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Multi-element determination of copper, iron, nickel, manganese, lead and zinc in environmental water samples by ICP OES after solid phase extraction with a C18 cartridge loaded with 1-(2-pyridylazo)-2-naphthol

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Multi-element determination of copper, iron, nickel, manganese, lead and zinc in environmental water samples by ICP OES after solid phase extraction with a C18 cartridge loaded with 1-(2-pyridylazo)-2-naphthol

Abstract

A pre-concentration solid-phase procedure has been developed for the sensitive and simple determination of copper, iron, nickel, manganese, lead and zinc in environmental water samples by inductively coupled plasma optical emission spectrometry (ICP OES). After pH adjustment, the samples were percolated with the aid of a peristaltic pump on a Sep-Pak C18 cartridge loaded with 1-(2-pyridylazo)-2-naphthol (PAN). The analyte elution was carried out with the passage of HCl through the cartridge for subsequent determination by ICP OES. The experimental conditions for pre-concentration were optimized considering the following factors: concentration and volume of the eluent, sample volume, flow-rate and pH. The optimized conditions corresponded to the use of 5 mL of 0.8 M HCl as the eluent, a sample volume of 50 mL, a flow-rate of 1.9 mL min⁻¹ and pH 9.0. In these conditions, the detection limits for Cu, Fe, Mn, Ni, Pb and Zn varied between 0.11 to 21 µg L⁻¹. The relative standard deviation (RSD) for the analytes of this study did not exceed 9%, after application of the proposed pre-concentration procedure (n=10, 0.50 mg L⁻¹). The effect of possible interfering species on the recovery of the analytes was also investigated. The accuracy of the method was evaluated by analysis of a certified reference material (SLEW-3 Estuarine Water Reference Material for Trace Metals) and the proposed method was applied to samples of ground water, drinking water and river water. The samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) as a comparative method and no significant differences among these results and the results obtained by the proposed method were observed.

Keywords: solid phase extraction; functionalized silica C18; PAN; determination of metals; ICP OES; water samples.
1. Introduction

In recent decades, population growth, industrial and technological development and the lack of proper treatment of generated waste have produced serious impacts on aquatic environments. Because of the resulting risks to human health and pollution, many studies have been conducted with the aim of developing strategies to monitor chemical species in natural water,\textsuperscript{1-3} including metallic species as copper, iron, nickel, manganese, lead and zinc.\textsuperscript{4} Metallic species can arise from natural or anthropogenic sources and can exhibit high toxicity in the environment presenting great risks to human health.\textsuperscript{5} Some metals such as copper, zinc, iron, cobalt, manganese are essential for the health of most organisms, forming integral components of proteins involved in all aspects of biological function. However, in excess they are toxic, binding to inappropriate biologically sensitive molecules or forming dangerous free radicals.\textsuperscript{6}

Atomic spectrometric techniques have been used for direct determination of metals ions; however, the use of these techniques for this purpose can be difficult due to low levels of analytes and matrix and spectral interferences.\textsuperscript{7} The determination of metals in environmental water samples can be carried out without a pre-concentration step by electrothermal atomic absorption spectrometry (ET AAS),\textsuperscript{8} or by inductively coupled plasma mass spectrometry (ICP-MS), which usually provide adequate sensitivity. However, when inductively coupled plasma optical emission spectrometry (ICP OES) is employed, a pre-concentration step is necessary due to the low concentrations in this type of sample.\textsuperscript{9-11} In this context, several methods have been proposed and used for pre-concentration and separation of trace elements according to the nature of the samples, the concentrations of analytes and the measurement techniques to meet the detection limit of the prescribed method and to eliminate the interference of the matrix elements.\textsuperscript{12-16}
There are several efficient methods for carrying out the pre-concentration of analytes in low concentrations.\textsuperscript{17,18} Solid phase extraction (SPE) is an important technique for the separation and pre-concentration of trace elements in different samples and features several advantages such as minimal waste generation and reduction of sample matrix effects, as well as sorption of the target species on the solid surface in a more stable chemical form.\textsuperscript{19} Selective solid phase extractors can be obtained from the immobilization of organic compounds on the surface of solid supports, such as Amberlite XAD,\textsuperscript{20} ion exchange resins,\textsuperscript{21} and functionalized silica C18.\textsuperscript{22} Among these, C18 is typically employed to fill columns in solid phase extraction functionalized sorbents and is widely used in the preparation and analysis of a varied number of samples because it exhibits great versatility in the extraction of organic and inorganic species\textsuperscript{21}.

