DETERMINATION OF ZINC (II), CADMIUM (II), LEAD (II) AND COPPER (II) IN COMMON AND BALSAMIC VINEGAR BY STRIPPING CHRONOPOTENTIOMETRY

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Abstract

A method for the determination of zinc (II), cadmium (II), lead (II) and copper (II) in common and balsamic vinegar by stripping chronopotentiometry is described. The metal ions were concentrated as their amalgams on the glassy carbon working electrode that was previously coated with a thin mercury film and then stripped by a suitable oxidant. Potential and time data were digitally converted into $dt\,dE^{-1}$, and E was plotted vs. $dt\,dE^{-1}$, thus increasing both sensitivity of the method and resolution of the analysis. Quantitative analysis was carried out by the method of standard additions. A good linearity was obtained in the range of concentrations examined. Recoveries of 90-98% for zinc (II), 91-97% for cadmium (II), 94-98% for lead (II) and of 93-97% for copper (II) were obtained from a sample spiked at different levels. The detection limits were 10.6 ng g^{-1} for zinc, 2.2 ng g^{-1} for cadmium (II), 3.4 ng g^{-1} for lead (II) and 4.2 ng g^{-1} for copper (II) and the relative standard deviations (mean of nine determinations) were 4.8, 6.5, 3.2 and 5.3%, respectively. Results obtained on commercial common and balsamic vinegar were not significantly different from those obtained by atomic absorption spectrometry.

Keywords: Stripping Chronopotentiometry; Zinc; Cadmium; Lead; Copper; Common Vinegar; Balsamic Vinegar.

1. Introduction

Vinegar is an aromatic condiment produced by acetic fermentation of wine or cooked juice, promoted by microorganism called "microderma aceti" (mother of vinegar). For the italian law vinegar is divided in three categories: common vinegar, Traditional Balsamic vinegar from Modena and Reggio Emilia and Balsamic vinegar from Modena. Common vinegar are obtained by vinegar fermentation of red or white wines. Traditional Balsamic vinegar from Modena and Reggio Emilia is obtained by sugar and acetic fermentation of

cooked grape juice which is then subjected to an ageing period. Balsamic vinegar from Modena is produced following a "particular traditional technique of acetic and alcoholic fermentation of grape juice. Law gives full details about the composition of vinegar and the rules to be observed in their production (1,2).

Heavy metals like cadmium (II) and lead (II) in food produce toxic effects on the consumer. Zinc (II) and copper (II) are normally classified as essential trace elements for the human body because their presence are fundamental for the biochemistry of metalloproteins and metalloenzymes but high concentration levels may produce toxic effects. In vinegar these metals may produce also "hazy phenomena" with undesirable effects on the organoleptic characteristics (3-5). Environmental contamination and the contact with the materials used during the vinegar making process are the causes of their presence in these foodstuffs. Recently law have reduced the Provisional Tolerable Weekly Intake (PTWI) for lead (II) to 25 $\mu g Kg^{-1}$ body weight and for cadmium (II) to 7 $\mu g\ Kg^{-1}$ body weight (6-8).

Therefore the analytical dosage of these metals in food is a theme of great importance in order to estimate the toxicological parameters and to guarantee a good quality of the aliments as well sensitive, precise, accurate and cheap methods are required for their determination. Quantitative determination of heavy metals in foods and condiments is usually carried out by atomic absorption spectrometry (AAS) after a wet ash method to release metals from the organic matrix (9-10).

In this paper a method for the determination of zinc (II), cadmium (II), lead (II) and copper (II) in different samples of common and balsamic vinegar by stripping chronopotentiometry (SCP) using a mercury film-plated electrode was set up previous digestion of the sample by dry ash.

2. Experimental

2.1. Standards and Reagents

All glassware was rinsed with 10% (v/v) pure nitric acid (C. Erba, Milan, Italy). Ultra-pure water obtained by the Pure Lab RO and the Pure Lab UV systems (USF, Ransbach-Baumbach, Germany), ultra-pure and certified hydrochloric acid, pure mercury (II) chloride and pure sodium acetate for analysis (C. Erba), zinc (II), cadmium (II), lead (II) copper (II) and gallium (III) standard solution (1,000 mg L^{-1}) (Panreac Quimica, Barcelona, Spain) were used. By dilution with water, the solutions containing 10.0 ng μL^{-1} of zinc (II), 0.1 ng μL^{-1} of cadmium (II), 1 ng μL^{-1} of lead (II) 4.0 ng μL^{-1} of copper (II) and 4.0 ng μL^{-1} of gallium (III) were prepared.

2.2. Instrumentation and Software

Determinations were carried out by a potentiometric stripping analyzer, PSA ION^3 (Steroglass, S. Martino in Campo, Perugia, Italy), connected to an IBM-compatible personal computer. The analyser operated under control of the NEOTES software package (Steroglass).

