THE DETERMINATION OF IRON IN WINE BY SQUARE WAVE VOLTAMMETRY

K.Stojanova; I.Spirevska; S.Petrovska-Jovanović

Institute of Chemistry, Faculty of Science, University "St. Kiril and Metodij", POB 162, 91000 Skopje, Arhimedova 5, Macedonia; Tel: 398 91 221 033

Abstract

A new square wave voltammetric method for the determination of iron(III) content in aqueous solutions is developed. The iron(III) ions give well defined voltamogram ($E_p = -1.592$ V, vs Ag/AgCl) in kaliumnatriumtartarate ($c = 0.20$ mol dm^{-3}) and ammoniacal buffer ($c = 0.15$ mol dm^{-3}) as supporting electrolyte. The relative standard deviation is about 4% and the detection limit is 0.1 ppm. Other ions, such as Pb(II), Cd(II), Ni(II), Co(II) and Cu(II) do not interfere. The method is applied to determine the iron content in some sorts of wines from Macedonia. The mass concentration of iron in wines varies from 0.35 mg dm^{-3} to 4.38 mg dm^{-3}. The obtained results are very close to those obtained by atomic absorption spectrophotometric method.

Introduction

The reliable knowledge of the level of heavy metals in human being accumulation and level in the food chains and environment of human populations have been recognized in their significance and are a matter of great concern for national authorities responsible for environmental protection.

The wine contamination by heavy metals can come from various sources. The grapes may be contemned by atmospheric fallouts, or by the use metal-containing pesticides. The iron is mineral element that is present in wine and is important to the wine technologist. It may cause cloudiness or a color change when is present in a large excess.

Several authors have already investigated the determination of iron in wine. In recent years atomic absorption spectrophotometry has been recommended for the analysis of iron in wine [1,2]. In the routine analyses of iron in wine spectrophotometric methods are often used [3], but the spectrophotometric procedures are usually rather complicated and time consuming. Then, paper chromatography [4] and chelating resin [5,6] are used for separation and concentration of iron in wine. Some workers [7], employed combined detection system for HPLC, which consists of an electrochermal detector for iron(II) detection and an online flame-AAS detector for total iron in wine.

Polarography and related techniques have rarely been used in this analyses [8,9]. However, the high sensitivity and selectivity of these techniques, combined with inexpensive instrumentation, make them eminently suited for this task.

In this work an approved electroanalitical method for the determination of iron, with a new much more efficient approach is described. The measurements are performed by square wave voltammetry (SWV), at the static mercury drop electrode (SMDE). This new method is applied to the determination of iron content in some wines from Macedonia.

Experimental

A Princeton Applied Research (PAR) Model 348 B Polarographic Analyzer System with three electrodes was used. The static mercury drop electrode was used as a working electrode, the reference was a saturated (KCl), Ag/AgCl electrode and a Pt-wire was auxiliary electrode.

A standard iron(III) solution ($\gamma_{Fe3+} = 0.1$ g dm^{-3}) was prepared by dissolving $NH_4Fe(SO_4)_2$ .12 H_2O in redestilled water. The iron content was determined volumetrically using EDTA as a titrant [10].

Ammoniacal buffer (c=0.5 mol dm^{-3}) was prepared from aqueous ammonia (25%) and NH_4Cl. Kaliumnatriumtartarate ($KNaC_4H_4O_6..4H_2O$) and the other chemical were analytical grade (Merck).

The voltametric measurements were performed under the following experimental conditions:.

- initial potential   -1.10 V; .
- final potential   -1.80 V;
- frequency   100 Hz;
- scan increment   2.0 mV;
- pulse height   20 mV;
- deposition time   0 s;
- equilibrium time   5 s.

All experiments were performed at a room temperature, and the solutions were degassed with highly purified nitrogen during 240 s.

The samples of wine were prepared on the following way: In a porcelain crucible 50 cm^3 of investigated wine was evaporated on water bath. The residue was heated to 600°C in a muffle furnace for 2 hours. After being cooled, the ash was treated with 2 cm^3 of conc. HCl and evaporated on a water bath. This operation was repeated. The residue was dissolved in a HCl and added 2 g of kaliumnatriumtartarate and some Na_2SO_3. The solution was neutralization with a slight excess of conc. NH_4OH.

To the aliquot of 7 cm^3 of that solution, 3 cm^3 ammoniacal buffer (0.5 mol dm^{-3}) was added for analyses.

For the statistical treatment of the data, the programme package Statgraph was used.

The content of iron was determined in samples of the ten white and red wines from different region of Macedonia.

Results and discussion

The iron(III) ions in aqueous solution of kaliumnatriumtatarate (c = 0.20 mol dm^{-3}) and ammoniacal buffer (c = 0.15 mol dm^{-3}) as supporting electrolyte give two SW peaks (Fig.1). The more positive one ($E_P = -1,216$ V) is derived by the reduction of iron(III) from tartarate complex to iron(II), and the other ($E_P = -1.592$ V) by the reduction of iron(II) to elementary iron. As seen, the more negative peak is very well defined and can be used for analytical purpose.

