

Digestion-Free Determination of Trace Cu, Cd, Pb, and Zn Ions in Egyptian Cane Sugar by Differential Pulse Anodic Stripping Voltammetry

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Anodic differential pulse stripping voltammetry with a hanging mercury drop electrode has been used for the determination of trace amount of Cu, Cd, Pb, and Zn ions in different Egyptian white cane sugar samples. Experiments have been made directly, *i.e.* without digesting and pretreating the sugar samples. The best conditions for the determination of traces of these metal ions in sugar, *i.e.* deposition potential, supporting electrolyte composition, effect of pH, and deposition time have been studied. The concentration of each metal ion is determined using the standard addition method. It has been found that the metal content is varied according to the quality of the sugar samples distributed in the market.

The main source of toxic elements for humans nowadays is food. Husbandry practices and food processing methods are commonly responsible for the contamination of human food by toxic metals. The FAO/WHO Joint Expert Committee on Food Additives [1] recommended a provisional maximum tolerable daily intake for Cd and Pb from all sources (food, air, and water) of 1–1.2 μg and 3.5–4 μg in 1 kg of body mass, respectively. The National Research Council of America [2] established a maximum tolerable dietary level of 500 μg Cd and 30 mg of Pb in 1 kg of sugar. Control of trace metal content in sugar is very important since it is a major ingredient of various foodstuffs and because of its fundamental nutritional role in the diet of infants and the elderly. At present, the level of toxic metals allowed by European legislation in refined sugar is in the 1 mg/kg range, but it is likely that these levels will be lowered in near future, moreover, sugar quality and hence sugar price are closely related to metal content.

The determination of heavy metal ions in cane sugar is not only of interest for quality control but also for purposes of environmental monitoring. UV VIS spectrophotometry has been recommended by ICUMSA (International Commission for Uniform Methods of Sugar Analysis) for the determination of several trace elements [3]. But the detection limits of this technique (above the 1 mg dm^{-3} level) are not low enough to determine accurately the metal con-

tents usually found in sugar of good quality (in the $\mu\text{g dm}^{-3}$ range). More sensitive flame and electrothermal atomic absorption spectrometric (FAAS and ETAAS) methods have been described for the determination of metals in sugar [4–6]. However, the analytical matrix of sugar causes strong interference in these techniques, thus hindering the direct measurement of the element in the sample, which must be digested prior to the determination. This inconvenience causes these procedures to be time-consuming and increases the risk of sample contamination and loss of analyte. Multielemental instrumental neutron activation analyses (INAA), inductively coupled plasma atomic emission spectrometric (ICP-AES) and atomic absorption spectrophotometric (AAS) analyses had been utilized for the determination of several metal ions in sugar cane plant and raw juice [7]. Also, few reports are proposed for the determination of other metal ions in some sugar samples using different techniques [8, 9].

Traces of zinc, cadmium, lead, and copper had been determined in refined sugar by anodic stripping voltammetry with the hanging mercury drop electrode including modified method for the oxygen flask combustion [10]. The determination of copper, lead, cadmium, and zinc in very concentrated sucrose solutions and in raw industrial sirups coming directly from the first extraction step of beet roots by water vapour and lime treatment had been studied using differential pulse anodic stripping voltammetry and poten-

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tiometric stripping analysis [11, 12]. Trace amounts of zinc, lead, and copper in sugar cane spirits from different sources had been determined by anodic stripping voltammetry with a hanging mercury drop electrode without previous treatment and in the absence of a supporting electrolyte [13]. Differential pulse anodic stripping voltammetry and potentiometric stripping analysis techniques had been applied for the determination of lead, copper, and cadmium in honey directly without digesting and pretreating the sample [14]. Low levels of Cd, Pb, and Zn in untreated solutions of refined beet sugar have been determined using DPASV [15]. Stripping electrochemical techniques such as anodic stripping voltammetry (ASV) can be used to simultaneously measure Cu, Cd, Pb, and Zn ions in solution. This technique combines low maintenance costs with high sensitivity and selectivity that allows the determination of low levels of metals without prior treatment of the sample.

In the present paper the use of differential pulse anodic stripping voltammetry is examined for the determination of Cu, Pb, Cd, and Zn ions directly without pretreating the samples from different Egyptian cane sugar refineries (crystalline sugar (S_1), commercial sugar (S_2), and cubic sugar (S_3)). This technique is rapid, highly sensitive, precise, reproducible, simple and cost-effective electroanalytical technique for measuring heavy metal ions in several materials [16].

EXPERIMENTAL

All chemicals used were of anal. grade. All glassware was soaked in 6M- HNO_3 (Merck) for 24 h prior to use to avoid the presence of anions, which have complexing effects, then washed with bidistilled water. Solutions were prepared with doubly distilled water. Sodium nitrate and nitric acid solutions (BDH Analar) were prepared and diluted as required (10 cm^3 of 10 mmol dm^{-3} nitric acid or sodium nitrate as supporting electrolyte were needed for the determination). 1 mmol dm^{-3} of metal ions *viz.* Cu(II), Cd(II), Pb(II), and Zn(II) was prepared from their anal. grade (BDH) nitrate salts and dissolving the appropriate mass for each in doubly distilled water.

The sample preparation consisted of dissolving commercially available white cane sugar samples, *i.e.* crystalline sugar (S_1), commercial sugar (S_2), and cubic sugar (S_3) directly (without treatment) in redistilled water (50 g of sugar dissolved in 100 cm^3 of water) individually.