Regarding the reagent to be immobilized on the solid phase, it is important to use complexing reagents that allow the simultaneous extraction of various metals, creating methods which allow simultaneous or sequential determinations.\textsuperscript{23} PAN is an indicator in complexometry and a reagent for the extraction and spectrophotometric determination of many transition metals; the complexant is soluble in methanol, ethanol and insoluble in water.\textsuperscript{24} These features make it an excellent reagent for multi-element complexation in aqueous media. The PAN associated with solid supports has been explored in mono-elements determinations;\textsuperscript{25-27} however PAN can be exploited in SPE systems in association with ICP OES for multi-element determination.\textsuperscript{28-30}

In this paper, a pre-concentration system is proposed for the determination of copper, iron, nickel, manganese, lead and zinc in water samples by ICP OES using a Sep-Pak C18 cartridge loaded with PAN as the solid phase.
2. Materials and Methods

2.1. Apparatus

An ICP OES with an axially viewed configuration (VISTA PRO, Varian, Mulgrave, Australia), equipped with a solid-state detector, Stumar-master mist chamber nebulizer and a V-Groove nebulizer, was employed for copper, iron, nickel, manganese, lead and zinc determinations. The metal determinations were carried out under manufacturer-recommended conditions for power (1.2 kW), plasma gas flow (15.0 L min\(^{-1}\)), auxiliary gas flow (1.5 L min\(^{-1}\)) and nebulizer gas flow (0.80 L min\(^{-1}\)). The emission lines for analysis by ICP OES were chosen according to previous interference studies. The emission lines employed were Cu(I): 327.395, Fe(II): 238.204, Ni(II): 216.555, Mn(II): 257.610, Pb(II): 220.353 and Zn(I): 213.857 nm.

A quadrupole ICP-MS Xseries II (Thermo, Germany) equipped with a hexapole collision cell (CC) and a standard concentric nebulizer was employed as a comparative method. Ge, Rh, Tl, In, Bi, and Sc were employed as internal standards to compensate for instrument drift or any acid effects. The measurements were performed under manufacturer recommended conditions for power (1350 W) with the nebulizer, plasma and auxiliary argon flow rates at 0.87 L min\(^{-1}\), 13.0 L min\(^{-1}\) and 0.70 L min\(^{-1}\), respectively.

2.2. Reagents and solutions

All chemical reagents used in the experiment were of analytical grade. Ultrapure water (18.2 M\(\Omega\) cm) from a Milli-Q system (Millipore, MA, USA) was used to prepare all solutions. Glass apparatus elements were maintained in nitric acid solution (10\%, v/v) during 24 h for decontamination prior to use.
Acetate (pH 3.8–5.7), borate (pH 10.0), TRIS/HCl (pH 8.0–9.0) and hexamine/HCl (pH 7.0) buffers were used to adjust the pH of the solutions (0.01–0.05 mol L\(^{-1}\)). Cu, Fe, Ni, Mn, Pb and Zn standard solutions (1000 µg mL\(^{-1}\)) were purchased from Merck (Darmstadt, Germany). Working solutions were prepared daily by appropriate dilution. Hydrochloric acid solution used as the eluent was prepared by direct dilution from the concentrated solution (Merck).

2.3. Preparation of the C18 cartridge

The Sep-Pak C18 cartridge (Millipore Waters) was washed multiple times with methanol solution (10%, v/v) and then with water using a peristaltic pump. A 0.001% (m/v) ethanolic solution of PAN (Merck) was percolated through the cartridge containing approximately 500 mg of octadecyl-functionalized silica gel phase for 15 min. After this, the cartridge was washed with water again.

2.4. Optimization strategy

The experimental conditions for the pre-concentration procedure have been optimized utilizing the unvaried method for evaluation of the variables affecting the system efficiency and considering the following factors: concentration and volume of the eluent, sample volume, flow-rate and pH. The concentration of the analytes was maintained at 0.50 mg L\(^{-1}\) for all optimization experiments.
2.5. General procedure

Prior to the pre-concentration procedure, all water samples were filtered through a 0.45 µm pore size membrane filter to remove suspended particulate matter and were stored at 6 °C until analysis.