It is well known that the peak current and peak potential depend on parameters of excitation SW signal [11]. Therefore, working condition were varied and the optimal experimental parameters were found.
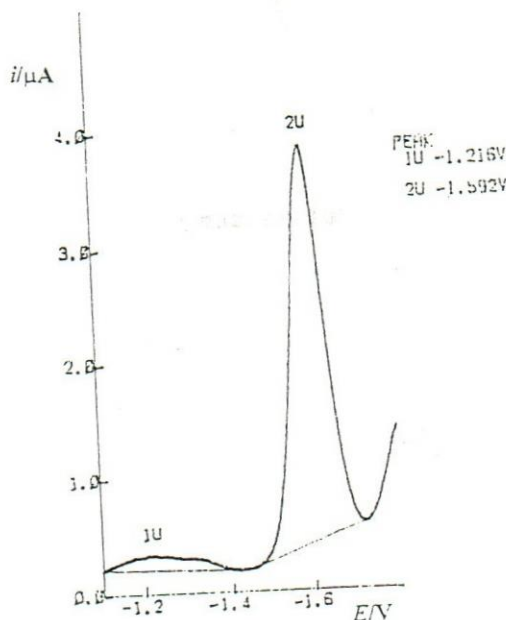
Fig.1 Square wave voltamogram of iron(III) in kaliumnatriumtartarate and ammoniacal buffer

In the order to examine the effect of some other metal ions solutions containing Co(II), Ni(II), Pb(II), Cu(II) or Cd(II) and Fe(III) ions were studied. It is found that, their effect on the peak current and peak potential is negligible.

The further investigation showed that there is a good linear relationship between peak current and concentration of iron(III) ions in the range of 10^{-6} mol dm^{-3} to 10^{-4} mol dm^{-3}.

The linear regression analyses of the calibration curve (in the range of 1 ppm to 30 ppm) gave a correlation coefficient of 0.997. The equation of calibration curve is following:

$$i_p \ / \ \mu A = 0.200 \ \gamma(Fe) \ / \ ppm + 0.203$$

Measurement on seven solutions (containing 5 ppm iron(III)) gave a relative standard deviation below 4%. The detection limit was about 0.1 ppm.

The described method was applied to the determination of the iron content in a different samples of wines produced in Macedonia. Standard additions methods were employed to quantify the peak currents. The results showed that the iron content in the studied wines varied from 0.35 to 4.38 mg dm^{-3} (Table 1).

165

Table 1
Iron content in the analyzed wines from Macedonia

Number	Name of wine	χ(Fe) ppm
1	Red wine Gostivar 1992	0.35
2	Red wine Gostivar 1993	3.93
3	Red wine Tetovo 1991	2.86
4	Macedonian Royal Reserve 1985	1.35
5	Merlot-Ohrid	3.47
6	Smederevka 1990	4.38
7	Ohridia 1991	1.69
8	Red wine Bitola 1992	1.20
9	White wine Bitola 1992	1.25
10	Red wine Skopje 1992	1.61

For comparison purposes, the iron content in the wines determined by the atomic absorption spectrophotometric method. The obtained results were very close to those obtained by square wave voltammetric method.

Also, to confirm the accuracy of the voltammetric method a known amount of iron(III) ions was added to samples of wine. The results showed a mean recovery of about 98%.

Conclusion

It can be concluded that the described square wave voltammetric method with kaliumnatriumtartarate and ammoniacal buffer as supporting electrolyte is rapid and very convenient to obtain reliable information on the iron content in aqueous solutions. The relative standard deviation is below 4%. The cobalt(II), nickel(II), copper(II), lead(II) and cadmium(II) ions do not interfere.

The method was successfully used to determine the iron content in different wines from Macedonia.

166

References

[1] Lipis B. V., Pchelintsev A. M., Spector L. A.: Atomic -Absorption Determination of Iron and Copper in Wines and Juices, Sadovod. Vinograd. Vinodel. Mold., 5, p.38-40 (1968)

[2] Harju K., Ronkainen P.: Analysis of Wines for Metals Using Atomic-Absorption . Spectrophotometry, Z. Lebensm.-Unters. Forsch., 170(6) p.445-8 (1980)

[3] Konrad H.: Colorimetric Determination of Iron in Wine with Sulfosalicylic Acid, Nahrung, 4, p.365-73 (1960)

[4] Mokhnachev I. G., Serdyuk L. C.: Determination of Iron in Wine, Vinodelie I Vinogradarstvo, 24(1), p.22 (1964)

[5] Chizuko S., Mitsuhiko T.: Separation and Concentration of Trace Heavy Metals in Food with Chelating Resin, Bunseki Kagaku 33(9), p.500-3 (1984)

[6] Ajlec R., Stupar J.: Determination of Iron Species in Wine by Ion-exchange Chromatography-Flame Atomic Absorption Spectrofotometry, Analyst, 114, p.137-142 (1989)

[7] Weber G.: Speciation of Iron Using HPLC with Electrochemical and Flame-atomic Absorption Spectrometric (AAS) Detection, Fresenius'Zeitchrift fur Analytische Chemii, 340(3), p.161-5 (1991)

[8] Agarwel S., Kumar A., Jain M.: Polarographic Determination of Copper, Iron and Bismuth after Extraction into Molten Naphthalene with Diacetyl Oxime Thiosemicarbazone, Zhurnal Analiticheskhoi Khimii, 46(5), 904-11 (1991)

[9] Wang J., Mannino S.: Application of Adsorptive Stripping Voltammetry to the Speciation and Determination of Iron(III) and Total Iron in Wines, Analyst, 114(5), p.643-5 (1989)

[10] Complexometric Assay Method with Titriplex, Ed. Merck, Darmstadt 1982, p.38

[11] O'Dea J., Osteryoung J., Osteryoung R.: Theory of Square Wave Voltammetry for Kinetic System, Analytical Chemistry, 53, 4. p.695 (1981)