



# Sequential multi-element determination of iron and zinc in water samples by high-resolution continuum source graphite furnace atomic absorption spectrometry after column solid-phase extraction onto multiwalled carbon nanotubes



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## ABSTRACT

A method for the sequential multi-element determination of iron and zinc in water samples by high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GFAAS) after column solid-phase extraction onto multiwalled carbon nanotubes (MWCNTs) was described. The influences of some analytical parameters (including pH of the sample solution, amount of MWCNTs, flow rate of sample, concentration and type of eluent, maximum sample volume and coexisting ions) were investigated for optimization of the proposed procedure. The concentration limits of detection were 4 and 0.5 ng L<sup>-1</sup> for Fe and Zn, respectively; the preconcentration factors achieved for Fe and Zn were 25 and 20, respectively. The relative standard deviations (RSDs) were 6% and 4% for Fe and Zn, respectively. The accuracy of this method was validated by analyses of NIST SRM 1643e (Trace Elements in Water) and ERM – CA011b (Hard Drinking Water) certified reference materials. The measured element contents in these reference materials were in satisfactory agreement with the certified values according to the *t*-test for a 95% confidence level. The presented method has been successfully applied for the determination of iron and zinc in four different water samples (seawater, lake water, mine water and tap water).

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## 1. Introduction

Iron is trace element for our organisms only in appropriate dosage – its neurotoxic effects have been recently reported [1,2]. Zinc, even in low concentration, could be toxic for plants, animals and human body due to its bioaccumulation, nonbiodegradable properties and its toxicity for brain [3]. The biological effects of Fe and Zn are exactly dose dependent and these elements have antioxidant properties at low concentrations but show potent prooxidant effects for human from moderate to high concentrations. These elements may modulate the toxic effect for the reason that the appropriate dosage is very subtle and this dosage depends on human genome/phenotype [4]. Zn and Fe as pollutants they damage and change the environment, especially in river flow [5].

Therefore in recent years the determination of Fe and Zn in water samples has been developed. It is essential to use simple analytical methods for determining elements at very low concentrations with excellent precision and accuracy. X-ray fluorescence, mass spectrometry, electrochemical methods, and the latest techniques in

atomic spectrometry for such elements as Fe and/or Zn have been developed. To improve these modern techniques the preconcentration treatment is very useful. The carbon sorbents, are very widely used, for example new activated carbon chemically modified with 2-((2-aminoethylamino)methyl)phenol was used to solid-phase extraction of Cu(II), Fe(III) and Pb(II) [6]. Since Ijima has found carbon nanotubes [7], this material was used as sorbent for i.e. Fe and/or Zn preconcentration [8–10]. Multiwalled carbon nanotubes (MWCNTs) modified with some organic compounds are expected to be more selective than untreated and oxidized-MWCNTs for the solid-phase extraction of metal ions. Therefore, ethylenediamine-modified multiwalled carbon nanotubes as a solid-phase extractant has been developed for simultaneous preconcentration of trace Cr(III), Fe(III) and Pb(II) prior to the measurement by inductively coupled plasma optical emission spectrometry. Modified MWCNTs for column preconcentration of Zn were also used to determine this element by flame atomic absorption spectrometry (FAAS) [11]. A solid phase extraction onto MWCNTs impregnated with D2EHPA-TOPO mixture was used to determine copper, nickel and zinc by FAAS [12].

The aim of this work was to improve the analytical potential of graphite furnace atomic absorption spectrometry (GFAAS) by using sequential multi-element determination of iron and zinc in water samples after preconcentration on multiwalled carbon nanotubes.

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## 2. Experimental

### 2.1. Spectrometer

An Analytik Jena ContraAA 700 high-resolution atomic absorption spectrometer equipped with a 300 W xenon short-arc lamp (Analytik Jena, Jena, Germany) as a continuum radiation source was used throughout these experiments. This new equipment comprises a compact high-resolution double echelle monochromator and a charge-coupled device (CCD) array detector with a resolution of about 2 pm per pixel in the far-ultraviolet range. In our research, a graphite furnace was used for atomization of analytes. After the measurement, data stored in the internal memory of the processing system were transferred to the computer for evaluation. The xenon short-arc lamp was operated at 9 A; 248.327 and 213.857 nm were selected as analytical lines for Fe and Zn, respectively. This spectrometer provides an efficient background correction by simultaneous measurement of atomic and continuous background absorption. The interference of fine-structured background of NO molecule on Zn 213.857 nm line was eliminated based on the reference spectrum registered for a 1 mol L<sup>-1</sup> HNO<sub>3</sub> solution and the least-squares background correction (LSBC). The primary line of iron was selected for the determination due to the highest sensitivity.

### 2.2. Reagents, chemical and gasses

Compressed high-purity argon obtained from Air Products (Warsaw, Poland) was used as a carrier gas.

Standard solutions of Fe and Zn were prepared from a 1000 mg L<sup>-1</sup> atomic absorption standard solutions (Merck, Darmstadt, Germany). Working standard solutions were prepared fresh each day by diluting appropriate aliquots of the stock solution in high-purity water.

