Tl. As can be seen in Figure 7, the influence of sample pH on the percentage recovery of Te indicates that decreasing the pH increases the %R. The pH value at the point of zero charge (pH_{pzc}) for the composite was 5.5, meaning that below this point the surface of the adsorbent acts as an anion exchanger. It should be noted that Te exists as the oxyanion in water systems, implying that it has a negative sign [32]. Therefore, as observed, at lower pH values, the surface of the adsorbent was positive, suggesting that more sites were available for the adsorption of Te, thus leading to more Te ions being extracted. Extraction times higher than the

minimum values were required for the preconcentration of Te. Therefore, higher recoveries were observed in the range of 12.5–20 min. It was also observed that increasing the mass of adsorbent enhanced the preconcentration of Te; hence, an increase in analytical response was observed.

Sample pH is an important and effective parameter in the preconcentration process. Therefore, the effect of pH on the preconcentration of Tl was investigated in the range of 3–9 (Figure 8). It can be seen that sample pH had a positive influence on the preconcentration of Tl (Figure 8) because the results point out that increasing the pH leads to higher recoveries. In addition, it was observed that the recoveries increased when the pH ranged from 6 to 9. Extraction time did not have a significant influence on the analytical response. Finally,

the effect of mass of adsorbent on the preconcentration process shows that at 80–150%, more Tl ions were adsorbed and higher recoveries (>90%) were obtained.

Based on these results for both Te and Tl, the mechanism of sorption is possibly dominated by electrostatic attraction. This is because at low pH values (below $pH_{pzc} = 5.5$), the negatively charged Te oxyanion was adsorbed by the positively charged surface of the nanocomposite. This was also evident for Tl, which exists as a cation because its quantitative adsorption was achieved at higher pH values when the surface of the adsorbent was negatively charged. Therefore, it can be concluded that the extraction and preconcentration of Te and Tl were pH-dependent.

3.5.3 Optimization using the desirability function (DF)

The DF, as a preferred tool for estimating the optimal conditions, was constructed and applied for the selection of optimum values of operative variables. The desirability profile for the percentage recovery of Te and Tl versus the variables is shown in Figures 9 and 10. The desirability variation from 0.0 to 1.0 is known to correspond to the movement from undesirable to very desirable analytical response values. As shown in Table 3, the values of 46.3%, 62% and 99.7% were obtained for the minimum, median and

maximum %recovery of Te, respectively, while those of Tl were 67.5%, 83.2% and 98.7%, respectively. As shown in Figures 6 and 7, the desirability profile for the %recovery of target analytes versus the independent variables indicated that maximum recoveries of 99.7% and 99.3% for Te and Tl were obtained with $DF = 1.0$. These recoveries were obtained at optimal values: for Te, sample pH, 3–4.5; extraction time, 12.5–16.5 min; and mass of adsorbent, 125–150 mg; and for Tl, sample pH, 7.5–9; extraction time, 9–20 min; and mass of adsorbent, 75–150 mg. Therefore, the optimum conditions for the preconcentration of Te were set to be 4.5, 12.5 min and 125 mg for sample pH, extraction time and mass of adsorbent, respectively, whereas those for Tl were sample pH = 7.5, extraction time = 10 min and mass of adsorbent = 100 mg. For validation of the model, the preconcentration experiments were carried out in triplicates using the optimum conditions. The confirmatory/validation experiments revealed the %recoveries of $99.8 \pm 1.2\%$ and $99.7 \pm 1.5\%$ for Te and Tl, under optimal conditions. These results were comparable with the predicted results obtained using the DF. They implied that the RSM model based on the BBD combined with DFs was suitable and accurate. In addition, these findings suggested that the RSM model can be successfully used to optimize the experimental parameters for the preconcentration of Te and Tl by the $MPC@SiO_2@Fe_3O_4$ nanocomposite.

Figure 9: Profile for the predicted values and DF for the percentage recovery of Te.

Figure 10: Profile for the predicted values and DF for the removal percentages of Tl.

3.6 Analytical performance of the method

Under the determined optimum experimental conditions, the analytical performances of the developed method for the preconcentration and determination of Te and Tl were investigated. The calibration curves were obtained after a set of standard solutions ($0\text{--}200\text{ }\mu\text{g L}^{-1}$) were processed using the described extraction procedure. The limits of detection (LOD) and limits of quantification (LOQ) were calculated using the following expressions: $\text{LOD} = 3 \times \text{SD}$ and $\text{LOQ} = 10 \times \text{SD}$, where SD is the standard deviation of five replicate measurements at the lowest concentration of calibration curves. Dynamic linear ranges, precision, preconcentration

factors, correlation coefficient (R^2), LOD and LOQ determined using the developed method are presented in Table 4. The results obtained showed that the UASDME method was precise, sensitive and had a relatively wide linearity and high preconcentration factor.

