ANALYSIS OF MILK SAMPLE: A VOLTAMMETRIC APPROACH

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ABSTRACT

A convenient and accurate analytical procedure has been developed for the determination of the different metal ions present in milk. This investigation showed that concentration of different metal ions found in milk samples depend on their source, i.e., buffalo, cow, goat and human. Direct current polarography (DCP), differential pulse polarography (DPP) and differential pulse anodic stripping voltammetry (DPASV) were used for the purpose of analysis.

1% Seignette salt (sodium potassium tartrate) (pH 2.6 ± 0.02) was used as a supporting electrolyte. The sample produced three well defined polarographic/voltammetric signals with $E_{1/2}/E_p$ values equal to –0.22V/–0.20V, –0.50/–0.52V and –1.20V/–1.24V vs SCE indicating the presence of Cu(II), Pb(II)/Sn(II) and Fe(III).

The second signal with $E_{1/2}/E_p$ values equal to –0.5V/–0.52V vs SCE in the polarogram may be due to Pb or Sn. To confirm the presence of

Pb(II)/Sn(II) or both in the sample, differential complexation was used with EDTA as complexing agent. This single peak/wave split into two with $E_{1/2}/E_p$ values equal to –0.52V/–0.54V, –0.62V/–0.64V, confirming the presence of both Pb(II) and Sn(II) in the sample.

The method of standard addition was used for quantitative analysis and observed results were subjected to statistical analysis.

INTRODUCTION

Milk contains different metal ions in traces /1,2/. The analysis of milk for its trace metal content is very important because, in the study of the role of metals in health and disease, the two most important considerations to clinicians and basic scientists are the areas of metal deficiency and excess /3/. In milk, copper is the most abundant heavy metal in the human body and indispensable for normal metabolism in man and most animals. Its deficiency or excess in the body is found to be associated with a large number of diseases /4,5/.

In view of the importance and utility of the work we have designed voltammetric methods /6,7/ for an analysis of milk sample for its metal content.

EXPERIMENTAL

Sample

Cow, buffalo and goat milk samples were collected from a local dairy farm. A human milk sample was collected from a maternity home in Sagar (M.P.).

Chemicals and Reagents

All the chemicals used were of Anal R/BDH grade. Stock solutions of Seignette salt (sodium potassium tartrate) (10%), Cu(II), Pb(II), Sn(II) and Fe(III) (0.01 m), EDTA (etthylenediamine tetraacetic acid, disodium salt) (0.1m) were prepared by dissolving a requisite quantity of their soluble salt in deionised water. The solutions were standardised by known methods /8/ and diluted as required.

Instrumentation

Voltammetric and polarographic measurements were made on an Elico Pulse Polarograph model CL-90, coupled with X-Y Polarocard model LR-108. The electrode system consisted of a dropping mercury electrode (DME) as a working electrode in DCP and DPP mode, whereas glassy carbon fibre electrode was used in DPASV mode, a coiled platinum wire as an auxiliary electrode and a saturated calomel electrode (SCE) as a reference electrode. pH measurements were made on a Systronic digital pH meter 335.

Preparation of Analyte and Recording of Voltammogram

10 ml of each milk sample, obtained from different sources, was evaporated to dryness on a water bath and then ignited in a platinum crucible. The resulting ash was moistened with water and heated several times until the weight became constant and the ash became completely white. Several drops of concentrated sulfuric acid were added to this material and it was fumed off by heating over a small flame. In order to remove the excess sulfuric acid, the residue was treated with water and again evaporated to dryness; the residue was then heated. After the addition of several drops of nitric acid, fuming off of the excess acid was repeated. The resulting nitrates were dissolved in 10 ml of 10% Seignette salt solution and the total volume was made up to 100 ml with distilled water. The pH of the test solution was adjusted to 2.60 ± 0.02 using HCl/NaOH solution. Pure nitrogen gas was bubbled through the test solution for 15 minutes and the voltammogram/polarogram was recorded.

RESULTS AND DISCUSSION

The DC and DP polarogram (Fig. 1a and 1b) and DPASV voltammogram (Fig. 1c) of the milk sample solution showed three well defined polarographic/voltammetric signals with $E_{1/2}/E_p$ values equal to –0.22V/ –0.20V, , –0.50V/–0.52V and –1.20V/–1.24V corresponding to Cu(II), Pb(II)/Sn(II) and Fe(III).

