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Determination of iron in natural and mineral waters by flame atomic absorption spectrometry

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Abstract: Simple methods for the determination of Fe in natural and mineral waters by flame atomic absorption spectrometry (AAS) are suggested. The results of the investigation of selectivity of the proposed AAS method proved that this procedure is not affected by high concentrations of other metals. The calibration graph for iron was linear at levels near the detection limit up to at least 0.10 μg ml^{-1}. For the determination of microamounts of iron in mineral waters, an extraction AAS technique was developed. Iron was retained as Fe-8-oxyquinoline complex and extracted into chloroform. The optimal conditions for the extraction of the iron complex were determined. The AAS method was applied to the determination of Fe in mineral waters and natural waters from different areas of Lithuania. The accuracy of the developed method was sufficient and evaluated in comparison with a photometric method. The obtained results demonstrated that the procedure could be successfully applied for the analysis of water samples with satisfactory accuracy.

Keywords: iron determination, flame atomic absorption spectrometry, preconcentration, water analysis.

INTRODUCTION

Metals are natural constituents of the environment. At high concentrations, trace metals can become toxic for living organisms and behave as conservative pollutants.[1–3] Metals enter the environment mainly by two means: (*i*) natural processes (for example, erosion of rocks, volcanic activity, forest fires) and (*ii*) processes due to human activities. An anthropogenic activity may add considerable amounts of polluting compounds, which will influence the existing natural aquatic system. Metals are frequently released in large quantities during different processes derived from human activities and may lead to major destruction of aquatic ecosystems. Moreover, human beings located at places contaminated by heavy metals could be especially sensitive to these contaminants due to bioaccumulation.

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The metals can accumulate in bone, hair and in some soft tissues, such as the liver, kidney, brain or lungs.[4,5]

At low concentrations, iron plays an important role in metabolic and fermentation processes, as an enzyme activator, stabilizer and functional component of proteins. Above trace levels, however, iron has other roles. It has been stated that for all trace elements that considered to be essential, including iron, there exists a fairly narrow "concentration window" between the essential and toxic levels. Iron is a moderately toxic element when compared with other transition metals. However, the toxic doses of iron and its compounds can lead to serious problems, including depression, rapid and shallow respiration, coma, convulsions and cardiac arrest.[6–8] Iron and its compounds have widespread industrial applications (constructional material for drinking-water pipes, food colours, coagulants in water treatment, pigments in paints and plastics); hence, large quantities of iron are discharged into the environment. Thus, appropriate knowledge of the iron content of natural water is very desirable. So, the toxicity of this element demands a fast and accurate method for its determination in water.

For the determination of trace metals in natural and mineral waters different spectrochemical methods are used. However, flame atomic absorption spectrometry (FAAS) is one of the most extensively used techniques for determining various elements with significant precision and accuracy. This analytical technique is remarkable for its selectivity, speed and fairly low operational cost.[9] However, in some cases there are many difficulties in determining traces of heavy metals in environmental samples due to insufficient sensitivity or matrix interferences. Thus, a preconcentration and/or separation step is necessary.[10–13]

Also the iron content in mineral water samples is usually lower than the detection limits reported for this element by AAS. Thus, a preconcentration of analytes should be performed before their final analytical quantification. For the AAS determination of different metals, including iron, many methods, such as extraction, coprecipitation, electrodeposition, ion exchange and accumulation with biological organisms, have been used for preconcentration of trace elements.[6,14–17] The aim of the present study was to propose an extraction procedure for the preconcentration of iron ions in water prior to their AAS determination. The experimental conditions for the extraction of the 8-oxyquinoline complex of Fe into chloroform (extraction time, amount of extractant, pH of the aqueous solution, *etc.*) were optimised. This paper also reports the application of the proposed method to the determination of Fe in mineral and natural water samples from different areas of Lithuania. The obtained results are compared with the results of photometric determination.[18,19]