3.7 Application of the analytical procedure to water samples

The UA-DSPM/ICP-OES technique was applied to the water samples collected from a river in Soweto for the analysis of Te and Tl. The analytical results obtained from the six investigated water samples are presented in Table 5. It can be seen that the concentrations of Te and Tl ranged from $2.4\text{--}2.6\text{ }\mu\text{g L}^{-1}$ and $1.7\text{--}4.1\text{ }\mu\text{g L}^{-1}$. As can be seen from Table 5, the concentrations of Tl in samples 1, 3 and 4 were below the maximum contaminant level ($2.00\text{ }\mu\text{g L}^{-1}$) of Tl in surface water set by the United States Environmental Protection Agency, while in samples 2 and 5, the concentrations were above the allowable limit.

To evaluate the accuracy of the developed method, the river samples were analyzed using ICP-MS as a

Table 4: Analytical parameters investigated for the performance of the method

Analytical parameters	Te	Tl
Limits of detection ($\mu\text{g L}^{-1}$)	0.05	0.02
Limits of quantification ($\mu\text{g L}^{-1}$)	0.17	0.07
Precision (%RSD)	2.3	2.8
Linear range ($\mu\text{g L}^{-1}$)	0.3–150	0.1–200
Correlation coefficient	0.9994	0.9989
Preconcentration factor	50	75

Table 5: Determination of Te and Tl in real samples (mean $\pm$ SD, $n = 4$)

Samples	UA-DSPM/ICP-OES	² -MS	-DSPM/ICP-OES	² -MS
	Te	Tl	Te	Tl
Site 1	2.65 $\pm$ 0.01	2.67 $\pm$ 0.09	1.68 $\pm$ 0.02	1.71 $\pm$ 0.12
Site 2	2.40 $\pm$ 0.02	2.38 $\pm$ 0.13	4.13 $\pm$ 0.08	4.11 $\pm$ 0.15
Site 3	1.78 $\pm$ 0.03	1.80 $\pm$ 0.15	1.01 $\pm$ 0.01	0.98 $\pm$ 0.15
Site 4	2.71 $\pm$ 0.09	2.73 $\pm$ 0.10	1.31 $\pm$ 0.04	1.29 $\pm$ 0.16
Site 5	1.02 $\pm$ 0.01	0.97 $\pm$ 0.22	ND	ND
Site 6	ND	ND	2.23 $\pm$ 0.02	2.25 $\pm$ 0.08

Table 6: Comparison of the analytical performance of UADSPME/ICP-OES with other analytical methods for the preconcentration and determination of Te and Tl

Analytes	Matrix	Analytical method	LOD ($\mu\text{g L}^{-1}$)	LOQ	%RSD	Ref.
Tl(I)	Water	GFAAS	0.087	0.287	6.4	[33]
Tl(I)	Wastewater	DSPE/FAAS	0.85	2.80	—	[34]
Te(IV)	Water	USAE-SFODME/GFAAS	0.08	0.26	3.4	[35]
Te(IV)	Water	HF-LPME/ETAAS	0.004	0.013	3.5	[4]
Te(IV)	Water	DLLME-ETV-ICP-MS	0.00056	0.0018	9.7	[36]
Tl	Water	UADSPME/ICP-OES	0.00025	0.00084	2.4	[37]
Te(IV)	Water	HG-ETAAS	0.086	0.29	46	[38]
Te, Tl	Water	UADSPME/ICP-OES	0.05, 0.05	0.17, 0.07	2.3, 2.8	This work

GFAAS = graphite furnace atomic absorption spectrometry; FAAS = flame atomic absorption spectrometry; ETAAS = electrothermal atomic absorption spectrometry; ETV-ICP-MS = electrothermal vaporization inductively coupled plasma-mass spectrometry; HG = hydride generation; DLLME = dispersive liquid-liquid microextraction; USAE-SFODME = ultrasound-assisted emulsification-solidified floating organic drop microextraction; DSPE = dispersive solid-phase extraction; UADSPME = ultrasound-assisted dispersive solid-phase

reference method. The samples were acidified and filtered using a 0.22 μm syringe filter and then analyzed by ICP-MS. The results are presented in Table 5. The results obtained using the developed and the reference methods were compared using Student's *t*-test. The results of the developed method were in agreement with those obtained using ICP-MS. These findings revealed that the UA-DSPM/ICP-OES method was accurate and precise.

3.8 Comparison with previous studies

The developed UADSPME/ICP-OES method was compared with other methods reported in the literature for their analytical performances (Table 6). It can be seen that this study reports lower detection limits, lower quantification limits and relatively low standard deviations than those reported by other researchers [33–35,38].

Based on the observed data in Table 5, it can be concluded that the analytical performance of the UADSPME/ICP-OES method exhibits outstanding effectiveness and efficiency compared to other methods.

4 Conclusion

The MPC@SiO₂@Fe₃O₄ nanocomposite was synthesized and successfully applied as a solid-phase material in the UA-DSPME method for the preconcentration of Te and Tl in water samples prior to ICP-OES determination. The XRD and EDS results revealed that the SiO₂@Fe₃O₄ nanoparticles were incorporated in mesoporous carbon. The BBD was successfully employed to optimize parameters affecting the extraction and preconcentration efficiency that assisted in choosing optimum conditions for application. Under optimized conditions, the UA-DSPME preconcentration method demonstrated good

analytical qualities such as rapidity, simplicity, relatively low detection limits and high preconcentration factors as well as high precision. The method can be successfully applied to the extraction, preconcentration and determination of Te and Tl in environmental water samples.

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