Oxidized multiwalled carbon nanotubes with purity greater than 98% were purchased from Sigma-Aldrich (Sigma-Aldrich, Steinheim, Germany) and characterized by 6–13 nm outer diameter, 2.5–20 nm length, 10 μm average length and 220 m<sup>2</sup> g<sup>-1</sup> surface area.

The following chemical modifier solutions were used: magnesium modifier stock solution, 10.0 ± 0.2 g L<sup>-1</sup> Mg(NO<sub>3</sub>)<sub>2</sub>, palladium/magnesium modifier stock solution, 10.0 ± 0.2 g L<sup>-1</sup> Pd + Mg(NO<sub>3</sub>)<sub>2</sub>. All chemical modifier solutions were obtained from Merck, Darmstadt, Germany.

Nitric acid 65% (v/v), hydrochloric acid 32% (v/v) and sodium hydroxide 30% (v/v) of the highest quality (Suprapur, Merck, Darmstadt, Germany) were used.

High-purity water was used throughout the research: deionized water (DEMIWA 5 ROSA, Watek, Czech Republic) and doubly distilled water (quartz apparatus, Bi18, Heraeus, Hanau, Germany). The resistivity of the water was 18 MΩ cm.

### 2.3. Reference materials and water samples

Validation of the method described in this work was performed using two certified reference materials. The following materials were chosen: NIST SRM 1643e (Trace Elements in Water) supplied by the National Institute of Standards and Technology (NIST), Gaithersburg, USA and ERM – CA011b (Hard Drinking Water) supplied by LGC Limited, Teddington, UK. The certified reference values are available for elements for the assessment of the method accuracy.

In the research, four different water samples (seawater, lake water, mine water and tap water) were analyzed. The water samples were stored at 4 °C in polyethylene flasks maximum for 7 days.

### 2.4. Preconcentration procedure

MWCNT cartridge was prepared by placing 50 mg of the MWCNTs in an empty 1 mL polypropylene SPE-tube (Supelco, Bellefonte, USA). The

MWCNTs were weighed using an M2P microanalytical balance (Sartorius, Göttingen, Germany) with a resolution of 1 μg (electronic weighing range up to 2 g). The ends of the column were plugged with polyethylene frits of 20 μm porosity (Supelco, Bellefonte, USA) to hold adsorbent packing in the right place. Cartridge was preconditioned by washing with 10 mL of 1 mol L<sup>-1</sup> HNO<sub>3</sub> and double distilled deionized water. Then column was conditioned to the desired pH by buffer solution. A 12-port vacuum manifold BAKER SPE-12G (J.T. Baker, USA) connected to the vacuum pump (KNF NEUBERGER D-7800, Berlin, Germany) was used to control a flow rate during the preconcentration procedure. 150 mL of sample solution was passed through the column at a flow rate of 1 mL min<sup>-1</sup>. Then the metal ions retained on the column were eluted with 1 mL of 1 mol L<sup>-1</sup> HNO<sub>3</sub> at a flow rate of 1 mL min<sup>-1</sup>. The analytes in the eluent were determined by HR-CS GFAAS. Schematic diagram of the optimized analytical procedure is shown in Fig. 1.

### 2.5. Analytical procedure for sequential measurements with HR-CS GFAAS

The use of the spectrometer with a continuum source and a double monochromator with an echelle grating allows to perform a fast sequential multi-elemental determination. This makes it possible to reach any line within an extremely short period of time, much less than 1 s, as both the grating and prism are stepper motor controlled. This means that elements are determined sequentially under optimized but not compromised conditions, as would be the case for simultaneous multi-element determination.

The temperature programs used for determining selected elements in water samples and certified reference materials are shown in Table 1. The transient absorbance signals were integrated and both peak height and peak area signals were recorded. It was observed that the precision of the peak height measurement is better than that obtained using the peak area. For this reason, the peak height measurement was chosen for further analysis. Analytical blanks were also carried through the whole procedure to correct possible contamination from the reagents used for the sample preparation. The mean blank value was subtracted from the sample value after all calculations. Quantification of Fe and Zn was based on linear calibration curves verified by the method of standard addition. All limits of detection were calculated for unsmoothed data based on a three times the standard deviation replicate readings (n = 5) of the blank counts.

## 3. Results and discussion

The study included an investigation of the preconcentration of Fe and Zn using multiwalled carbon nanotubes, the atomization into the graphite furnace, and its application to practical analysis. The optimization parameters affecting the preconcentration of selected elements, atomization, and analysis technique will be discussed separately.

### 3.1. Analytical blank

There are several possible sources of contamination, for example multiwalled carbon nanotubes used as an adsorbent and the reagents used to optimize pH of sample solution. Blanks were determined using the same treatment procedure used for samples (solid-phase extraction procedure). The absolute blanks achieved for Fe and Zn were 0.01 and 0.005 ng, respectively.

### 3.2. Selection of instrumental conditions

The temperature programs used for Fe and Zn determination in water samples are shown in Table 1. The temperature of pyrolysis was optimized in the range of 300–1200 °C for all selected elements (Fig. 2). The pyrolysis curves were obtained using the atomization temperatures recommended by the producer of the instrument (2000 °C for Fe and 1300 °C for Zn). It was observed that absorbance increased with

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