EXPERIMENTAL

A Hitachi 170-50 (Japan) flame atomic absorption spectrometer equipped with hollow cathode lamps was used for the analyses. The instrumental parameters were adjusted according to the manufacturer's recommendations. An Fe hollow cathode lamp operating at 248.3 nm was used as the radiation source. The lamp current was set at 15 mA. The flame composition was: propane–butane (gas pressure 0.1 kg/cm^2), and air (gas pressure 1.5 kg/cm^2). For comparison, the amount of iron in the samples was determined by photometric analysis with a KFK-3 photometer. Fe was determined in aqueous medium with 1,10-phenanthroline. The method is based on the complexation reaction between Fe^{2+} ions at pH 3–3.5. The reduction of Fe^{3+} to Fe^{2+} was performed in acidic medium using hydroxylamine. The photometric measurements were carried out at a wavelength of $\lambda = 510$ nm. A pH meter Mettler-Toledo MP220 was employed for measuring the pH values of the aqueous phase.

Double-distilled water and analytical-grade reagents were used in all the experiments. A stock standard solution of iron, 1 mg ml^{-1}, was prepared by dissolving an appropriate amount of metallic iron (99.99 % purity) in dilute nitric acid (1:1). The iron ion standard solution was diluted daily to obtain a working standard solution of iron (100 μg ml^{-1}). Standard solutions of other metals, 2×10^4 μg ml^{-1}, were prepared by dissolving an appropriate amount of: (*i*) metallic Cd, Co, Cu, Mn, Ni, and Pb or ZnO in dilute nitric acid (1:1); (*ii*) metallic Al and Mg or CaO in dilute hydrochloric acid (1:1); (*iii*) metallic Cr in dilute sulfuric acid (1:4) ; (*iv*) metallic Bi in aqua regia; (*v*) salts $BaCl_2$, KCl, Li_2SO_4, NaCl, and $Sr(NO_3)_2$ in double-distilled water.

Solutions of iron, 0.2 μg ml^{-1}, along with appropriate amounts of interfering ions were prepared for the evaluation of the selectivity. An iron solution of the same concentration without additives was used as the reference solution. To determine the influence of pH, solution of 2 M HCl or NH_3 (1:1) were added to the to be analysed solutions.

A calibration curve for the determination of iron in mineral water samples by AAS was established using the following procedure. First, an appropriate amount of working standard solution of iron was transferred to an extraction tube containing 100 ml of double-distilled water. Then, 1 ml of a 10 % 8-oxyquinoline solution was added to the extraction tube. The obtained solutions were extracted for 2 min with chloroform. Finally, after removing the organic solvent by slow evaporation, the residue was dissolved in 10 ml of nitric acid (1:1), transferred to a 100-ml volumetric flask and filled to the mark with double-distilled water. The calibration solutions were prepared in the concentration range of 0.1–2.0 μg ml^{-1} Fe. For the determination of iron in mineral waters, the to be analysed sample (100 ml) was transferred into an extraction tube and the same preconcentration procedure was followed.

The amount of iron in natural water samples was found to be higher than the detection limits. Therefore, the determination of iron was performed directly without preconcentration. To establish the calibration curve for the determination of iron in natural water samples by AAS, an appropriate amount of working standard solution of iron and 5 ml of 2 M HCl was transferred to a 100-ml volumetric flask and filled to the mark with double-distilled water. The calibration solutions were prepared over the concentration range of 0.1–4.0 μg ml^{-1} Fe. For the determination of iron in natural waters, 25 ml of the to be analysed sample and 5 ml of 2 M HCl were mixed in a beaker. The mixture was boiled gently and partially evaporated (to approximately one half of the initial volume), cooled to room temperature, transferred to a 25-ml volumetric flask and filled to the mark with double-distilled water.

RESULTS AND DISCUSSION

The analytical features of the developed procedure were found to be comparable to those reported in previous papers for the determination of iron in environmental samples. The calibration curve obtained under the best conditions showed a linear correlation within the concentration range from 0.1–4.0 μg ml^{-1}. The influence of the different inorganic acids (HCl, HNO_3, and H_2SO_4) used in the analytical procedure on the absorbance of iron was estimated. It was determined that the nature of the acid does not influence the analytical signal significantly. It is inter-