The second signal created some confusion as to whether it was due to Pb or Sn because its halfwave potential was –0.50V which, according to the literature /9,10/, is between those of Pb and Sn. To overcome this problem,

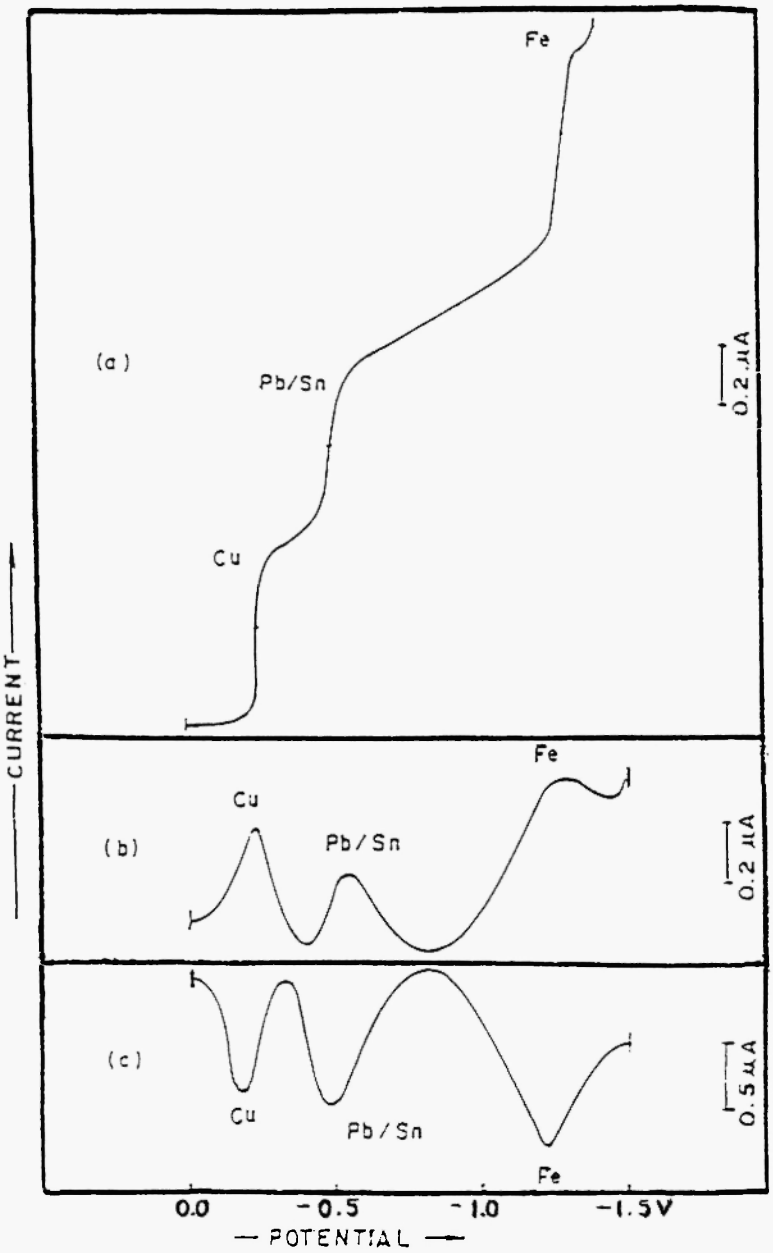

Fig. 1. Milk Sample in 1% Seignette Salt at pH 2.6 ± 0.02
(a) - Direct Current Polarogram
(b) - Differential Pulse Polarogram
(c) - Differential Pulse Anodic Stripping Voltammogram

advantage was taken of differential complexation with EDTA. On recording the voltammogram of EDTA-complexed sample solution, this single wave split into two, with $E_{1/2}/E_p$ values equal to –0.54/–0.56V and –0.62V/ –0.64V respectively, indicating the presence of both Pb and Sn in the sample. Separate experiments on 1:1 Pb-EDTA and Sn-EDTA complexes were carried out and the results showed that these complexes produced polarographic waves with the same $E_{1/2}/E_p$ values, thus confirming the presence of Pb and Sn in the sample (Fig. 2).

