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Fast and simultaneous detection of heavy metals using a simple and reliable microchip-electrochemistry route: An alternative approach to food analysis

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Abstract

This paper reports, for the first, the fast and simultaneous detection of prominent heavy metals, including: lead, cadmium and copper using microchip CE with electrochemical detection. The direct amperometric detection mode for microchip CE was successfully applied to these heavy metal ions. The influences of separation voltage, detection potential, as well as the concentration and pH value of the running buffer on the response of the detector were carefully assayed and optimized. The results clearly show that reliable analysis for lead, cadmium, and copper by the degree of electrophoretic separation occurs in less than 3 min using a MES buffer (pH 7.0, 25 mM) and L-histidine, with 1.2 kV separation voltage and −0.8 V detection potential. The detection limits for Pb^{2+}, Cd^{2+}, and Cu^{2+} were 1.74, 0.73 and 0.13 μM (S/N = 3). The %R.S.D. of each peak current was <6% and migration times <2% for prolonged operation. To demonstrate the potential and future role of microchip CE, analytical possibilities and a new route in the raw sample analysis were presented. The results obtained allow the proposed microchip CE-ED acts as an alternative approach for metal analysis in foods.

Keywords: Microchip CE; Electrochemical detection; Heavy metals; Microanalysis

1. Introduction

The traditional format of capillary electrophoresis is quickly being replaced by microdevice platforms in modern analytical chemistry, offering improvements in cost, resolution, speed, quantitation and automation. This aspect of miniaturization is well matched with the ultimate goal of rapid screening and simultaneous detection of a large number of samples [1,2]. The miniaturization of an integrated system improves the advantages inherent to capillary electrophoresis.

Heavy metals are particularly worrisome contaminants in foods and the environment. In general, they are not biodegradable and they have long biological half-lives. Heavy metals have potential for accumulation in humans from various plants and other natural sources, posing serious health hazards for conditions such as renal failure, symptoms of chronic toxicity, and liver damage. According to the World Health Organization (World Health Organization, 1995), lead, cadmium, chromium, and other heavy metals must be controlled in food sources in order to assure public safety.

Lead and cadmium are among the most abundant heavy metals on earth, and are particularly toxic. Excessive concentrations of these metals in food is associated with the etiology of a number of diseases, especially with cardiovascular, renal, neurological, and bone diseases [3,4]. In addition, they are also implicated in causing carcinogenesis, mutagenesis, and teratogenesis [5]. Copper, another important metal, is an essential trace element for the human body and contributes to important intracellular metabolic events [6]. A copper imbalance can result in a severe human ailment, from either an excess or deficiency of this key element [7]. A major reason to monitor levels of toxic metals in foods follows from the fact that contamination of the general environment has increased. The sources of this environmental pollution are quite varied, ranging from industrial

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and traffic emissions to the use of purification mud and agricultural expedients. In order to study the toxicity of heavy metals in food, a simple, sensitive and accurate detection method is required.

Many analytical methods have been developed for determination of individual metals in food products, including: titration [8], colorimetric analysis [9,10], UV–vis spectroscopy [11–13], and either flame or graphite furnace atomic absorption spectrometry (AAS) [14–17]. In addition to these techniques, methods for multi-elemental determination have been developed; these are ion chromatography (IC) [18–20] and inductively coupled plasma combined with either atomic emission spectrometry (ICP–AES) [21,22] or mass spectrometry (ICP–MS) [23–25]. Although these methodologies are rapid and sensitive for the determination of trace amounts of metals, they require complicated instrumentation with high capital and operational costs. Furthermore, these methods are not easily implemented into fully portable analytical tools for screening, detecting, identifying, and quantifying metal ions.

Capillary electrophoresis (CE) has been widely applied to the separation and determination of different metal species, and has proved to be a fast, high-resolution separation technique [26–31]. The detection methods typically used in combination with CE separation technique are ultraviolet light (UV), fluorescence or laser-induced fluorescence (LIF) detection. The lack of a strong chromophore from metal ions has certainly been one of the major limitations in the analysis of most metals by these methods. In addition, these detection modes suffer from lack of sensitivity when a miniaturized device is used. Electrochemical detection (ED) offers high sensitivity and selectivity for metals that are readily oxidized or reduced. This technique is readily suitable and compatible with microfabrication technology that has been successfully employed in microchip CE.

