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STRIPPING CHRONOPOTENTIOMETRIC DETERMINATION OF CADMIUM (II) AND LEAD (II) IN EQUINE KIDNEY, BOVINE AND POULTRY MEAT

Filippo Lo Coco[*], Paolo Monotti[**], Veronica Novelli[***], Luciano Ceccon[*], Luigi Ciraolo[****], Silvia Rizzotti[*****]

[*]Department of Economic Sciences, University of Udine, Via Tomadini 30/A, Udine, filippo.lococo@dse.uniud.it luciano.ceccon@dse.uniud.it
[**]Consultant of the Chemical Laboratory of Steroglass, Via Romano di Sopra 2/c, S. Martino in Campo, Perugia, paolo.monotti@libero.it
[***]Department of Chemical Sciences and Technologies, University of Udine, Via Cotonificio 108, Udine, v.novelli@dstc.uniud.it
[****]Department of Studies on Resources, Enterprise, Environment and Quantitative Methodologies, University of Messina, Piazza S. Pugliatti 1, Messina, luigi.ciraolo@unime.it
[*****]Chemical Laboratory of Customs of Venice, Via Ca' Marcello 15, Mestre, Venice, lab1venezia@finanze.it

Abstract

Stripping chronopotentiometric determination of cadmium (II) and lead (II) in equine kidney, bovine and poultry meat 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 cadmium (II) and of 91-98% for lead (II) were obtained from a sample spiked at different levels. The detection limits were 1.2 ng g^{-1} for cadmium (II) and 2.4 ng g^{-1} for lead (II) and the relative standard deviations (mean of nine determinations) were 5.8 and 4.2%, respectively. Results obtained on different samples of equine kidney, bovine and poultry meat were not significantly different from those obtained by inductively coupled plasma atomic emission spectrometry.

Keywords: Stripping Chronopotentiometry; Cadmium; Lead; Equine kidney; Bovine Meat; Poultry Meat.

1. Introduction

Environmental pollution by heavy metals is a serious problem. Among heavy metals especially cadmium and lead play a major role for their toxicological importance to man and animals (1,2). Cadmium and lead are used in many industrial processes and cadmium is also a contaminant in some fertilizers and in urban sewage sludges used to fertilize

pasture or crops (3,4). Therefore these metals are present in all parts of the environment including sea and fresh water, soils, sediments and air (5,6). Food-producing animals may be a source of cadmium and lead in human alimentation. World Health Organisation has indicated the necessity of reducing to a minimum the content of toxic metals in food and in Europe many countries have fixed limits for levels of heavy metals in different food matrices and in organic farming the use of mineral fertilizers is restricted (7-10).

The determination of cadmium (II) and lead (II) in bovine and poultry meat is important owing to both nutritional interest and incidence in the diet of these foodstuffs. We have done the determination also in animal offal because in these organs toxic elements concentrate (4). The analytical technique frequently used for their determination is atomic absorption spectrometry after a wet ashing or microwave sample processing (11).

In this paper a stripping chronopotentiometric determination of cadmium (II) and lead (II) in different samples of equine kidney, bovine and poultry meat using a mercury film-plated electrode was set up previous digestion of the sample by wet 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 (C. Erba), pure mercury (II) chloride for analysis, cadmium (II) and lead (II) standard solution (1,000 mg L^{-1} in 0.5 M HNO_3) (Panreac Quimica, Barcelona, Spain) were used. By dilution with water, a solution containing 0.1 ng μL^{-1} of cadmium (II) and a solution containing 2.0 ng μL^{-1} of lead (II) 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 analyzer operated under control of the NEOTES software package (Steroglass).

Inductively coupled plasma mass spectrometry (ICP-MS) measurements were carried out with an ICP-MS ELAN 5000 Perkin Elmer instrument.

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 10-g amount of sample was exactly weighed in a quartz crucible and dried at 120 °C for approximately 3 h. Afterward the sample was moistened with 1-2 mL of concentrated sulphuric acid and carbonised in a hot plate. The sample was transferred in a cold muffle oven and the temperature was slowly increased to up 500 °C. The muffle oven was kept at this temperature 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 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) and lead (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 electrolyzing 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) and 100 μL of a solution containing 2.0 ng μL^{-1} of lead (II).

