

TOTAL IRON DETERMINATION IN DRINKING WATER USING STRIPPING VOLTAMETRY TECHNIQUE

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Abstract

The paper describes the development and optimization of an analytical technique based on stripping voltammetry for iron determination in drinking water. The method is based on AdSV technique and HMDE electrode. Along with the complexing agent, the catechol, a pH buffering phosphate solution (pH 7) is added. The reference electrode is Ag/AgCl/KCl. The principle of the method is the following: iron complexation by the catechol, adsorption of the complex on the drop of the electrode followed by the stripping stage and practical resolubilization of the complex. Two concentration ranges were tested: from 10 to 50µg/L and between 25 and 150µg/L. After calibration curves were plotted, real drinking water samples enriched with iron standard solution were analysed.

Laboratory test results indicate a very good recovery rate for the analytical trials performed (100.44%, 104.07%, 103.49%). However, the average value of the recovery rate following all additions and replicates – the precision grade is 102.66%. The correlation factor between the two curves was 0.9936 for the interval of 10- 50µg/l and 0.9989 for the interval of 25-150µg/L. The optimised method can be easily applied in case of drinking water resources both surface and underground water.

Keywords: *stripping voltammetry, iron speciation, HMDE*

Introduction

Various techniques may be used for the determination of metals in water samples [1]. Given their toxicity of metals and ability to bioaccumulate [2], the legislation is imposing lower maximum concentration limits. Because of that reason analytical techniques with higher sensitivity and selectivity [3, 4] is needed. Electrochemical techniques are successfully suitable for such determinations having certain advantages: are simpler, sensitive, precise, present a fast response and imply lower financial costs [5-7]. Among these, electrochemical stripping voltammetry is frequently used [8, 9]. Stripping voltammetry allows not only the determination of trace iron in water but also the determination of iron species [10]. In this paper is presented a method based on stripping voltammetry for the determination of total iron and iron species in drinking water samples. It should be noted that in the case of iron, both Fe (II) and Fe (III) are electrochemically active. The iron is complexed by catechol. The complex formed is adsorbed on the drop of working electrode followed by the stripping step and practical resolving of the complex in solution. In addition to the complexing agent, which is catechol, a phosphate buffer solution is used. The pH of the buffer solution is 7. The reference electrode is Ag / AgCl / KCl.

Next, to determine the iron species, the following steps are respected: bipyridyl is added to the water sample in order to selectively and totally complex and mask Fe (II). In this case, electrochemical signal will be given only by Fe (III). A reaction time of 20-30 minutes is required.

In all literature studies is recommended to keep the natural pH of surface or drinking water as appropriate. Therefore, a sodium phosphate buffer solution with a pH of 7 is used. After the addition of buffer, the analysis is performed on the sample following the same procedure as for the determination of total iron. After determining the total iron and Fe (III) in the sample, the Fe (II) can be calculated.

Increasing the concentration of bipyridyl leads to an increased degree of masking Fe II. Studies have shown that to mask Fe II 2 nM by 100% in necessary to use a 10 μ M solution of bipyridyl. Below this value, the degree of masking decreases to 70% at a concentration of 2 μ M bipyridyl while excessive increase of the bipyridyl concentration leads to inhibitory effects for the electrochemical processes.

Experimental part

Following the laboratory tests, the series of parameters presented in table 1 were selected.

Table 1. Working parameters set for determining total iron in drinking water for different working domain

Working electrode	HMDE
Stirrer	2000rpm
Purging time	300s
Deposition potential	Without deposition
Deposition time	0s
Equilibration time	10s
Pulse amplitude	50mV
Start potential	-250mV
End potential	-600mV
Voltage step	6mV
Sweeping time	0,3s
Peak potential	-360mV

UV digestion of sample in the presence of hydrogen peroxide and hydrochloric acid is required, prior to analysis, only for groundwater or surface water samples to remove the influence of organic compounds that can either mask and complexate iron or have surfactant properties and thus can be adsorbed on the mercury drop of the work electrode. The working domain was chosen between 10 and 50 micrograms / L.

A calibration curve was drawn, and a sample of tap water was analyzed. The analyzed sample was then enriched with increasing concentrations by standard iron solution. So when plotting the calibration curves or for sample determinations, as such or in enriched sample, at least two replicates for each point on the curve were performed.

Figure 1 shows the voltamogram for iron calibration curve over the range of 10-50 μ g/L obtained after five additions and three replicates and in Figure 2 is shown the calibration curve of total iron in the range 10-50 μ g/L.