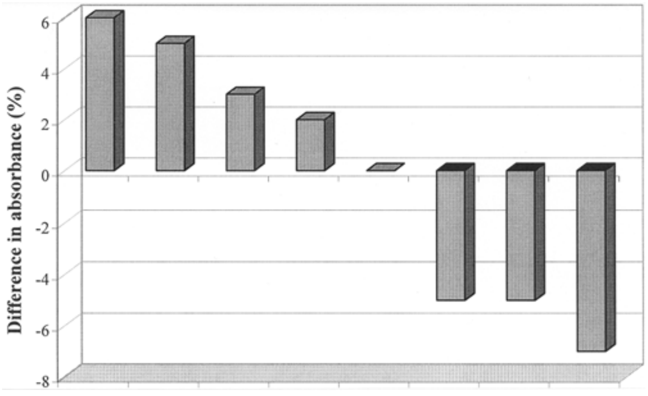

Fig. 1. Effect of the concentration of Zn, Li, Ca, Na, K, Ni, Mg, and Cu ions on the analytical signal of Fe (Fe:M = 1:10 000).

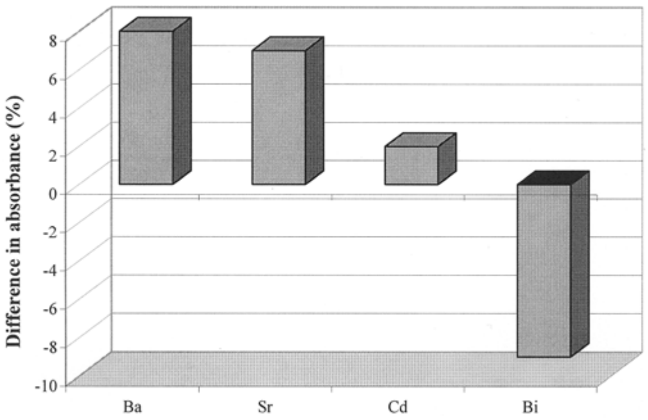

Fig. 2. Effect of the concentration of Ba, Sr, Cd, and Bi ions on the analytical signal of Fe (Fe:M = 1:5 000).

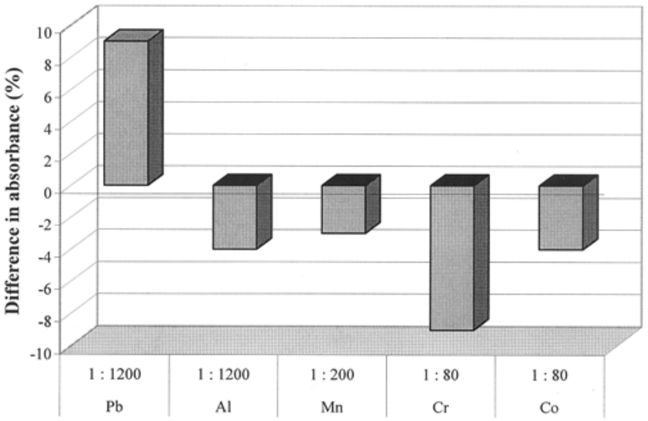

Fig. 3. Effect of the concentration of Pb, Al, Mn, Cr, and Co ions on the analytical signal of Fe.

esting to note that the absorbance of the iron solutions showed no difference for approximately three months.

An attempt was also made to examine the effects of representative potential interfering species[1,3,4] on the determination of iron by FAAS. In order to determine the selectivity of the method, solutions containing iron and other metal ions were prepared and analysed. The Fe/M interfering ratios were considered as limiting when the error of the determination did not exceed ±10 %.[9] The selectivity studies are summarized in Figs. 1–3.

Evidently, Zn, Li, Ca, Na, K, Ni, Mg, and Cu have the lowest influence on the absorbance of iron (Fig. 1). These metals did not interfer with the determination of iron by AAS even if their concentrations were 10 000 times higher than that of Fe. A two times higher influence on the determination of iron was observed for Ba, Sr, Cd and Bi (see Fig. 2). From Fig. 3, the conclusion can be drawn that Cr and Co have the highest interfering effects on the determination of iron. These metals could only be tolerated up to concentrations 100 time higher than that of Fe. According to their interfering effect, the examined metals can be ordered as Cr, Co > Mn > Pb, Al > Cd, Ba, Bi, Sr > Zn, Li, Ca, Na, K, Ni, Mg, Cu. These results clearly indicate the high level of selectivity of the AAS method and no masking reagents are required for the successful determination of iron in water samples.

