ACTA TECHNICA CORVINIENSIS – BULLETIN OF ENGINEERING

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THE HEAVY METALS MONITORING IN CANNED VEGETABLES MIX

Abstract:
The paper proposes some possibilities for heavy metals detection in canned vegetables mix: Cr, Fe, Pb, Cd, Sn, Al, Zn, As . The heavy metals concentrations have been determinate by AA spectrometry and electrochemical methods: cyclic voltammetry. The monitoring of heavy metals in canned vegetables mix can help evaluate and improve the insufficiently developed technology.

Keywords:
vegetables mix, heavy metals, AA spectroscopy, cyclic voltammetry

INTRODUCTION

Vegetables mix and similar products are widely used for taste enhancement of various food products. Apart from their taste properties they also have a high nutritive value due to the content of easily retainable sugars, vitamin C, carotenoids and mineral salts.

Vegetables mix is a produce conserved through decrease in humidity, thus preventing the evolution of microorganisms. Microorganisms require a certain minimum amount of water to develop; bacteria require 35%, yeasts 25% and molds only need 10%.

EXPERIMENTAL

Samples preparation

Vegetables mix products have been weighed and treated by concentrated nitric acid (67%, Merck, heavy metals free). Samples digestion has been achieved in a 1000W MWS-2 – Berghof type microwave oven using a three-step program: $T_1=160^oC$, $t_1=15$ min., $P_1=40\text{-}60\%$ from total power, $T_2=210^oC$, $t_2=15$ min., $P_2=60\text{-}80\%$, $T_3=210^oC \rightarrow 100^oC$, $t_3=15$ min., $P_3=0\%$.Thus resulted solutions have been completed with ultrapure water (RO System Operating Barnstead apparatus) to equal volumes in 25 ml calibrated flasks.

Methods of analysis. AA Spectrometry

The heavy metals content has been determinated by AA spectrometry (International Standard ISO 15586:2003) and cyclic voltametry (Koryta , 1993), $i=f(E)$. AA spectrometry has been achieved with novAA 400 G type spectrometer - Analytik Jena - Germany, equipped with graphite furnace, WinAAS 3.17.0 software for evaluation, control and result presentation, a so-called cookbook, for every element, and a HS 55-1 hydride generator. Calibration curves have been plotted using standard solutions of metals in search.

Electrochemical Methods

Heavy metals such as Sn, Fe, Zn at the electrode surface are affcted by characteristic redox phenomena with can be used to determine their concentration. The voltammograms i=f(E) are obtained using PGZ 402 Voltalab, with VoltaMaster 4, version 7 software (User's manual, Voltalab®,2008). A 50 cm^3 BEC/EDI X51 V001 electrochemical cell, from Radiometer Copenhagen is part of the Voltalab system. Platinum electrodes (S_{work}=7.85 mm^2, S_{aux}=50 mm^2) and standard calomel electrode (SCE) with 0.1M HNO_3 support electrolyte have been used in experiments. Recording speed was 50 mV/min. at an apparatus sensitivity of 10 mA. Calibration curves for Fe and Sn have been plotted using metals standard solutions as I_{peak}=f(conc.).

RESULTS AND DISSCUTIONS

Vegetables mix products are obtained through processing of fully mature tomatoes, beans, onions, papricas. Vegetables concentrates are used in the food industry to enhance the taste and nutritive value of various products. There are three phases in the vegetables mixt production technology: obtaining the brute vegetables mixt, conditioning and packaging the product (HOTARARE nr.1197, 2002; ORDIN 1050, 2006**)**. When packaging into metallic cans the heavy metals content may exceed the safety limits, and in turn may be detrimental to public health. The two proposed analysis methods have the advantage of being fast and reliable (result accuracy). Five types of these products have been studied, both local and imported: four of them packaged in metallic cans and one in glass bottle, for reference.

It has been remarqued the high Cd concentration in Maxim's vegetables mix (Italian product).

For the determination of heavy metals by electrochemical methods, the first step was plotting the calibration curves. The methods used for Fe and Sn by means of cyclic voltametry i=f(E) are presented in Fig.1., Fig.2., Fig.3. and Fig.4.

The electrochemical method has only been applied for the higher concentration of metals Fe and Sn. Extracting Fe from the vegetables mixt products using this method has had no results. (Fig. 5.). Note that the Fe voltamogram is lower than the base line of the support electrolyte.

Sn, on the other hand, is present in the Italian vegetables mixt canned in high concentrations Fig.6 and Fig.7. (samples were taken from right next to where the can is welded, for all samples).The heavy metal concentrations in vegetables mixt determined by AA spectroscopy are presented in Table 1. High values are noted in the case of Fe (which although beneficial to the human body may become an energetic catalyst for some chemicalor biochemical processes), of Sn and of Al, especially in the Italian products.