The pre-concentration system was carried out using a peristaltic pump fitted with Tygon tubes and a cartridge containing C18 phase loaded with PAN. The samples, after pH adjustment (pH 9.0 with 0.05 mol L\(^{-1}\) TRIS buffer), were percolated at 1.9 mL min\(^{-1}\) with the aid of the peristaltic pump in the cartridge. The analyte elution was carried out with the passage of the HCl through the cartridge for subsequent determination by ICP OES. The flow system was operated in a volume-based mode, in which a sample volume of 50.0 mL was percolated through the cartridge. In the pre-concentration procedure, 5 mL of 0.8 mol L\(^{-1}\) HCl was used as the eluent. The calibration curves were obtained employing standard solutions and a blank submitted to the same procedure.
3. Results and Discussion

3.1. Optimization

The effect of acidity on the solid phase extraction was investigated because this parameter affects the extraction of metallic ions and, consequently, the analytical signals. Most of pyridylazo reagents interact with metals at slightly acidic to alkaline pH values. Acidic medium creates unfavorable conditions for the metal–ligand interaction.\textsuperscript{31} Then, this study was carried out under pH values ranging from 4.0 to 10.0. The efficiency of retention was low for all cations tested when the pH ranged between 2 and 4. The highest extraction efficiency was achieved between pH 4.0–10.0 for copper, pH 6.0–10.0 for iron, pH 7.0–10.0 for zinc, and pH 8.0–10.0 for manganese, nickel, lead. Formation of precipitate was not observed in the experiments at pH 9.0. The pH adjustment of the samples was performed with tris(hydroxymethyl)aminomethane (TRIS). TRIS can act as a ligand complexing metal ions.\textsuperscript{32,33} Since precipitation was not observed in the system, the reagent may have acted as an auxiliary complexing, preventing the hydrolysis of the iron. Therefore, a pH value of 9.0 was chosen for the subsequent experiments.

The concentration of the HCl eluent has been studied ranging from 0.10 to 1.0 mol L\textsuperscript{-1}. This parameter is important because the analytes are desorbed by the lowering of the pH. Efficient elution for iron, zinc, manganese, nickel and lead was observed when the eluent concentration was higher than 0.4 mol L\textsuperscript{-1}. However, for copper desorption, an eluent concentration of 0.7 mol L\textsuperscript{-1} was necessary. Therefore, in the subsequent experiments, a concentration of 0.8 mol L\textsuperscript{-1} was chosen. In terms of the eluent volume, metal ions adsorbed on the column were completely eluted when eluent volumes were from 5.0 mL. This volume was employed in the proposed procedure to guarantee a better enrichment factor.
The amount of analyte retained on the solid phase depends on the sample flow rate. Sample flow rates below 1.9 mL min\(^{-1}\) would significantly impair the analytical frequency of the method, while flow rates above 2.8 mL min\(^{-1}\) increased the back-pressure resulting in joint leakage. The leakages were observed in the joint between the tube and the cartridge, even when larger diameter tubes (purple/purple, 2.06 mm i.d.) were used. Thus, the flow rate was varied from 1.9 mL min\(^{-1}\) to 2.8 mL min\(^{-1}\). As seen from the experimental results shown in Figure 1, the retention of all analytes was significantly affected by the sample flow rate. It was observed that a flow rate of 1.9 mL min\(^{-1}\) gave higher intensities for all analytes. The decrease of signal for higher flow rates can be attributed to the kinetics of sorption because the increased flow decreases the contact time of ions in the active sites of the solid phase, adversely affecting the retention of the analytes. The sample flow rate was therefore fixed at 1.9 mL min\(^{-1}\) to maximize the sensitivity of the method.

The sample volume is one of the important parameters influencing the pre-concentration factor. The effect of the sample volume on the recoveries of the analyte was investigated in the range of 10 to 100 mL, keeping constant the amount of the analytes. The obtained recoveries values of copper, iron, nickel, manganese, lead and zinc were efficient (>95%) in this sample volume range. In addition, to study the effect of the analyte concentrations on the pre-concentration system, the volume of the aqueous phase containing 0.5 µg L\(^{-1}\) of each analyte was varied in the range of 10–100 mL, since high enrichment factors can be obtained by exploiting higher sample volumes. Further improved sensitivity can be achieved by increasing the volume of the sample subjected to the pre-concentration process. This fact can be employed to regulate the sensitivity of the process as a function of the concentration of the analytes in the sample. Evaluation of the influence of the volume in the pre-concentration process was carried out by varying the sample volume between 10 and 100 mL and measuring the emission intensity obtained after the pre-concentration procedure.
with these different volumes of solution containing the same concentration of analytes (0.50 mg L\(^{-1}\)) passed through the solid phase. Linear relationships were observed between the emission intensity \((I, \text{ cps})\) and the sample volume \((V, \text{ mL})\), as described by the following equations:

\[
I = 1696 \, V + 3226 \quad (r = 0.998), \text{ for copper} \tag{1}
\]
\[
I = 1602 \, V - 2099 \quad (r = 0.996), \text{ for iron} \tag{2}
\]
\[
I = 6432 \, V + 14646 \quad (r = 0.998), \text{ for manganese} \tag{3}
\]
\[
I = 489 \, V + 254 \quad (r = 0.999), \text{ for nickel} \tag{4}
\]
\[
I = 46 \, V + 453 \quad (r = 0.985), \text{ for lead} \tag{5}
\]
\[
I = 1274 \, V + 1313 \quad (r = 1.00), \text{ for zinc} \tag{6}
\]

High enrichment factors can be obtained by exploiting higher sample volumes, but is more time-consuming. Because a compromise condition should be reached to obtain a good pre-concentration factor while simultaneously providing a proper sampling rate, a sample volume of 50 mL was considered sufficient to obtain an appropriate sensitivity and was chosen for the proposed procedure.

3.2. Analytical features and application

The established experimental conditions were as follows: pH 9.0, sample volume of 50 mL, eluent volume of 5 mL, eluent concentration (HCl solution) of 0.8 mol L\(^{-1}\) and sample flow-rate of 1.9 mL min\(^{-1}\). To check the effect of other ions on the method under the established conditions, a solution containing copper, iron, nickel, manganese, lead and zinc with potential interferents (As, Mo, V, Cd, Bi, Co, Se, Hg, Cr) at concentrations five times
higher than the analytes was analyzed. The concentration of analytes was determined according to the proposed procedure and the achieved results showed that these species did not interfere in the analyte determination at this proportion. The presence of NaCl was evaluated, and concentrations up to 5% (m/v) did not interfere. Acetate, borate, TRIS and hexamine were also tested and, in the final concentration range 0.01–0.05 mol L\(^{-1}\), did not interfere. The adequate performance of the method in the presence of potential interferents was confirmed with the results obtained for the reference sample and the comparison with the alternative method.

Using the proposed procedure, experiments were performed to obtain the calibration curves and precision and detection limits for each analyte. The analytical curves were obtained with seven points and good coefficients of correlation, as described by the following equations:

\[ I = 162.42 C - 1.45 \quad (r = 0.9996), \text{ for copper} \]  
\[ I = 146.8 C + 931.4 \quad (r = 0.9977), \text{ for iron} \]  
\[ I = 714.3 C - 160.9 \quad (r = 0.9990), \text{ for manganese} \]  
\[ I = 42.1 C - 48.1 \quad (r = 0.9990), \text{ for nickel} \]  
\[ I = 5.99 C + 2.72 \quad (r = 0.9994), \text{ for lead} \]  
\[ I = 132.1 C + 1046.3 \quad (r = 0.9970), \text{ for zinc} \]  

where \( I \) is the intensity signal (cps) and \( C \) is the concentration (\( \mu g \) L\(^{-1}\)).

The limits of detection (LOD), defined as the analyte concentrations that provide a response equivalent to three times the standard deviation of the blank (\( n = 10 \)), varied from 0.11 to 21 \( \mu g \) L\(^{-1}\), and the quantification limits (LOQ) varied from 0.4 to 69 \( \mu g \) L\(^{-1}\). Precision,
expressed as relative standard deviation (RSD), ranged from 2 to 9% (Table 1). The enrichment factors (EF) of the proposed procedure are also shown in Table 1 and were calculated as the ratio of the slopes of the calibration curves with and without pre-concentration.

Table 2 shows the analytical parameters of the previous methods that used ICP OES for the determination of metals in waters samples after preconcentration procedure employing PAN in association with different solid supports. According to the Table, the combination between PAN and C18 has been little explored for multi-element determination in water samples. In addition, the recovery values were similar to those reported in the literature and the determination can be performed with good limits of detection.