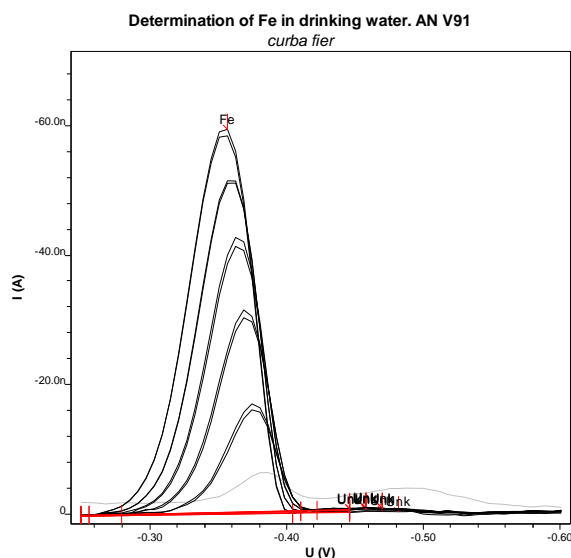


Fig. 1. The voltammogram of the calibration curve

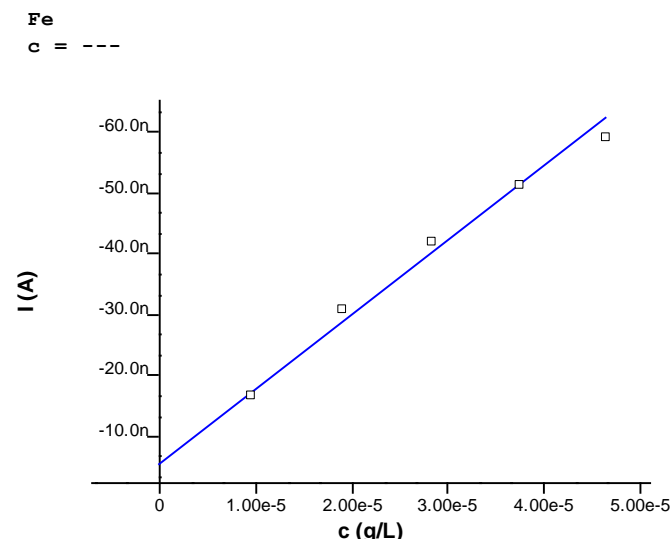


Fig. 2. The calibration curve of total iron in the range 10-50 µg/L

For the calibration curve with the field work in the domain of 10-50µg/L, a very good correlation coefficient of 0.994 is obtained. After plotting the calibration curve, tap water sample was subjected to analysis (Fig.3.si Fig.4)