Table 1. The heavy metal concentrations

No.	Sample	Concentration, ppm							
		Cr	Fe	Pb	Cd	Sn	Al	Zn	As
1.	Vegetables mix Sultan (Romanian product, Turkish licence, metalic can)	0.20	29.5	0.02	0.009	4.45	33.45	7.1	**
2.	Vegetables mix Conserv frig (Romanian product, metallic can)*	0.15	218.00	0.20	0.034	70.78	36.1	4.03	**
3.	Vegetable mix Mib (Romanian product, metallic can)	0.13	16.93	**	0.003	12.5	23.1	6.5	**
4.	Vegetable mix Maxim's, (Italian product, metallic can)*	0.18	41.31	1.9	0.109	14.8	80.2	9.0	**
5.	Vegetables mix Buftea (Romanian product, glass bottle)	0.26	27.61	0.16	0.017	8.24	48.56	8.79	**

* before the samples were taken the vegetables mix was homogenized at 1500 rpm with an IKA-LABORTECHNIK stirrer, with adjustable rotations and display unit observation

** under limit detection

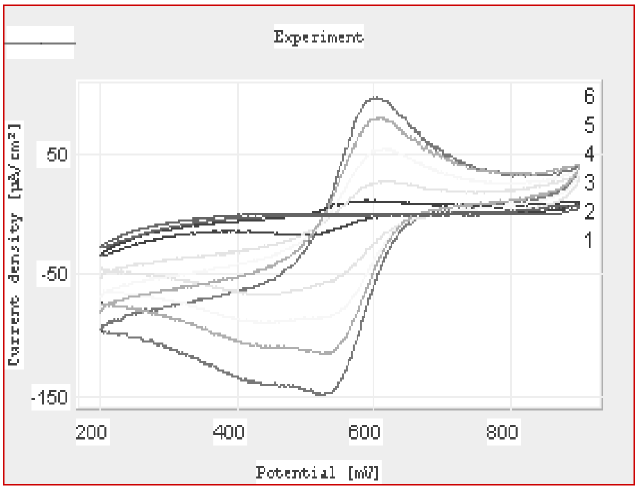

Fig.1. Cyclic voltammogrames for equilibrium $Fe^{3+} + e^- \rightarrow Fe^{2+}$. 1 – support electrolyte HNO3 0.1 M; 2 - c=25.64 mg/L; 3 - c=50.00 mg/L;4 - c=95.24 mg/L; 5 - c=136.36 mg/L; 6 - c=173.91 mg/L

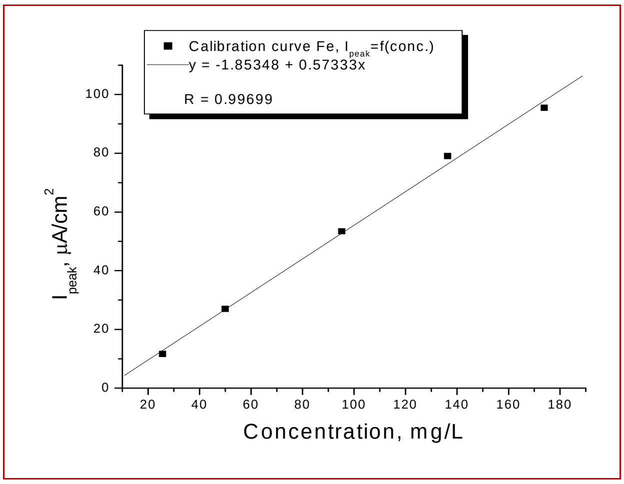

Fig.2. Calibration curve for iron concentration determination in canned vegetables mix, I_{peak}=f(conc.), E_{ESC} = 608 mV

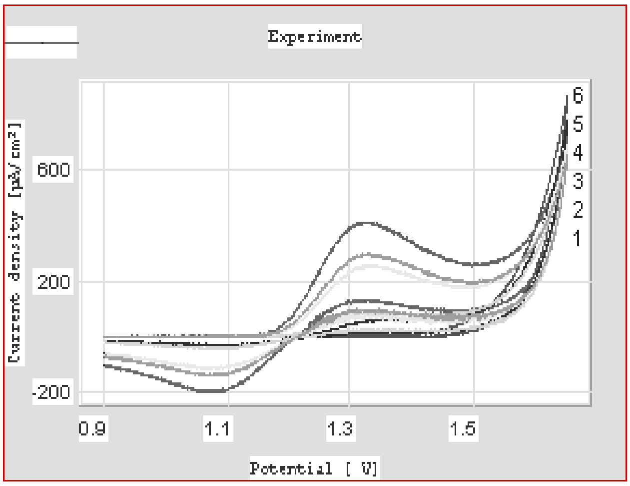

Fig.3. Cyclic voltammogrames for equilibrium $Sn^{4+} + 2e^- \rightarrow Sn^{2+}$. 1 – support electrolyte HNO3 0.1 M; 2 - c=6.8333 mg/L; 3 - c=13.5257 mg/L; 4 - c=20.0816 mg/L; 5 - c=26.5050 mg/L; 6 – c=32.8000 mg/L