The method was evaluated through spike recovery tests in three water samples under the optimized conditions. The results are shown in Table 3 and show quantitative recoveries between 90 and 110%. In addition, copper, manganese and zinc were determined in a standard reference material (SLEW-3 Estuarine Water Reference Material for Trace Metals) to confirm the accuracy of the method (Table 4). The paired t-test (95% confidence level) did not show a significant difference between the concentrations for the species determined in this sample.

The proposed method was applied for copper, iron, nickel, manganese, lead and zinc determination in samples of groundwater, drinking water and river water collected in Cachoeira and São Félix cities, Bahia, Brazil. The obtained results can be seen in Table 5. The samples were also analyzed by ICP-MS as a comparative method and no significant differences among the results were observed by applying the paired t-test and F test (95% confidence level).
4. Conclusion

Solid phase extraction with a C18 cartridge loaded with 1-(2-pyridylazo)-2-naphthol was successfully applied as a pre-concentration step for the determination of copper, iron, nickel, manganese, lead and zinc by ICP OES. The method provides a simple, precise and accurate approach for metals determination in environmental water samples.

Acknowledgements

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Figure Caption

Figure 1. Effect of flow rate on the analytical signal for (a) copper, (b) iron, (c) manganese, (d) nickel, (e) lead and zinc determination by ICP OES after solid phase extraction with a C18 cartridge loaded with PAN.
Table 1. Analytical characteristics of the proposed method for determination of metals in water samples by ICP OES after a pre-concentration procedure employing a C18 cartridge loaded with PAN.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>LOD, µg L(^{-1})</th>
<th>LOQ, µg L(^{-1})</th>
<th>RSD, % (n=10)</th>
<th>EF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.02</td>
<td>0.07</td>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td>Fe</td>
<td>1</td>
<td>4</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Mn</td>
<td>0.5</td>
<td>2</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>Ni</td>
<td>0.8</td>
<td>3</td>
<td>7</td>
<td>16</td>
</tr>
<tr>
<td>Pb</td>
<td>4</td>
<td>14</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>Zn</td>
<td>1</td>
<td>4</td>
<td>9</td>
<td>9</td>
</tr>
</tbody>
</table>

EF: Enrichment factors.
Table 2- Methods for metals determination in waters samples by inductively coupled plasma optical emission spectrometry after solid phase extraction using 1-(2-pyridylazo)-2-naphthol as complexing agent.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Solid phase</th>
<th>Limit of detection, µg L⁻¹</th>
<th>Recovery range, %</th>
<th>% RSD</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce, Dy, La, Sm, U, Y</td>
<td>C18-cartridge</td>
<td>11 to 69ᵃ</td>
<td>95–106</td>
<td>1.0–7.9</td>
<td>29</td>
</tr>
<tr>
<td>Mn</td>
<td>Magnetic nanoparticles</td>
<td>0.11</td>
<td>98–102</td>
<td>4.6</td>
<td>25</td>
</tr>
<tr>
<td>Zr</td>
<td>Clinoptilolite</td>
<td>0.1</td>
<td>95–104</td>
<td>0.9–2.3</td>
<td>26</td>
</tr>
<tr>
<td>Cd, Pb</td>
<td>Magnetic nanoparticlesᵇ</td>
<td>0.147, 2.02</td>
<td>98.0–104.1</td>
<td>2.96, 1.3</td>
<td>30</td>
</tr>
<tr>
<td>Cu, V</td>
<td>Active carbonᵇ</td>
<td>94, 73ᵃ</td>
<td>92–105</td>
<td>1.37, 1.22</td>
<td>28</td>
</tr>
<tr>
<td>Ni</td>
<td>Amberlite XAD-2</td>
<td>94–103</td>
<td></td>
<td>3.9</td>
<td>27</td>
</tr>
<tr>
<td>Cu, Fe, Mn, Ni, Pb and Zn</td>
<td>C18-cartridge</td>
<td>0.11 to 21</td>
<td>92–109</td>
<td>2–9</td>
<td>This work</td>
</tr>
</tbody>
</table>

