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Publisher:
Facoltà di Economia. Università "La Sapienza"

Published
DOI:

DETERMINATION OF CADMIUM (II) AND LEAD (II) IN WHOLE AND SKIM MILK BY STRIPPING CHRONOPOTENTIOMETRIC ANALYSIS

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Abstract

A method for the determination of cadmium (II) and lead (II) in whole and skim milk by stripping chronopotentiometric analysis 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 94-100% for cadmium (II) and of 91-98% for lead (II) were obtained from a sample spiked at different levels. The detection limits were 4.4 ng g^{-1} for cadmium (II) and 8.6 ng g^{-1} for lead (II) and the relative standard deviations (mean of nine determinations) were 4.1 and 5.6%, respectively. Results obtained on commercial whole and skim milk were not significantly different from those obtained by inductively coupled plasma atomic emission spectrometry.

Keywords: Stripping Chronopotentiometry; Cadmium; Lead; Whole Milk, Skim Milk.

1. Introduction

Cadmium is an harmful environmental pollutant; it is classified into Group I substances, carcinogenic to humans (1). The Provisional Tolerable Weekly Intake (PTWI) for cadmium is 7 μg Kg^{-1} body weight (2). Cadmium in soils is derived from both natural and anthropological sources by aerial deposition and sewage sludge, manure and phosphate fertiliser applications. The use of cadmium-containing fertilisers and sewage sludge is most often quoted as the primary reason for the increase in the cadmium content of soils over the last 20 to 30 years in Europe (3). The major factors governing cadmium absorption and distribution in soils are pH, soluble organic matter content, hydrous metal oxide content, presence of organic and inorganic ligands and competition with other metal ions (4).

Also lead is a harmful environmental pollutant; it is used for petroleum products, glass panels, crafts, batteries, jewellery, pencils, coloured newsprint, etc. (5). The PTWI for lead is 25 µg Kg^{-1} body weight (6). Health risks are particularly associated with exposure in uterus and the early years of life, since the developing organism is at greater risk from permanent damage, and both absorption and retention can be considerably greater in infants than in adults; but if lead is hazard for all humans, children under the age of six are more at risk for lead poisoning (7).

Whole and skim milk is the major source of food especially for infants and children and also relatively low levels of toxic elements can contribute significantly to cadmium and lead intakes and are hazardous for public health (7).

The monitoring of toxic and essential trace elements in biological materials is very important and several methods are available for the determinations of heavy metals in milk. The most widely used are based on atomic absorption spectroscopy (AAS) (8-11), on neutron activity and inductively coupled plasma atomic emission spectrometry (ICP-AES) (5), on voltammetric techniques as differential pulse anodic stripping voltammetry and potentiometric stripping analysis (12, 13).

In this work we have investigated the content of Cd (II) and Pb (II) in different sample of whole and skim milk by chronopotentiometric stripping analysis using a mercury film-plated electrode previous digestion of the sample by dry ash. The aime of this work is to set up a stripping chronopotentiometry (SCP) method for this foodstuffs so important for human health.

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 mgL^{-1}) (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 analyser 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 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) 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 milk by SCP is described. Preliminary sample processing was carried out as described in the section 2.5.1 to prevent volatilisation losses (14). It is only necessary that an electrolysis time of 300 s is adopted. In Figure 1 the stripping curves for a sample of milk, 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), are reported. Cadmium and lead were oxidised at approximately - 0.63 V and - 0.45 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 concentration examined, as is shown by both the equations of the lines $Y = 1.08 \times 10^{8} X (\pm 3 \times 10^{4}) + 3.04 \times 10^{3} (\pm 367)$ for cadmium (II) and $Y = 1.21 \times 10^{7} X (\pm 5 \times 10^{4}) + 1.23 \times 10^{3} (\pm 179)$ for lead (II), where Y is the integrated areas (ms) and X is the analyte mass (mg), and the correlation coefficient that were 0.986 (n=5) and 0.999 (n=6), respectively.

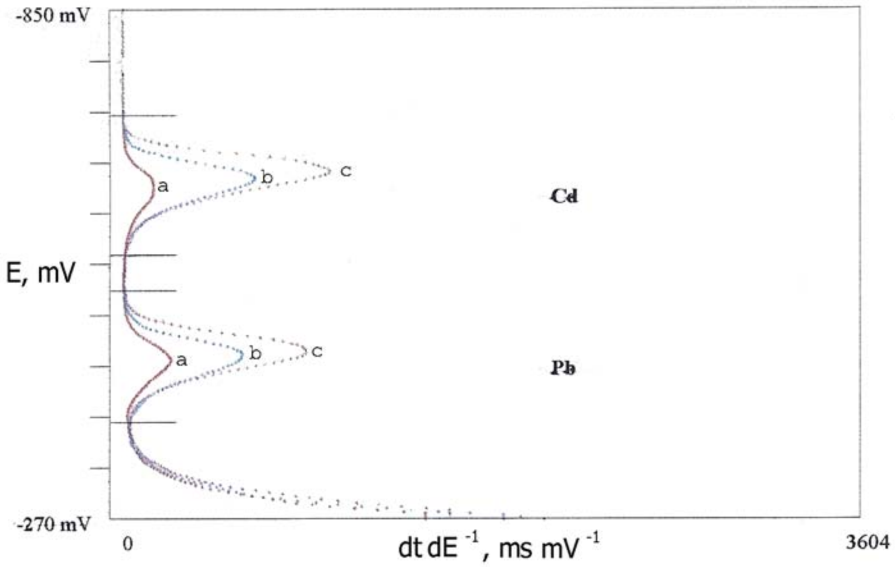

Fig. 1- Stripping curves relative to cadmium (II) and lead (II) determination in a sample of whole milk: (a) sample added with a cadmium (II) amount of 10 ng g^{-1}; (b) and (c) sample added with one and two standard additions, respectively, as decribed in Experimental.

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 milk; 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 94 to 100% and that of lead (II) from 91 to 98%. Repeatibility of the method was evaluated by carrying out three indipendent determinations on the same sample of milk added with a cadmium (II) amount of 10 ng g^{-1}; each determination 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 9.7 ng g^{-1} for cadmium (II), with a relative standard deviation of 4.1%, and 40.8 ng g^{-1} for lead (II), with a relative standard deviation of 5.6%. By using the working conditions stated above, the detection limits were 4.4 ng g^{-1} for cadmium (II) and 8.6 ng g^{-1} for lead (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 the sensitivity obtained from the calibration graph and   is the peak threshold (15). The method was applied to cadmium (II) and lead (II) determination in ten different commercial samples of whole and skim milk. Cadmium (II) was not found in all the examined samples while the average content of lead (II) was in the range 8.3 - 68.1 ng g^{-1} and only three samples had lead (II) levels greater than 20 ng g^{-1} that is the allowed maximum amount fixed by the european community (16). 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 whole and skim milk 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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