3. Results and Discussion

In this paper the simultaneous determination of cadmium (II) and lead (II) in different samples of equine kidney, bovine and poultry meat by SCP is described. Preliminary sample processing was a proper wet digestion as described in the section 2.5.1 to prevent volatilization losses (2). An electrolysis time of 300 s is adopted for the two analytes at the potential of – 0.9 V. In Figure 1 the stripping curves for a sample of equine kidney are reported. Cadmium and lead were oxidised at approximately - 0.63 V and - 0.44 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) and lead (II) amount, a straight line was obtained. A good linearity was obtained in the range of concentrations examined, as is shown by both the equations of the lines $Y = 1.82 \times 10^7 X (\pm 3 \times 10^5) + 1.44 \times 10^4 (\pm 43)$ for cadmium (II) and $Y = 4.71 \times 10^7 X (\pm 1 \times 10^5) + 1.23 \times 10^3 (\pm 115)$ for lead (II), where Y is the integrated areas (ms) and X is the analyte mass (mg), and the correlation coefficient which were 0.999 (n=5) and 0.999 (n=5) respectively.

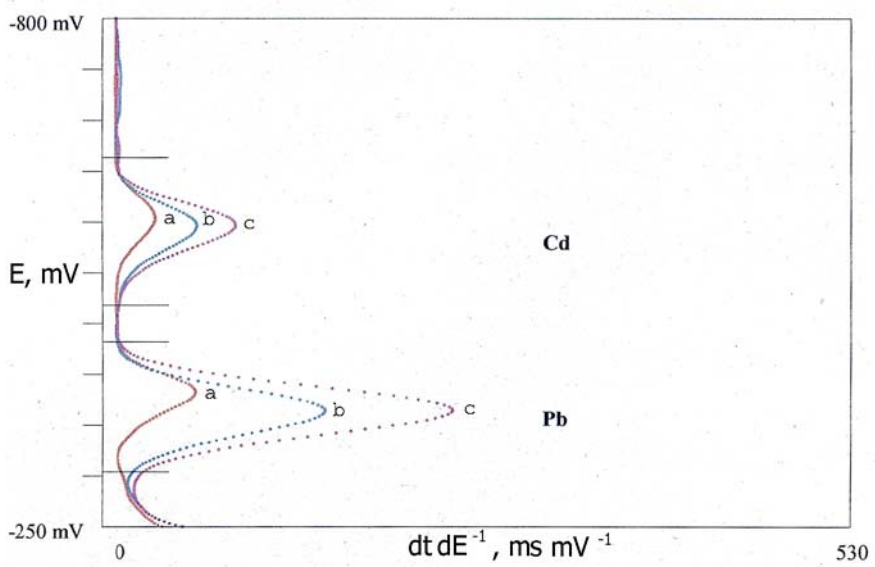

Fig. 1- Stripping curves relative to cadmium (II) and lead (II) determination in a sample of equine kidney: (a) sample; (b) and (c) sample added with one and two standard additions, respectively, as decribed in Experimental.

To determine the recoveries of cadmium (II) and lead (II), appropriate volumes of a cadmium (II) and lead (II) solution were added to a sample of equine kidney; both spiked and unspiked samples were analysed in triplicate by the proposed method. The results obtained showed that the recovery of cadmium (II) ranging from 90 to 98% and that of lead (II) from 91 to 98%. Repeatibility of the method was evaluated by carrying out three independent determinations on the same sample of equine kidney; 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 7.9 ng g^{-1} for cadmium (II), with a relative standard deviation of 5.8%, and 19.2 ng g^{-1} for lead (II), with a relative standard deviation of 4.2%. By using the working conditions stated above, the detection limits were 1.2 ng g^{-1} for cadmium (II) and 2.4 ng g^{-1} for lead (II) by setting three times the standard deviation of the intercept as the peak threshold and by utilizing the expression 3 S^{-1}, were S is the sensitivity obtained from the calibration graph and the peak threshold (12). The method was applied to cadmium (II) and lead (II) determinations in fifteen different commercial samples of equine kidney, bovine and poultry meat. Cadmium (II) was not found in all the examined samples of bovine and poultry meat while the average content in equine kidney was in the range 5.1 –15.3 ng g^{-1} ; the content of lead (II) was in the range 10.4 - 58.3 ng g^{-1} and only four sample had lead (II) levels greater than 20 ng g^{-1} that is the allowed maximum amount fixed by the european community (13). The results were compared with those obtained by an ICP-MS method. A paired Student's t-test showed that there is no significant differences in the method used at the 95% confidence level.

4. Conclusions

The proposed method provides a sensitive and convenient procedure for the determination of cadmium (II) and lead (II) in equine kidney, bovine and poultry meat 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.

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