Voltammetric measurements were performed with an EG & G Princeton Applied Research Corp (PAR) Model 264A stripping analyzer, coupled with a PAR 303A static mercury drop electrode (SMDE) (drop size medium). The polarographic cell (PAR Model K 0060) was fitted with an Ag/AgCl saturated KCl reference electrode and a platinum wire counter electrode. A PAR 305 stirrer was connected to the 303A SMDE.

The SMDE and the stirrer were controlled by the instrument. A PAR RE 0089 x-y recorder was used for the collection of the experimental data.

Procedure

10 cm^3 of 10 mmol dm^{-3} nitric acid as supporting electrolyte ($\text{pH} \approx 2.01$) were transferred to the voltammetric cell for the determination of Cd(II), Pb(II), and Cu(II). For Zn(II) determination, 10 mmol dm^{-3} sodium nitrate ($\text{pH} \approx 6.4$) was used instead. The sample solutions were purged with purified nitrogen for ≈ 16 min prior to the electrochemical measurements and maintained above the solution surface during measurements. The solution was stirred during the accumulation time and anodic scan was carried out in the quiescent solution (after 15 s as equilibrium time). Deposition potentials (-1.3 V, -0.7 V, -0.6 V, and -0.3 V) *vs.* Ag/AgCl (reference electrode) were applied for Zn, Cd, Pb, and Cu ions determination, respectively. The scan rate was 5 mV s^{-1} , pulse height 50 mV, and duration time 1 s. The voltammograms were recorded for the original sugar solution and then after spiking the standard metal ion solutions (individually). Nitrogen was passed through the solution for 30 s after each addition. The standard addition technique was chosen because the matrix effects were less influenced by this procedure. The peak current values were plotted against the standard concentration added to obtain the metal ion content in the sample.

RESULTS AND DISCUSSION

The effect of different supporting electrolytes, *viz.* universal buffer, acetic acid—sodium acetate buffer, sodium nitrate, and nitric acid, was investigated for all metal ions Cu, Cd, Pb, and Zn in the presence of 5 cm^3 of sugar sample (S_2) (2.5 g of sugar in 5 cm^3 of bidistilled water). The highest signal was obtained in the presence of 10 mmol dm^{-3} nitric acid in the case of Cu, Pb, and Cd and 10 mmol dm^{-3} sodium nitrate for Zn(II) determination. Also, different concentrations of nitric acid (10 mmol dm^{-3} , 50 mmol dm^{-3} , and 100 mmol dm^{-3}) have been studied at $\text{pH} \approx 2$ for Cu, Cd, and Pb on one sugar sample S_2 (2.5 g of sugar in 5 cm^3 of H_2O). It was noticed that as the concentration of the acid increased, the peak height of the metal decreased as shown in Fig. 1. Therefore, the ideal concentration for the determination of these metal ions is 10 mmol dm^{-3} HNO_3 . Also the concentration of NaNO_3 has been tested for the detection of Zn(II) ion for the same sample (S_2) and it was noticed that 10 mmol dm^{-3} NaNO_3 gives the highest peak signal. The suitable deposition time was studied and fixed in the standard addition of the metal ions to the samples. However, the optimum pH for the detection of Cu, Cd, and Pb metal ions is $\text{pH} \approx 2$ and for Zn $\text{pH} \approx 6.2$. Furthermore, the optimum of an initial poten-

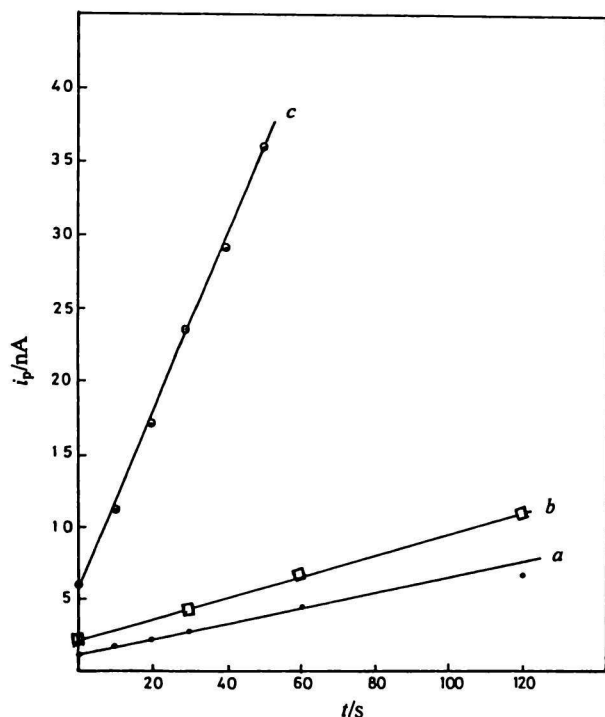


Fig. 1. Effect of nitric acid concentration on the differential pulse anodic stripping voltammetric current of Pb(II) ion in sugar sample S_2 (2.5 g of sugar in 5 cm^3 of H_2O), initial potential -0.6 V . a) 100 mmol dm^{-3} , b) 50 mmol dm^{-3} , c) 10 mmol dm^{-3} .

tial is -0.3 V , -0.7 V , -0.6 V , and -1.3 V for Cu(II), Cd(II), Pb(II), and Zn(II) ions, respectively. The optimal conditions for the detection of these metal ions in sugar samples are summarized in Table 1.