The content of iron was determined in several natural water samples from different regions of Lithuania. Since the amount of iron in the natural water samples was found to be higher than the detection limit, the determination of iron by AAS was performed directly without preconcentration. The results obtained for iron determination by AAS method were compared with those achieved by a conventional photometric method and are summarized in Table I.

TABLE I. Results obtained for the determination of iron in natural water samples ($n = 5$, $P = 0.95$), with standard deviations (%) in parentheses

Sample	Iron found by the AAS method/mg l^{-1}	Iron found by the photometric method/mg l^{-1}
Drinking water (Vilnius city)	0.32 (2.8)	0.36 (5.0)
River Neris (Vilnius city)	2.20 (2.0)	1.95 (5.2)
River Muse (Vilnius region)	0.75 (3.2)	0.83 (4.5)
Lake Gulbinai (Vilnius region)	0.58 (3.5)	0.52 (4.)
Lake Žalieji ežerai (Vilnius region)	0.98 (2.5)	0.88 (6.3)

As can be seen, the concentration of Fe in the natural water samples ranged from 0.32 mg 1^{-1} (drinking water of Vilnius city) to 2.2 mg 1^{-1} (rives Neris). Besides, the comparison of the results obtained by both methods suggests that the agreement between the two methods is satisfactory.

Preconcentration of iron from mineral water samples was necessary because its concentration is usually too low to be determined directly by AAS. In order to obtain accurate and precuse analytical results, an efficient preconcentration step should be performed before conducting the measurement. In the present study, an extraction procedure for the concentration of the analyte has been suggested. To demonstrate the suitability of the proposed method, the conditions for the extraction of the Fe-8-oxyquinoline complex sith chloroform have been investigated.

Knowing that the extraction procedure involves the transfer of the complex through the aqueous/organic phase interface and that the efficiency of this procedure depends on the contact time, the effect of extraction time on the analytical signal of the iron was estimated (Fig. 4).

As can be seen, the absorbance is stable already after 2 min. Consequently, this time could be considered as the time necessary for complete extraction.

The effect of extractant volume on the analytical responses is shown in Fig. 5.

A variation of the analytical signal as a function of the extractant volume is evident. From these results, 10 ml of chloroform was chosen as the otpimum volume.

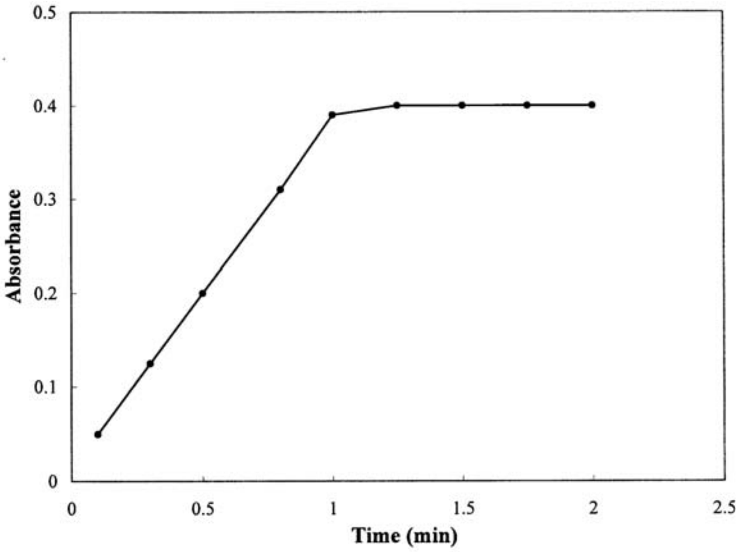

Fig. 4. Influence of the extraction time on the analytical signal of Fe. Preconcentration step: 0.2 μg ml^{-1} Fe; pH 5.0; 10 ml $CHCl_3$.

In order to optimize the preconcentration conditions, the extraction was also performed at different pH values of the aqueous solution.[14,20] Fig. 6 shows that the optimal pH values were in the range of 2.0–7.0. These results are understandable, since a better complexation occurs in this pH range.