ᵃ ng L⁻¹; ᵇ adsorption of metal ions after complexation with PAN.
<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Groundwater</th>
<th>Drinking water</th>
<th>Drinking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample without copper addition</td>
<td>15.6 ± 0.6</td>
<td>5.5 ± 0.1</td>
<td>2.4 ± 0.1</td>
</tr>
<tr>
<td>Sample with copper addition a</td>
<td>35 ± 2</td>
<td>24 ± 1</td>
<td>24 ± 1</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>97</td>
<td>92</td>
<td>108</td>
</tr>
<tr>
<td>Sample without iron addition</td>
<td>31 ± 1</td>
<td>15 ± 1</td>
<td>(3.8 ± 0.9)</td>
</tr>
<tr>
<td>Sample with iron addition a</td>
<td>52 ± 3</td>
<td>35 ± 2</td>
<td>24 ± 2</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>105</td>
<td>100</td>
<td>101</td>
</tr>
<tr>
<td>Sample without manganese</td>
<td>5.9 ± 0.4</td>
<td>8.8 ± 0.2</td>
<td>(0.7 ± 0.2)</td>
</tr>
<tr>
<td>Sample with manganese addition a</td>
<td>25.7 ± 0.4</td>
<td>30.6 ± 0.7</td>
<td>22.1 ± 0.6</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>99</td>
<td>109</td>
<td>107</td>
</tr>
<tr>
<td>Sample without nickel addition</td>
<td>(2.9 ± 0.2)</td>
<td>(2.3 ± 0.16)</td>
<td>(0.61 ± 0.08)</td>
</tr>
<tr>
<td>Sample with nickel addition b</td>
<td>22.4 ± 0.6</td>
<td>22.4 ± 0.6</td>
<td>21.0 ± 0.3</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>97</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Sample without lead addition</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
<td>&lt; LOD</td>
</tr>
<tr>
<td>Sample with lead addition b</td>
<td>86 ± 4</td>
<td>84 ± 3</td>
<td>85 ± 6</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>107</td>
<td>105</td>
<td>106</td>
</tr>
<tr>
<td>Sample without zinc addition</td>
<td>9.3 ± 0.9</td>
<td>15.7 ± 0.5</td>
<td>5.0 ± 0.1</td>
</tr>
<tr>
<td>Sample with zinc addition a</td>
<td>31 ± 2</td>
<td>34 ± 1</td>
<td>25 ± 1</td>
</tr>
<tr>
<td>Recovery, %</td>
<td>110</td>
<td>90</td>
<td>100</td>
</tr>
</tbody>
</table>

*a* addition of 20 µg L⁻¹ of the analyte; *b* addition of 80 µg L⁻¹ of the analyte. Uncertainties are estimates of relative standard deviation. Values below quantification limit are given in parentheses.
Table 4. Determination of copper, iron, manganese and nickel (µg L\(^{-1}\)) in a standard reference material by the proposed method.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Obtained value</th>
<th>Certified value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>1.57 ± 0.05</td>
<td>1.55 ± 0.12</td>
</tr>
<tr>
<td>Mn</td>
<td>1.66 ± 0.05</td>
<td>1.61 ± 0.22</td>
</tr>
<tr>
<td>Ni</td>
<td>(1.18 ± 0.16)</td>
<td>1.23 ± 0.07</td>
</tr>
</tbody>
</table>

Values below quantification limit are given in parentheses.
**Table 5.** Determination of metals (µg L\(^{-1}\)) in water samples by the proposed method and the comparative method (n=3).

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Groundwater</th>
<th>Drinking water</th>
<th>River water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ICP OES</td>
<td>ICP-MS</td>
<td>ICP OES</td>
</tr>
<tr>
<td>Cu</td>
<td>15.6 ± 0.6</td>
<td>16.7 ± 0.1</td>
<td>2.35 ± 0.09</td>
</tr>
<tr>
<td>Fe</td>
<td>10.8 ± 0.4</td>
<td>nd</td>
<td>32 ± 1</td>
</tr>
<tr>
<td>Mn</td>
<td>5.9 ± 0.4</td>
<td>6.02 ± 0.05</td>
<td>(0.70 ± 0.02)</td>
</tr>
<tr>
<td>Ni</td>
<td>(2.9 ± 0.2)</td>
<td>2.5 ± 0.3</td>
<td>(0.61 ± 0.08)</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;LOD</td>
<td>1.76 ± 0.16</td>
<td>&lt;LOD</td>
</tr>
<tr>
<td>Zn</td>
<td>9.3 ± 0.9</td>
<td>10.5 ± 0.6</td>
<td>5.0 ± 0.1</td>
</tr>
</tbody>
</table>

Uncertainties are estimates of relative standard deviation. Values below quantification limit are given in parentheses. nd: not determined.
References


Figure 1