The dependence of the peak signal of Pb(II) ion on the deposition time for the sugar sample S_2 was tested in the presence of 10 mmol dm^{-3} nitric acid, $\text{pH} \approx 1.9$, deposition potential -0.6 V and the effect of deposition time on the peak height was studied for three different volumes (2.5 cm^3 , 5 cm^3 , and 7.5 cm^3 , i.e. 1.25 g, 2.5 g, and 3.75 g of sugar, respectively) of S_2 sample diluted to 10 cm^3 aqueous solution (Fig. 2). It was observed that at the volume 2.5 cm^3 (1.25 g) of S_2 sample the peak is broad and there is no change of the

lead peak height with the deposition time (Fig. 2a). However, the peak is sharp at 5 cm^3 (2.5 g) and 7.5 cm^3 (3.75 g), but the increasing on the peak at 5 cm^3 of S_2 solution (Fig. 2b) is higher than that at 7.5 cm^3 as shown in Fig. 2c. The same behaviour was observed in the effect of S_2 volume for all metal ions under investigation. Therefore, 5 cm^3 (2.5 g) volume of sugar is taken to determine the metal ions in all sugar samples. It is noticed that the signal of Pb(II) ions at the deposition time 0.0 s is relatively high, this may be attributed to the fact that adsorption takes place during the equilibrium time [17, 18].

The influence of sugar concentration on the DPASV peaks of Cu, Cd, Pb, and Zn is investigated. It was observed that increasing amounts of pure sugar (S_1) sample were added to a solution of 10 mmol dm^{-3} nitric acid ($\text{pH} \approx 2$) in the case of Cu, Pb, Cd, 10 mmol dm^{-3} NaNO_3 ($\text{pH} \approx 6$) in the case of Zn, containing $50 \mu\text{g dm}^{-3}$ of all metal ions (Cu, Pb, Cd, and Zn), and peak currents of the four metals were recorded by DPASV as described in Experimental. The peak currents of Cd, Zn decreased by about 40 % in the presence of about 90 g dm^{-3} and 130 g dm^{-3} of sugar concentration, respectively, and were completely suppressed at sugar concentrations higher than 350 g dm^{-3} of sugar. For Cu and Pb, the interferences were more pronounced; the peak currents decreased by about 50 % in the presence of 70 g dm^{-3} of sugar concentration and were suppressed at higher concentrations. This interference is probably owing to the adsorption of sugar on the HMDE (hanging mercury drop electrode) which hinders metals approaching the electrode and hence their reductions [15]. The matrix effect caused by sugar can be overcome by using the standard addition method [16]. Irrespective of a slight decrease in the current observed in the concentrated sugar samples, the standard addition methods gave the same original concentration of metal ions. This conclusion is drawn from the results of some experiments done in the mineralized sample and it gives identical results as in the presence of matrix samples. The precision of the method is satisfactory with good standard deviation and correlation coefficients obtained for five replicate analyses. According

Table 1. The Optimal Conditions for the Determination of Cu, Cd, Pb, and Zn Ions in Sugar Samples Using DPASV Technique

Metal ions	mmol dm^{-3} supporting electrolyte	$E_{\text{acc.}}$ V	S_1		S_2		S_3	
			pH	$t_{\text{acc.}}$ s	pH	$t_{\text{acc.}}$ s	pH	$t_{\text{acc.}}$ s
Cu(II)	10 HNO_3	-0.3	2.01	60	1.81	10	1.75	120
Cd(II)	10 HNO_3	-0.7	2.01	30	1.81	60	1.75	30
Pb(II)	10 HNO_3	-0.6	2.01	20	1.81	0.0	1.75	10
Zn(II)	10 NaNO_3	-1.3	6.24	60	5.92	10	5.92	10