Atomic absorption spectrometry (AAS) measurements were carried out with a Spectra 110 instrument (Varian, Victoria, Australia).

2.4. Electrodes and Electrochemical Cell

A three-electrode system consisting of a 3-mm diameter glassy carbon working electrode, a platinum wire counter electrode and a silver/silver chloride//saturated potassium chloride reference electrode (Steroglass) were used for all measurements. The electrochemical cell consists of a 40-mL vessel supplied with an electrical spiral stirrer. All electrochemical measurements were made under stirring during plating and the first step (electrolysis) and under quiescent conditions during the second step (stripping).

2.5. Analytical Procedure

2.5.1. Preliminary Sample Processing

A 25-g amount of sample was exactly weighed in a quartz crucible and dried at 120 °C for approximately 12 h. The sample was transferred in a muffle oven and the temperature was slowly increased from 250 °C up to 350 °C. The muffle oven was kept at this temperature until the sample was completely carbonised. Afterward the temperature was raised to 500 °C and the sample was dry-ashed for 12 h until white ashes were obtained. If carbon particles remained, the crucible was cooled at room temperature, the residue was moistened with a few drops of water and 0.5-1 mL of concentrated nitric acid and the crucible was kept again in a muffle oven for 30 min at 500 °C. The crucible was then cooled at room temperature and the ashes were dissolved with small volumes of 2 M hydrochloric acid, that were quantitatively transferred to a 50-mL volumetric flask. The volume was filled up to the mark with 2 M hydrochloric acid.

2.5.2. Determination of cadmium (II), lead (II) and copper (II)

A 10-mL volume of the solution obtained as described in the preceding section was introduced into the electrochemical cell together with 10 mL of water and 1.0 mL of a mercury (II) chloride solution containing 1,000 mg L^{-1} of mercury (II) ion in 1 M hydrochloric acid. Before analysis, the working electrode was coated with a thin mercury film by electrolysing a mercury (II) chloride solution of a concentration equal to that added to the sample at - 0.9 V against the reference electrode for 1 min. For the subsequent determination, the electrolysis time was 300 s at the potential of - 0.9 V; the potential of the electrodes was monitored every 300 s. Quantitative analysis was carried out by the method of standard additions. Usually accurate results were obtained by adding 500 μL of a solution containing 0.1 ng μL^{-1} of cadmium (II), 200 μL of a solution containing 1.0 ng μL^{-1} of lead (II) and 500 μL of a solution containing 4.0 ng μL^{-1} of copper (II).

2.5.3. Determination of zinc (II)

A 10 mL volume of the solution obtained as described in the 2.5.1 section was buffered at pH 4.8 by adding a 10 mL volume of 4 M sodium acetate solution and spiked with 100 μL of a solution containing 1.0 ng μL^{-1} of gallium (III). The solution obtained was introduced into the electrochemical cell; from this point the procedure was the same as that described in the preceding section with the only differences concerning (i) the electrolysis potential, that was - 1.3 V, (ii) the time of electrolysis, that was 180 s and (iii)

the two standard additions, that spanned from 500 to 1500 μL of a solution containing 10.0 ng μL^{-1} of zinc (II).

3. Results and Discussion

In this paper the determination of zinc (II), cadmium (II), lead (II) and copper (II) in different samples of common and balsamic vinegar by SCP is described. Preliminary sample processing was carried out as described in the section 2.5.1 to prevent volatilisation losses (11). In Figure 1 the stripping curves relative to cadmium (II), lead (II) and copper (II) determination in a sample of common vinegar are reported.