The recovery of heavy metals when extracted as different complexes from water samples in some cases depends on the total volume of the to be analyzed sample.[21] Therefore, the limitting amount of sample, which would still be suitable for quantitative extraction, is a very important parameter. It can be seen from Fig. 7 that there is no significant effect on the analytical response for sample volumes up to 100 ml.

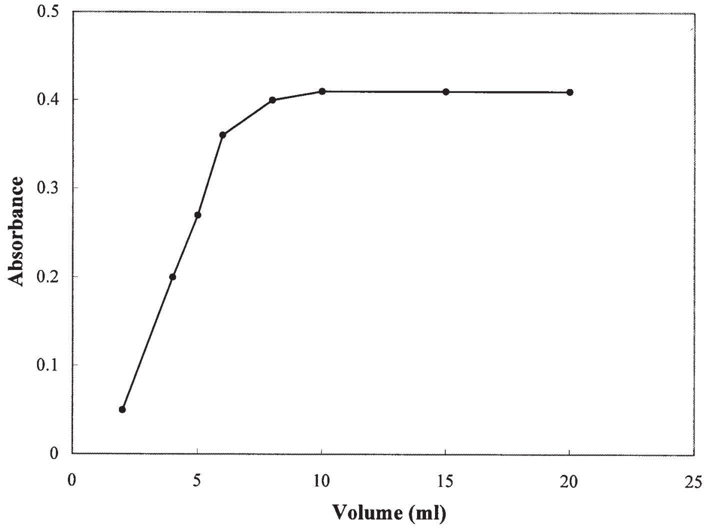

Fig. 5. Influence of the extractant volume on the analytical signal of Fe. Preconcentration step: 0.2 μg ml^{-1} Fe; pH 5.0; 2 min extraction time.

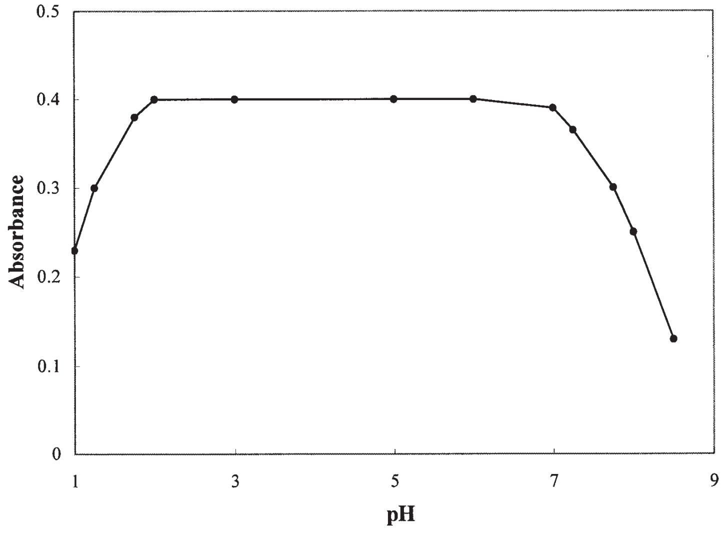

Fig. 6. Influence of the pH of the aqueous solution on the analytical signal of Fe. Preconcentration step: 0.2 μg ml^{-1} Fe; 2 min extraction time; 10 ml $CHCl_3$.

The developed preconcentration method was applied to determine Fe in various mineral water samples from Lithuania. The results obtained for iron with the proposed AAS method were compared with those achieved by a photometric method and are summarized in Table II.