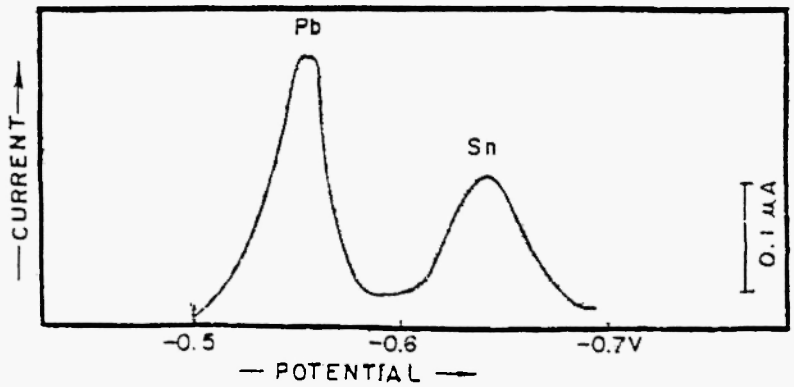

Fig. 2. Differential Pulse Polarogram of EDTA – Complexed Pb and Sn in 1% Seignette Salt. pH 2 6 ± 0·02

Each milk sample was spiked using the external standard addition method and the quantitative analysis of Cu, Pb, Sn and Fe of each sample was performed. The results have been tabulated in Table 1. The precision and percentage recovery of the spiked samples for the determination of the above mentioned metal ions has been reported in Table 1. The results indicated that the percentage recovery is over 99% for all the metal ions.

Minimum Tried Detection Limit

The minimum tried detection limits (smallest quantities that authors have used) of the techniques for measurement of the individual and

Table 1

Voltammetric (DPP) analysis for metal contents of milk samples obtained from different origins

Source sample	Metal ions	Spiked milk samples Added	Found*	Average Rec %	S.D. ±	C.V. %
Buffalo	Cu	–	0.62	99.9	0.008	0.63
		0.635	1.254			
	Pb	–	0.245	99.9	0.003	0.66
		0.207	0.452			
	Sn	–	0.002	100	0.0001	0.44
		0.023	0.045			
	Fe	–	0.223	99.9	0.002	0.39
		0.279	0.502			
Cow	Cu	–	0.39	100	0.004	0.57
		0.31	0.70			
	Pb	–	0.205	99.7	0.002	0.48
		0.207	0.411			
	Sn	–	0.040	100	0.0006	0.71
		0.044	0.084			
	Fe	–	0.108	99.5	0.002	0.81
		0.139	0.246			
Goat	Cu	–	0.10	99.6	0.002	0.78
		0.155	0.254			
	Pb	–	0.203	99.5	0.002	0.49
		0.207	0.408			
	Sn	–	0.022	100	0.0001	0.22
		0.023	0.045			
	Fe	–	0.017	100	0.0002	0.74
		0.010	0.027			
Human	Cu	–	0.24	99.7	0.003	0.68
		0.20	0.439			
	Pb	–	0.201	99.8	0.002	0.49
		0.207	0.408			
	Sn	–	0.012	100	0.0001	0.43
		0.011	0.023			
	Fe	–	0.017	100	0.0002	0.74
		0.010	0.027			

* mg/100 ml

combined metal ions are given in Table 2. Except for Pb(II) and Sn(II), all the metal ions could be determined in one run. For Pb(II) and Sn(II) differential complexation of the metals with EDTA was used. The detection limits were examined by preparing synthetic samples.

Table 2
Minimum tried detection limit

Metal ion	DCP (μg/10 ml)	DPP (μg/10 ml)	DPASV (ng/10 ml)
1. Cu Individual	6.0	0.06	6.0
Combined	6.0	0.06	6.0
2. Pb Individual	2.6	0.26	2.6
Combined	2.6	0.26	2.6
3. Sn Individual	1.1	0.11	1.1
Combined	1.1	0.11	1.1
4. Fe Individual	0.56	0.05	2.5
Combined	0.56	0.05	2.5

Table 3 shows the final analysis results of different milk samples. A perusal of this table clearly shows that buffalo milk has a higher concentration of Cu, Pb, Sn and Fe as compared to cow and goat milks, so it is too "heavy" for suckling children. It is also concluded that mother's milk is the safest for infants as regards its metal content.

Table 3
Final analysis results for metal contents of different milk samples

Source of milk	Metal ions (mg/100 ml)			
	Cu	Pb	Sn	Fe
1. Buffalo	0.62	0.245	0.22	0.223
2. Cow	0.39	0.205	0.040	0.108
3. Goat	0.10	0.203	0.022	0.017
4. Human	0.24	0.201	0.012	0.017

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