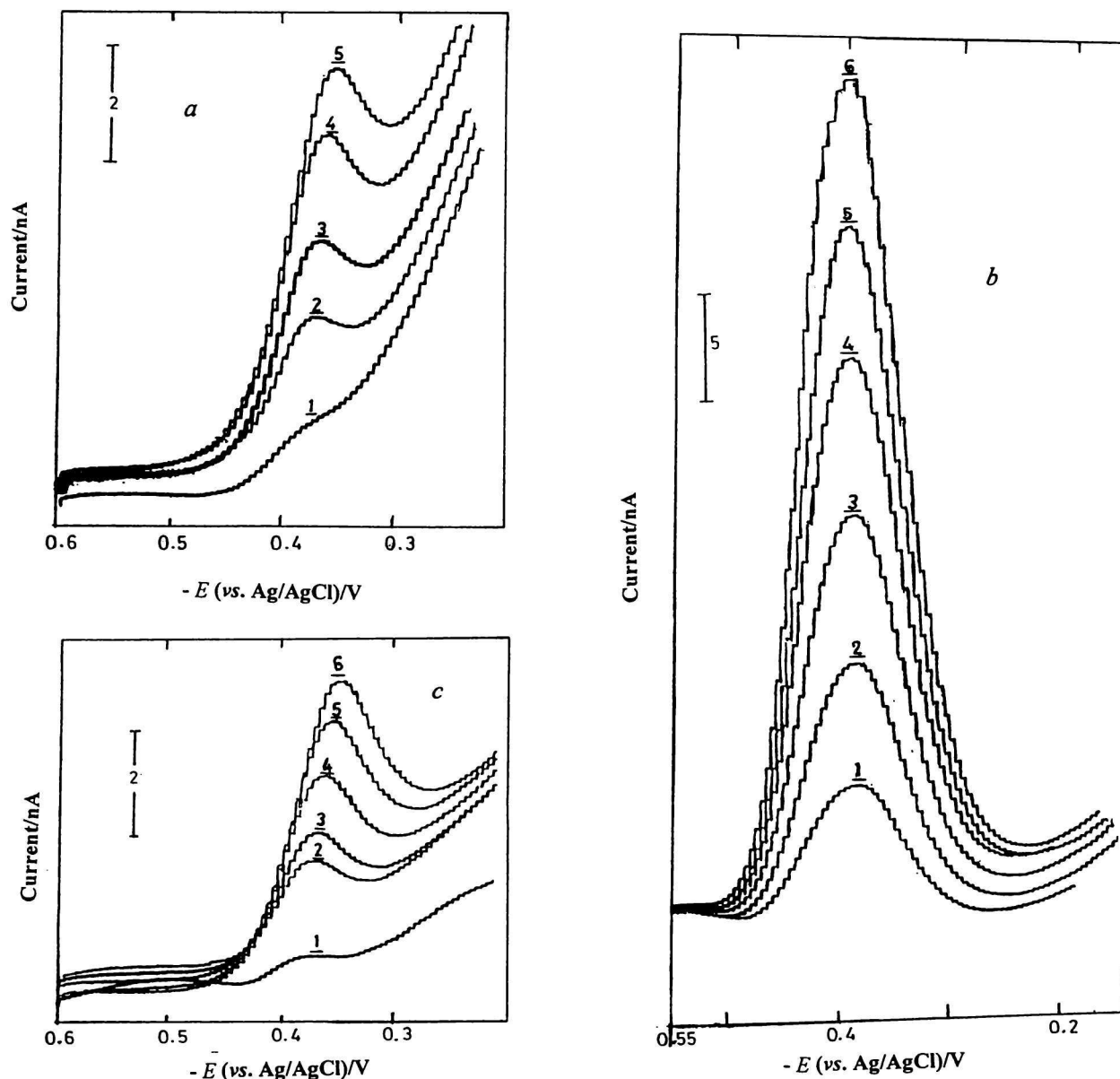


Fig. 2. DPAS voltammograms of Pb(II) ion in $10 \text{ mmol dm}^{-3} \text{ HNO}_3$, $\text{pH} \approx 2$, accumulation potential -0.6 V following different accumulation period using different sugar concentrations (S_2): a) 1.25 g sugar in $10 \text{ cm}^3 \text{ H}_2\text{O}$: 1. 0.0 s , 2. 30 s , 3. 60 s , 4. 120 s , 5. 180 s . b) 2.5 g sugar in $10 \text{ cm}^3 \text{ H}_2\text{O}$: 1. 0.0 s , 2. 10 s , 3. 20 s , 4. 30 s , 5. 40 s , 6. 50 s . c) 3.75 g sugar in $10 \text{ cm}^3 \text{ H}_2\text{O}$: 1. 0.0 s , 2. 30 s , 3. 60 s , 4. 120 s , 5. 180 s , 6. 240 s .

to our investigation [17, 19], a slight decrease in the signal in the presence of interfering ions, as a mixture, does not mean the failure of the analysis. The interference can be treated successfully by using the standard addition method, as seen in Figs. 5–7. However, polarographic techniques have been widely used in aqueous media, even in the presence of inert soluble organic compounds, provided that they were at low concentration levels [20–22]. Therefore, in these samples we can safely assume that there were no interferences since the concentrations of the interfering compounds are below the interfering concentrations.

Moreover, the organic impurities were less interfering at low pH values [11].

It has been reported [15] that Cd, Pb, and Zn ions were determined simultaneously in refined beet sugar by the DPASV method. Measurements were performed on samples without previous treatment. The performance of the procedure was compared with electrothermal atomic absorption spectrometry and DPASV applied to digested samples, and showed better accuracy. The same results were obtained in the white cane sugar samples [10]. Furthermore, these metal ions were also directly determined in sugar

DETERMINATION OF TRACES OF METALS

Table 2. Investigation of the Occurrence of Systematic Errors by Linear Regression for Different White Cane Sugar Samples

Regression parameter	Metal	S ₁	S ₂	S ₃
Numerical value of slope	Cu	1.3577	4.9165	0.5013
	Pb	2.9825	3.0616	2.2627
	Cd	1.8847	1.7647	0.7347
	Zn	4.5179	2.7380	0.8809
c(Intercept)/(10 ⁻⁸ mol dm ⁻³)	Cu	-5.7462	-22.5997	-12.8332
	Pb	-6.7457	-6.6700	-8.4505
	Cd	-0.6463	-0.8455	-1.7222
	Zn	-6.8410	-7.0385	-12.9782
Standard deviation/%	Cu	6.3141	10.01	10.02
	Pb	10.06	7.2559	9.2303
	Cd	2.0090	1.9961	5.8700
	Zn	9.1434	5.4420	10.01
Numerical value of confidence interval for STDEV, at 95 % significant levels	Cu	1.1158	1.7463	1.512
	Pb	1.6000	1.7445	1.3265
	Cd	0.5869	0.5707	1.5682
	Zn	1.5255	1.0263	1.6154

Table 3. Reproducibility of DPASV Applied in the Determination of Trace Metal Content in Untreated Sugar Samples (n = 5)