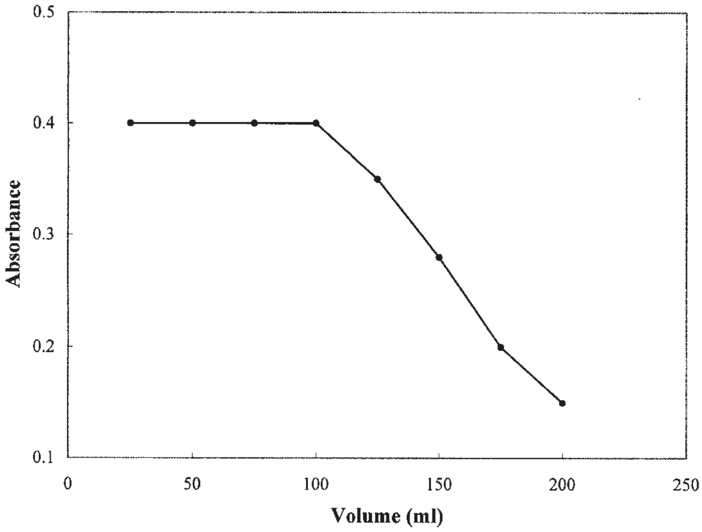

Fig. 7. Dependence of the analytical signal of Fe on the volume of the to be analyzed water sample. Preconcentration step: 0.2 μg ml^{-1} Fe; pH 5.0; 2 min extraction time; 10 ml $CHCl_3$.

TABLE II. Results obtained for the determination of iron in mineral water samples ($n = 5$, $P = 0.95$), with standard deviations (%) in parentheses

Name of the mineral water	Iron found by the proposed AAS method/mg l^{-1}	Iron found by the photometric method/mg l^{-1}
Tichė	0.025 (3.5)	0.020 (5.5)
Birštonas	0.032 (3.0)	0.036 (6.8)
Birutė	0.050 (3.0)	0.058 (7.8)
Druskininkai	0.054 (4.2)	0.050 (7.0)
Vytautas	0.085 (4.5)	0.079 (8.0)

As can be seen, the concentration of Fe in mineral water samples ranged between 0.025 and 0.085 mg l^{-1}. In addition, a comparison of the results obtained by both methods suggests that the agreement between the two methods is satisfactory. The results shown in Table II confirm that the developed extraction flame atomic absorption spectrometric methodology can be successfully applied to the determination of Fe in mineral water samples. In comparison with the photometric method, the proposed procedure is faster, more selective and not so labor intensive. Moreover, the determined relative standard deviations for the atomic absorption spectrometric measurements are smaller than those of the photometric method, indicating the developed method is more accurate.

CONCLUSIONS

A procedure for the determination of trace amounts of Fe in mineral water is described. The method combines atomic absorption spectrometry with preconcentration of analyte by extraction. The complexation of iron with 8-oxyquinoline was efficient enabling its preconcentrate from water. The developed preconcentration permitted the determination of iron in mineral water samples from Lithuania, the analysis of which would be restricted due to the poor sensitivity of direct flame atomic absorption spectrometry. The determination of iron in natural water samples (selected from different areas of Lithuania) was performed directly without preconcentration. Both methodologies showed excellent reproducibility and accuracy. In addition, the analytical costs of the proposed extraction method are low. It is also simple, quick and the operation techniques are fairly easy. Thus, the proposed preconcentration methodology offers a simple and sensitive alternative to other preconcentration techniques. Moreover, the procedure would appear to have potential for application in the determination of iron in seawater, groundwater and different manufacturing wastewater.[22–25] Consequently, this extraction atomic absorption spectrometric determination of iron can be suitable for routine application in water analysis.

ИЗВОД

ОДРЕЂИВАЊЕ ГВОЖЂА У ПРИРОДНИМ И МИНЕРАЛНИМ ВОДАМА ПЛАМЕНОМ АТОМСКОМ АПСОРПЦИОНОМ СПЕКТРОСКОПИЈОМ

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Предложена је једноставна метода за одређивање Fe у природним и минералним водама атомском апсорпционом спектроскопијом (AAS). Резултати испитивања селективности предложене AAS методе показали су да на ову процедуру не утиче присуство високих концентрација других метала. Калибрациони дијаграм за гвожђе је линеаран од детекционе границе до око 0,10 μg ml^{-1}. За одређивање микроколичина гвожђа у минералним водама разрађена је екстракциона AAS техника. Гвожђе се преводи у Fe-8-оксихинолнски комплекс и екстрахује хлороформом. Одређени су оптимални услови за екстракцију комплекса гвожђа. AAS метода је примењена за одређивање Fe у минералним и природним водама из различитих области Литваније. Тачност развијене методе је довољна и упоредива са фотометријском методом. Добивени резултати показују да се предложена процедура може успешно применити за анализу узорака воде са довољном тачношћу.

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