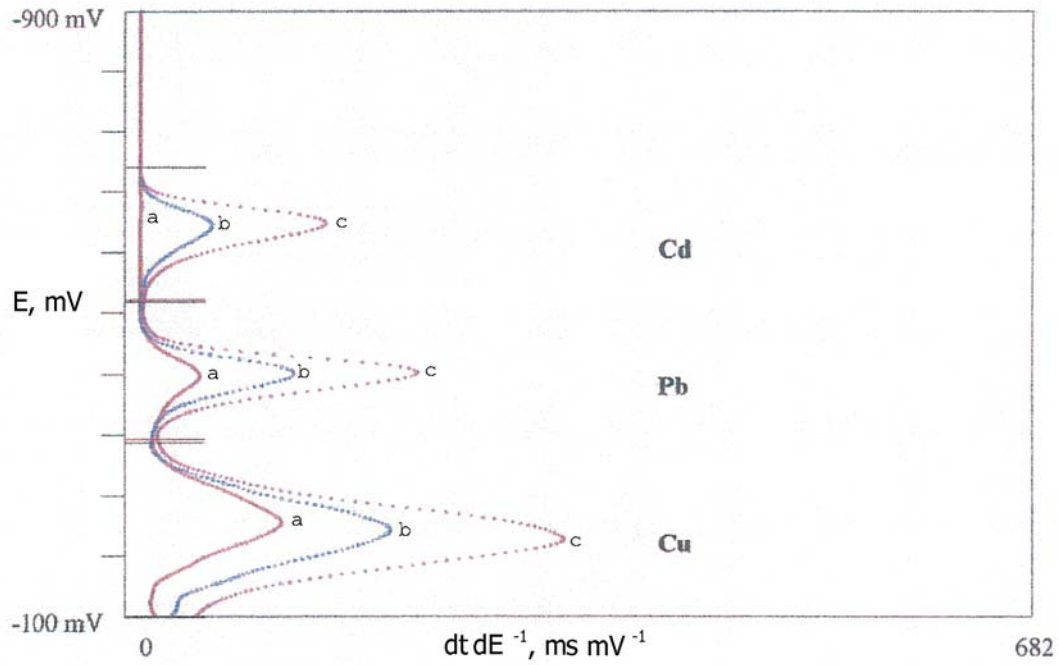

Fig. 1- Stripping curves relative to cadmium (II), lead (II) and copper (II) determination in a sample of common vinegar: (a) sample; (b) and (c) sample added with one and two standard additions, respectively, as decribed in Experimental.

Cadmium, lead and copper were oxidised at approximately - 0.62 V, - 0.42 V and - 0.24 V respectively, vs. a reference electrode under the conditions described and peak areas relative to both sample and two standard additions were measured. By plotting this area vs. total cadmium (II), lead (II) and copper (II) amount, a straight line was obtained. A good linearity was obtained in the range of concentration examined, as is shown by both the equations of the lines $Y = 9.91 \times 10^7 X (\pm 7 \times 10^5) + 3.21 \times 10^3 (\pm 388)$ for cadmium (II), $Y = 4.91 \times 10^7 X (\pm 3 \times 10^5) + 6.32 \times 10^4 (\pm 367)$ for lead (II) and $Y = 8.22 \times 10^7 X (\pm 9 \times 10^5) + 1.21 \times 10^4 (\pm 485)$ for copper (II), where Y is the integrated areas (ms) and X is the analyte mass (mg), and the correlation coefficient that were 0.996 (n=4) 0.986 (n=4) and 0.999 (n=4) respectively.

The determination of zinc (II) was carried out with an excess of gallium (III) to prevent the formation of Cu (II)-Zn (II) intermetallic compounds by forming more stable Cu (II)-Ga (III) intermetallics (12, 13). In Figure 2 the stripping curves relative to zinc (II) determination in the same sample of common vinegar are reported. Zinc was oxidised at approximately - 1.1 V vs. a reference electrode under the conditions described and peak

areas relative to both sample and two standard additions were measured. By plotting this area vs. total zinc (II) amount, a straight line was obtained. A good linearity was obtained in the range of concentration examined, as is shown by both the equation of the line $Y = 1.78 \times 10^7 X (\pm 2 \times 10^5) + 1.34 \times 10^5 (\pm 317)$ and the correlation coefficient that was 0.996 (n=4) .

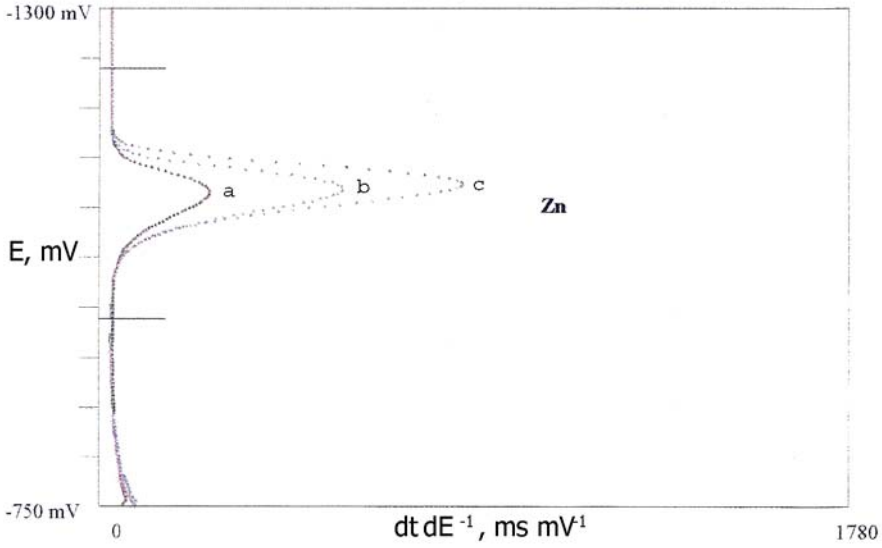

Fig. 2- Stripping curves relative to zinc (II) determination in a sample of common vinegar: (a) sample; (b) and (c) sample added with one and two standard additions as decribed in Experimental.