Sample	<i>m</i> (Metal in 1 kg sugar)/μg				Correlation coefficient			
	Cu	Cd	Pb	Zn	Cu	Cd	Pb	Zn
S ₁	14.606	2.904	55.861	17.966	0.9982	0.9981	0.9877	0.9884
S ₂	61.415	10.912	55.613	19.652	0.9923	0.9989	0.9998	0.9997
S ₃	35.715	7.742	70.034	33.92	0.9934	0.9925	0.9969	0.9989

Table 4. Assay of Zn, Cd, Pb, and Cu Ions Detected in Sugar Using the Suggested Method and Reported Method

Sample	<i>m_i</i> (i = ion, detected in 1 kg sugar)/μg					Ref.
	Zn(II)	Cd(II)	Pb(II)	Cu(II)		
S ₁	17.9	2.9	55.9	14.6		This paper
S ₂	19.6	10.9	55.6	61.4		This paper
S ₃	33.9	7.7	70.0	35.7		This paper
	34.0	1.0	6.0	57.0		[2]
	35.5	7.0	15.5	-		[13]

cane spirit without previous treatment using linear sweep anodic stripping voltammetry (LSASV) [13]. The large variation in organic content in the different samples caused some shift of the peak potential, but this did not affect the determination of the metals in the sugar cane spirits. The data obtained were compared with atomic absorption spectrometry. The discrepancies between the two methods were about 10 %.

Figs. 3 and 4 show the voltammograms obtained after successive standard additions of Cu, Cd, Pb, and Zn ions on the sugar samples, *i.e.* S₁ and S₃ (2.5 g in 5 cm³ of S₁ and S₃), under the same conditions summarized in Table 1. The addition of 10 mm³ of

standard metal ions did not alter the peak potential shifts of the voltammograms, but caused an increase in the current of the corresponding peak. The metal ions content in sugar sample S₁ is calculated from the graph of the peak currents and the standard addition solutions of Cu, Cd, Pb, and Zn as in Fig. 5a–d.

Figs. 6 and 7 give the graphs of the standard additions of all metal ions to the samples S₂ and S₃. It was noticed that the amount of Cu(II), Cd(II), Pb(II), and Zn(II) found in the three samples in the range of μg dm⁻³ varied from one sample to another which may be due to the difference in its quality. Table 2 demonstrates regression parameters obtained by the linear regression method for the determination of Cu, Pb,