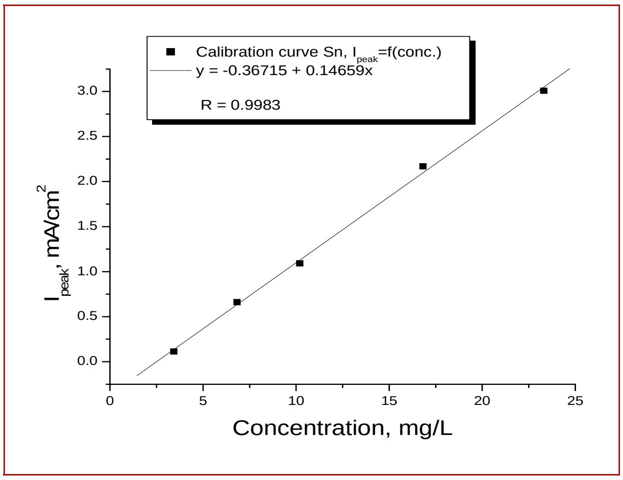

Fig.4. Calibration curve for tin concentration determination in canned vegetables mix, I_{peak}=f(conc.), , E_{ESC} = 1.375 V

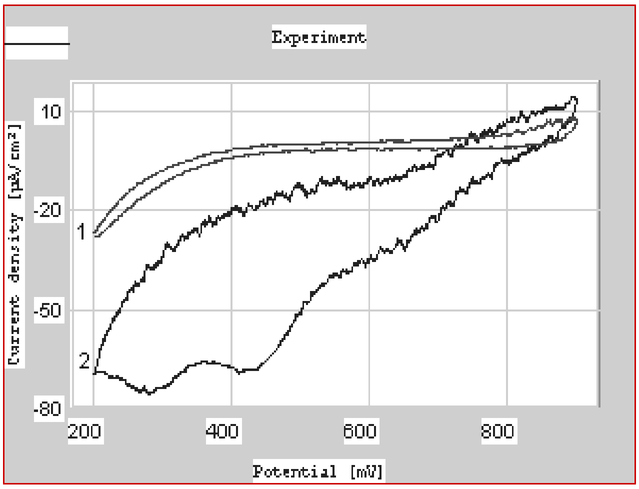

Fig.5. Fe determination in Conserv frig (vegetables mix)

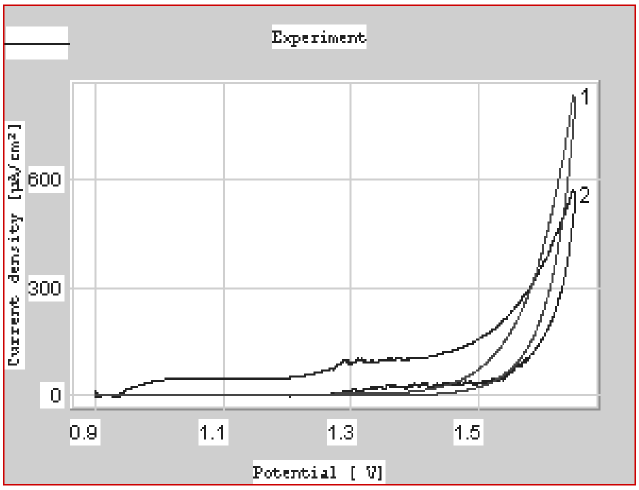

Fig.6. Sn determination in Conserv frig (vegetables mix), E_{ESC} = 1.375 V

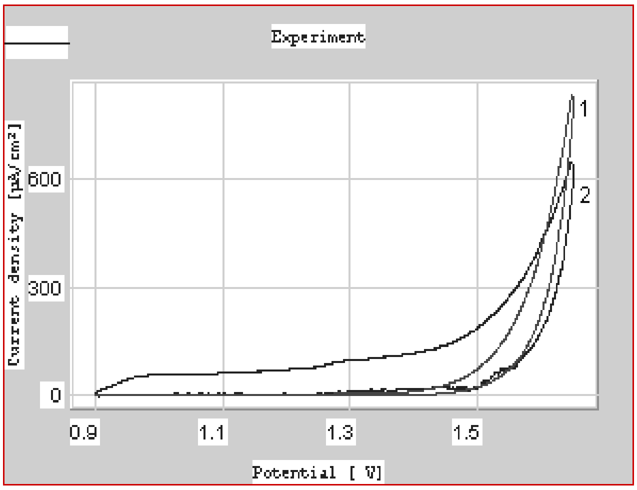

Fig.7. Sn determination in Maxim's (vegetables mix), E_{ESC} = 1.375 V

The values obtained using the electrochemical method are c = 3.60 ppm Sn for Conserv frig (I_{peak} = 0.1589 mA/cm^2) and c = 3.40 ppm Sn for Maxim's (I_{peak} = 0.1367 mA/cm^2). There are *obvious errors in using this method due to all the metal ions which can influence the electrochemical behavior.*

CONCLUSIONS

The environment pollution with heavy metals (Cr, Ni, Pb, Zn, Al, As, Cd, etc.) is due mainly to the activity of humans. Two heavy metals (Sn and Al) showed higher concentrations then legally admitted in canned vegetables mix. Concentration of heavy metals from the polluted environment in vegetables is influenced by different factors and stopped through several mechanisms. The monitoring of heavy metals in canned vegetables mix can help to evaluate and improve the insufficiently developed technology.

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