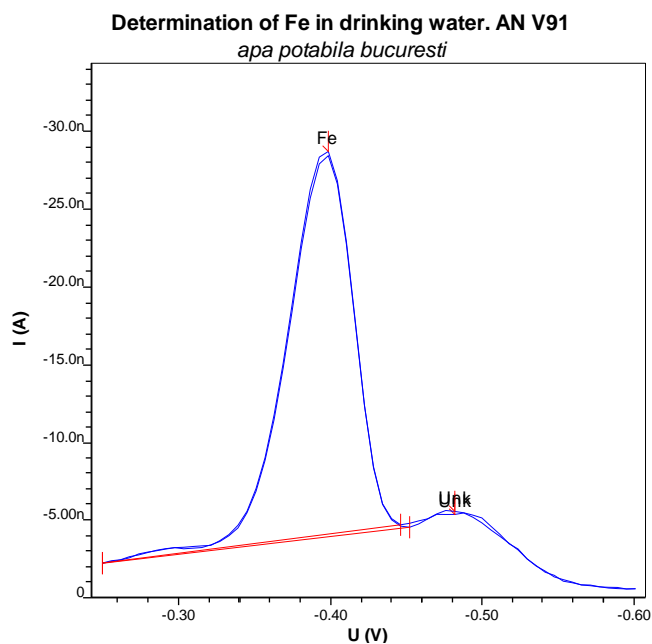


Fig.3. Voltamogram of total Fe determination in tap water

Fe
 $c = 16.191 \text{ ug/L}$
 $+/- 0.706 \text{ ug/L (4.36\%)}$

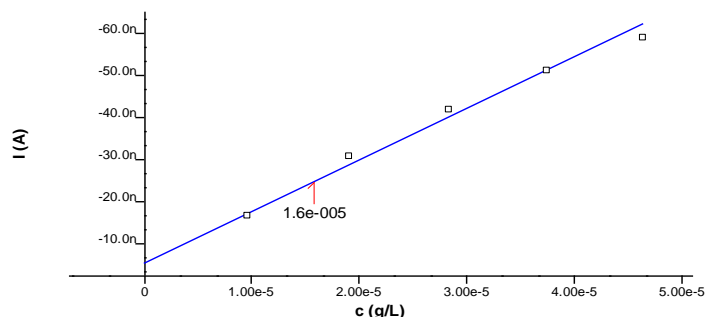


Fig.4. Determination of total iron in tap water

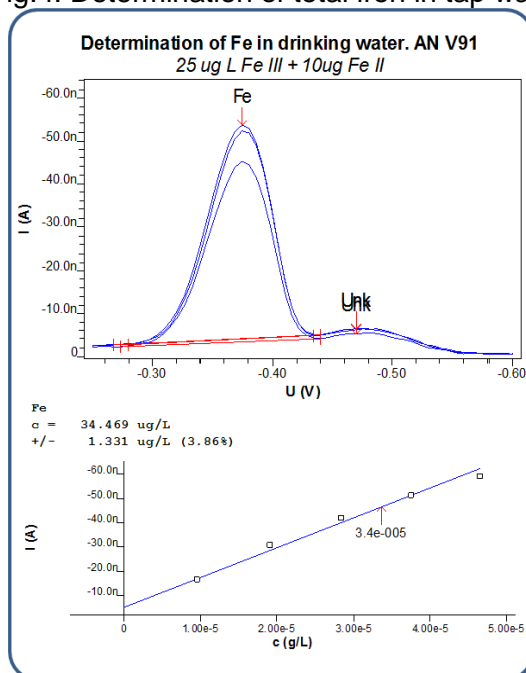


Fig.5. Determination of recovery following the addition of mixed standard solutions

To test the method for determination of iron species in drinking water, 25 µg/L Fe (III) and 10 µg/L of Fe (II) were added. Existing iron in the sample was set as blank, then switched to total iron determination.

After the addition of iron standard solutions, results obtained from three repetitions lead to a value retrieved of 34.47g /L. The results are shown in Figure 5.

The recovery grade is of 98.48% in case of tap drinking water. The values obtained represent the average of three replicates.

As described above, after determining the total iron in the sample followed the determination of Fe (III). For this purpose, the drinking water was treated with bipyridyl with the purpose of total masking and complexation of the Fe (II). After twenty minutes, the sodium phosphate buffer solution was added and the determination of Fe (III) was performed. The results are presented in the voltamograms from Fig.6..

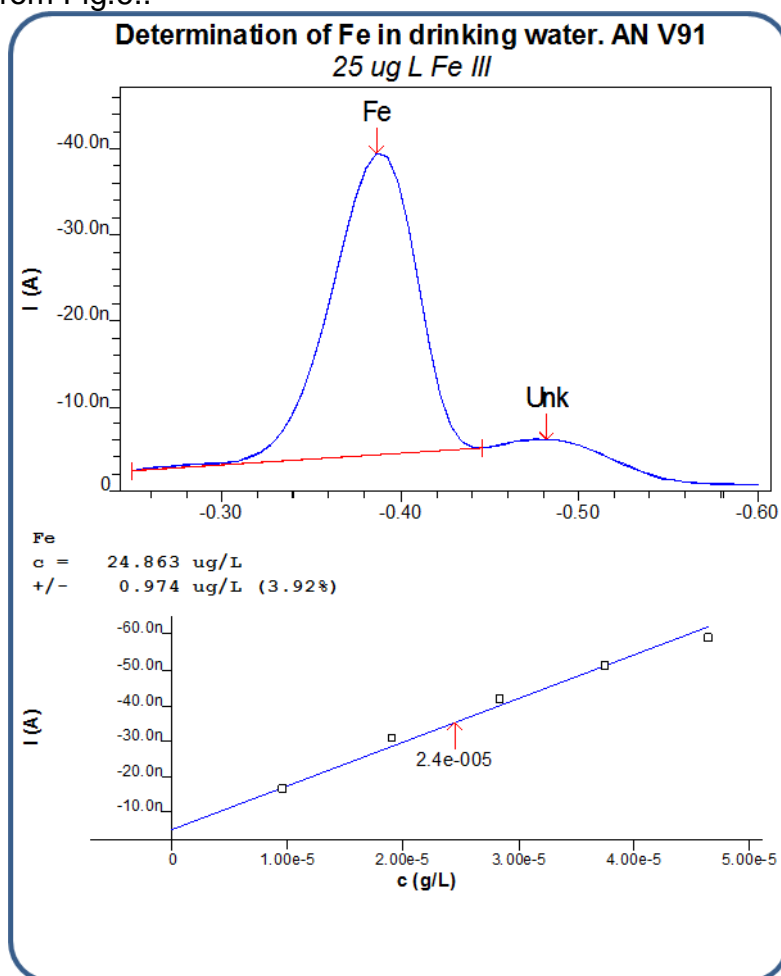


Fig 6. Determination of recovery following the addition of mixed standard solutions and complexation with bipyridyl

The recovery rate obtained after masking Fe (II) is 99.45% in the case of tap water. The values obtained represent the average of three replicates.

CONCLUSIONS

The laboratory tests were conducted using non-standardized methods. The results obtained from laboratory tests prove a very good recovery rate for measurements performed (98.48% for the

determination of total iron and 99.45% for the determination of Fe (III) by masking Fe (II) with bipyridyl).

The average degree of recovery after all additions and replicates performed, is 98.97%. The correlation coefficient for the calibration curve was 0.994 for the concentration interval of 10-50 µg/L. The method can be applied with confidence for drinking water analysis. The determinations performed using this method are achieved with low costs and requires little time.

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