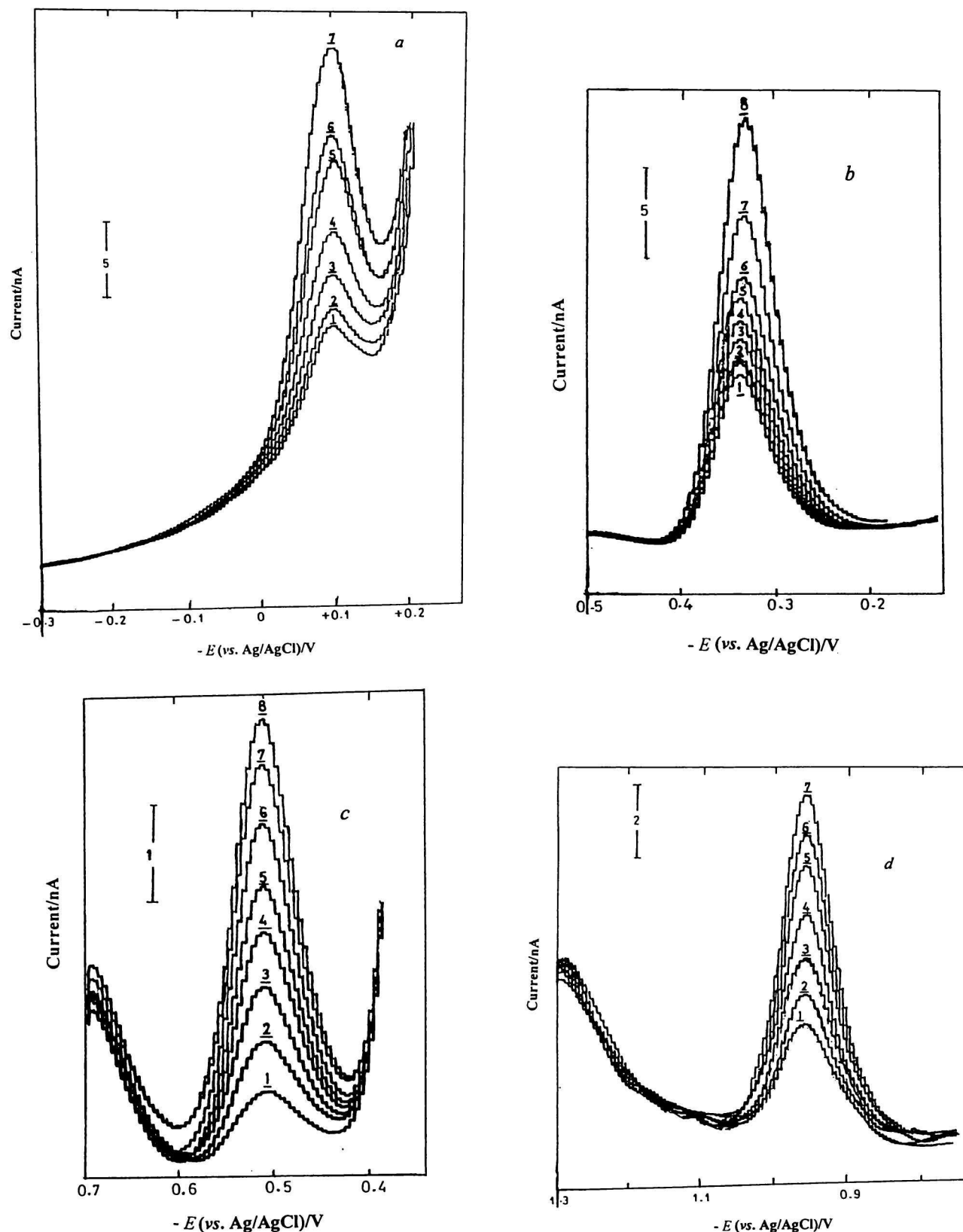


Fig. 3. DPAS voltammograms for successive standard additions to sugar cane (sample S_1): a) Cu(II), $t_{acc.} = 60$ s; $c/(10^{-8} \text{ mol dm}^{-3})$: 1. 0.0, 2. 1, 3. 3, 4. 6, 5. 10, 6. 14, 7. 20. b) Pb(II), $t_{acc.} = 20$ s; $c/(10^{-8} \text{ mol dm}^{-3})$: 1. 0.0, 2. 1, 3. 6, 4. 10, 5. 15, 6. 20, 7. 30, 8. 40. c) Cd(II), $t_{acc.} = 30$ s; $c/(10^{-8} \text{ mol dm}^{-3})$: 1. 0.0, 2. 1, 3. 3, 4. 4, 5. 5, 6. 6, 7. 7, 8. 8. d) Zn(II), $t_{acc.} = 60$ s; $c/(10^{-8} \text{ mol dm}^{-3})$: 1. 0.0, 2. 6, 3. 9, 4. 15, 5. 20, 6. 25, 7. 30. Conditions are summarized in Table 1.