To determine the recoveries of zinc (II), cadmium (II), lead (II) and copper (II), appropriate volumes of a zinc (II), cadmium (II), lead (II) and copper (II) solution were added to a sample of common vinegar; both spiked and unspiked samples were analysed in triplicate by the proposed method. Recoveries of 90-98% for zinc (II), 91-97% for cadmium (II), 94-98% for lead (II) and of 93-97% for copper (II) were obtained. Repeatibility of the method was evaluated by carrying out three indipendent determinations on the same sample of common vinegar added with a cadmium (II) amount of 10 ng g^{-1} (since the cadmium content was lower than the detection limit for all the examined samples); each solution was analysed three times. The values obtained were subjected to statistical analysis by employing the same software running all the analytical steps. The average concentration was 1215.6 ng g^{-1} for zinc (II) and a relative standard deviation of 4.8%, 9.8 ng g^{-1} for cadmium (II) and a relative standard deviation of 6.5%, 34.8 ng g^{-1} for lead (II) and a relative standard deviation of 3.2%, 350.2 ng g^{-1} for copper (II) and a relative standard deviation of 5.3%. By using the working conditions stated above, the detection limits were 10.6 ng g^{-1} for zinc (II), 2.2 ng g^{-1} for cadmium (II), 3.4 ng g^{-1} for lead (II) and 4.2 ng g^{-1} for copper (II) by setting three times the standard deviation of the intercept as the peak threshold and by utilising the expression $3\ S^{-1}$, were S is the sensitivity obtained from the calibration graph and the peak threshold (14). The method was applied to zinc (II), cadmium (II), lead (II) and copper (II) determinations in ten different commercial samples of common and balsamic vinegar. The average content of zinc (II) was in the range 1235.7 - 2458.1 ng g^{-1}, cadmium (II) was not found in all the examined samples, the average content of lead (II) was in the range 8.2 - 60.1 ng g^{-1} and the average content of copper (II) was in the range 180.2 – 480.3 ng g^{-1}. The results were compared with those obtained by an AAS method. A paired

Student's t-test showed that there is no significant difference in the method used at the 95% confidence level.

4. Conclusions

The proposed method provides a sensitive and convenient procedure for the determination of zinc (II), cadmium (II), lead (II) and copper (II) in common and balsamic vinegar by SCP. A proper procedure with respect to sample pretreatment was carried out. The analytical procedure is performed under computer control and the time of analysis is less than ten min for each analyte, including evaluation of the results and display. In addition, the cost and the size of the instrumentation are low. Furthermore, the extensive and flexible software supporting the instrumentation makes it possible not only to fully automate the analysis, but also to present the results digitally and graphically, and to store them for possible future processing and statistical treatment.

References

1) A. Morgante, *Rassegna di Diritto e Tecnica dell'alimentazione* **1988**, 23, 129.
2) A. Del Signore, B. Stancher, M. Calabrese, *It. J. Food Sci.* **2000**, 12, 317.
3) A. M. Troncosos Gonzales, M. Guzman Chozas, *Nahrung* **1988**, 32, 743.
4) P. Ribereau–Gayon, E. Peymand, P. Sudrand, P. Ribereau–Gayon, Tratado de Enologia, Ciencias y Tecnicas del vino, vol. I, Hemisferio Sup. **1980**.
5) A. Acosta Artiles, C. Diaz Romero, A. Hardisson, De la Torre, *Nahrung*, **1993**, 37, 72.
6) World Health Organization (WHO) Technical Report Series, "Evaluation of certain food additives and contaminants, Geneve, **1993**, N° 837.
7) Lead in Food, Health Protection on the Consumer, T. Berg, Council of Europe Press, **1994**.
8) International Agency for Research on Cancer (IARC), Biennal Report 1992-1993, Lyon, France **1993**.
9) F. Corradini, L. Marcheselli, A. Marchetti, C. Preti, *J. Assoc. Offic. Anal. Chem. Int*. **1994**, 77, 714.
10) A. Del Signore, B. Campisi, *J. Assoc. Offic. Anal. Chem*. **1998**, 81, 1087.
11) N. T. Crosby, *The Analyst* **1977**, 102, 225.
12) S. V. Psaroudakis, C. Efstathiou, *The Analyst* **1987**, 112, 1587.
13) S. V. Psaroudakis, C. Efstathiou, *The Analyst* **1989**, 114, 25.
14) D. L. Massart, A. Dijkstra, L. Kaufman, Evaluation and Optimization of Laboratory Methods and Analytical Procedures, Elsevier, Amsterdam (NL) **1978.**