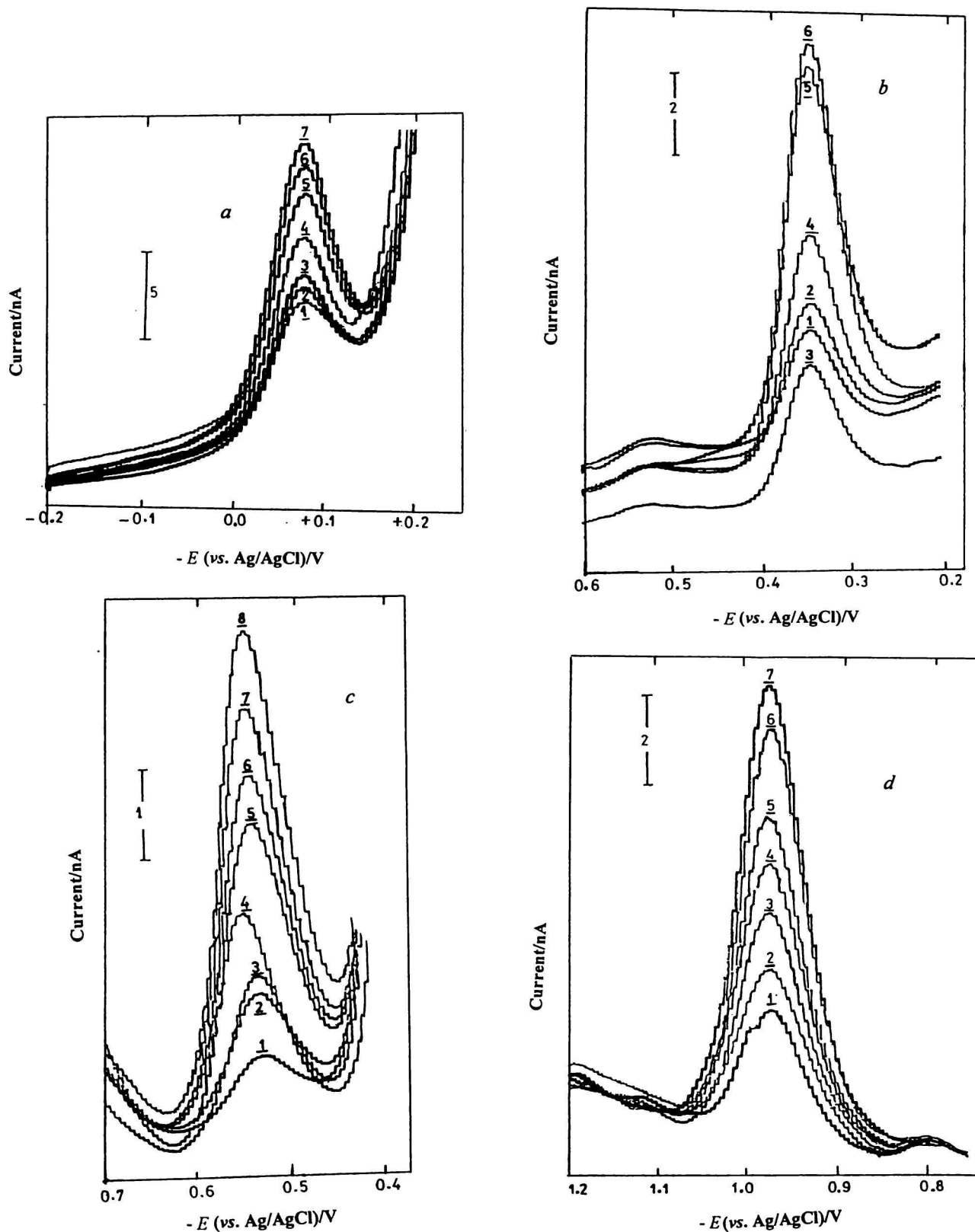


Fig. 4. DPAS voltammograms for successive standard addition to the sample (S_3): a) Cu(II), $t_{acc.} = 120$ s; $c/(10^{-8} \text{ mol dm}^{-3})$: 1. 0.0, 2. 2, 3. 5, 4. 10, 5. 20, 6. 30, 7. 40. b) Pb(II), $t_{acc.} = 10$ s; $c/(10^{-8} \text{ mol dm}^{-3})$: 1. 0.0, 2. 2, 3. 5, 4. 10, 5. 15, 6. 20, 7. 25. c) Cd(II), $t_{acc.} = 30$ s; $c/(10^{-8} \text{ mol dm}^{-3})$: 1. 0.0, 2. 1, 3. 2, 4. 3, 5. 4, 6. 5, 7. 6, 8. 7. d) Zn(II), $t_{acc.} = 10$ s; $c/(10^{-8} \text{ mol dm}^{-3})$: 1. 0.0, 2. 3, 3. 6, 4. 9, 5. 12, 6. 16, 7. 20. Conditions as in Table 1.

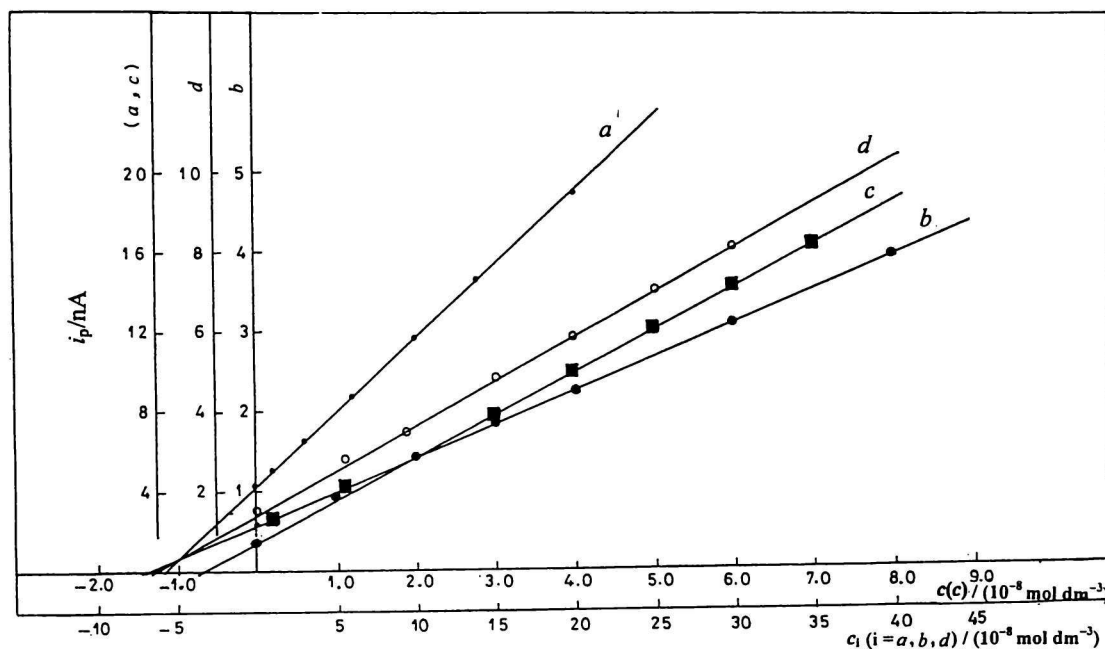


Fig. 5. i_p/nA vs. standard additions for: a) $c(\text{Cu(II)})/(10^{-8} \text{ mol dm}^{-3})$; b) $c(\text{Pb(II)})/(10^{-8} \text{ mol dm}^{-3})$; c) $c(\text{Cd(II)})/(10^{-8} \text{ mol dm}^{-3})$; d) $c(\text{Zn(II)})/(10^{-8} \text{ mol dm}^{-3})$; for sample S_1 conditions as given in Table 1.

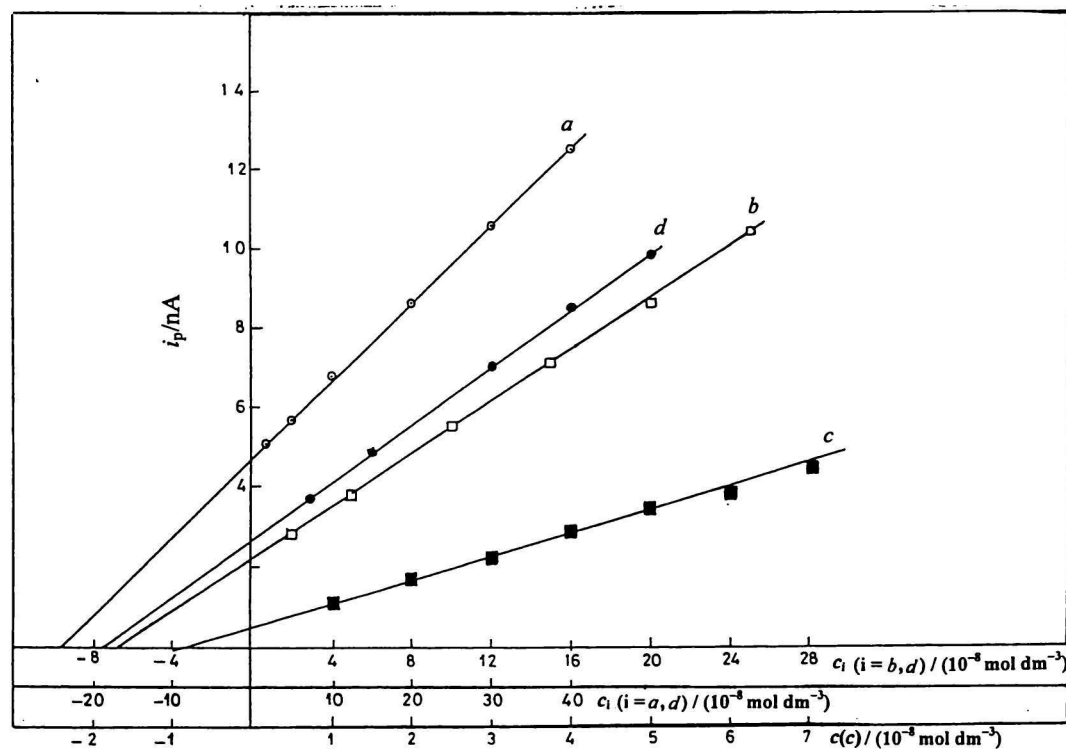


Fig. 6. i_p/nA vs. standard addition of a) Cu(II), b) Pb(II), c) Cd(II), d) Zn(II): $c_i(10^{-8} \text{ mol dm}^{-3})$; for sample S_2 conditions as given in Table 1.

Cd, and Zn in sugar using DPASV. The sensitivity of DPASV in untreated sugar sample solutions was computed from the slope of the regression line obtained by the standard addition method, and it is evident from Table 2. The precision and reproducibility of the se-

lected procedure were investigated by measuring the concentrations of Cu, Pb, Cd, and Zn in three different cane sugar samples. Five replicates were carried out and their confidence and the standard deviations obtained (≤ 10) indicate the good reproducibility of

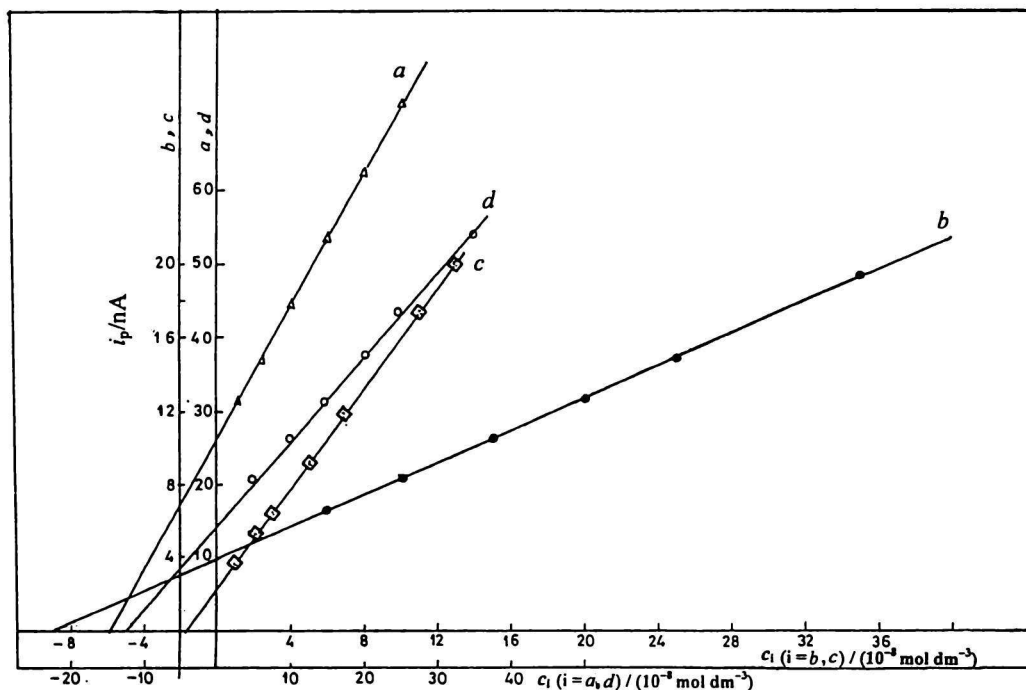


Fig. 7. i_p/nA vs. standard additions of a) Cu(II), b) Pb(II), c) Cd(II), d) Zn(II): $c_i(10^{-8} \text{ mol dm}^{-3})$; for sample S₃ conditions as given in Table 1.

the procedure. The metal ion contents obtained in the three white cane sugar samples and their correlation coefficients are tabulated in Table 3. The results obtained for the determination of Cu(II), Cd(II), Pb(II), and Zn(II) in the white cane sugar samples by the proposed method and the reported methods are shown in Table 4.

The proposed method (DPASV) using low scan rates allows the direct determination of metals in the white cane sugar without previous treatment and permits the determination of the metal ions mass in 1 kg of sugar in the range 1 μg which was not possible with other techniques.

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