Separation of metal ions by microchip CE has attracted significant attention, offering a number of advantages including speed of analysis, portability, flexibility, and compatibility with integrated analytical systems, allowing development of "micro-total-analysis systems (μTAS)" [1,32–38]. There are a few published examples of metal ion separation performed on a microchip CE. The detection methods are largely focused on the utilization of complexing agents, such as fluorescent metal complexation [39]. Although excellent separation of metal ions was obtained, the designs of microchip sensors were not compact or portable, but tedious and expensive. Unlike other researchers, Li et al. [40] reported the use of microchip CE with indirect amperometric detection of heavy metals. Their results demonstrated good separation and detection, unfortunately, the configuration of microchip and detector was still complicated. Alternatively, we have focused on the simple, direct quantitation of metals by electrochemical reaction, which will enable the incorporation of a portable, simple, and inexpensive detector.

This work addresses the need for developing an inexpensive and field portable analytical device for metal ions which would permit the rapid screening and detection of contaminated food or waste materials on site. The detection of metal ions was accomplished using a microchip CE/amperometric detection system, in which screen-printed carbon electrode is placed at the end of channel. This approach simplifies the fabrication of the working electrode and also provides a convenient and sensitive method for the determination of metal ions by amperometry. Furthermore, by simply changing the electrode, we can easily remove or clean the detection electrode, which is prone to contamination. In this manner, we propose an attractive portable device for screening and analyzing a complex system containing different metal species, such as food. The optimization, characterization, and attractive performance characteristics of a microchip CE, and its successful application to complex samples (such as vegetable juices) are reported in the following sections.

2. Experimental

2.1. Chemicals

Lead(II) nitrate was obtained from Aldrich (Germany). Cadmium(II) sulfate was obtained from Baker Analyzed (USA). Copper(II) sulphate was obtained from BDH (England). Standard stock solutions of all analytes were freshly prepared each day. The running buffer solution (BGE) for separation was prepared from 2-morpholinoethanesulfonic acid (MES), (s)-2-amiono-3-(4-imidazyl) propionic acid (L-histidine) which were obtained from Fluka (USA). Sodium hydroxide and Hydrochloric acid were purchased from Merck (Germany), and were used for pH adjustment of the electrolytic buffer solution. All reagents were used without further purification. Pure deionized water (Millipore, USA) was used to prepare all aqueous solutions. The sample solutions were prepared by diluting corresponding stock solutions in running buffer. All solutions for electrophoresis experiments were filtered through a 0.45 μm membrane filter (Altech) before use.

2.2. Apparatus

Borofloat glass chips with simple-cross single-separation channels (16 mm × 95 mm × 2.2 mm) were obtained from Micralyne (model MC-BF4-001, Canada). The microchip has a four-way injection cross that are connected to the three reservoirs and the channel. The original waste reservoir was cut off, leaving the channel outlet at the end of the chip, facilitating the end-column electrochemical detection. The chip had a 90 mm long separation channel (from injection cross to the channel outlet) and a 10 mm long injection channel (between the sample and buffer reservoir). All channels were etched to a depth of 20 μm and a width at the top of the channel of 50 μm.

The integrated CE-ED microchip system was described previously [36]. The CE microchip was placed in a laboratory-built Plexiglas holder for housing the separation chip and electrochemical detector, allowing convenient replacement. The holder consisted of a sample, running buffer, and unused reservoirs. Short pipette tips were cut and inserted into the fluidic ports of the various reservoirs on the glass chip for providing solution contact between the channel on the chip and the corresponding reservoir on the chip holder. Platinum wires were inserted into the compartments to provide the electrical contacts to a high-

voltage power supply. A home-made high voltage power supply, with an adjustable voltage range between 0 and +4000 V, was used for controlling the injection and separation. The amperometric detector, placed in the waste reservoir, at the separation channel outlet, consisted of an Ag/AgCl wire reference electrode, a platinum wire counter electrode, and a screen-printed carbon working electrode.

2.3. End-column amperometric detection

Amperometric detection was performed with a computer controlled electrochemical analyzer (Autolab potentiostat, PG-30, Methrom) using the "amperometric *i–t* curve" mode. The electropherograms were recorded at a fixed detection potential, −0.8 V versus Ag/AgCl wire. The screen-printed carbon working electrode was placed opposite the outlet of the separation channel through a plastic screw. The distance between the electrode surface and the channel outlet was controlled by a plastic screw and a thin-layer spacer. The electrochemical detection compartment was filled with 25 mM MES/L-histidine buffer solution (pH 7.0). All experiments were done at room temperature, sample injection were performed after the baseline current had stabilized.

2.4. Electrophoresis procedures

Before electrophoresis, the channels of each glass chip were treated by rinsing with deionized water, 0.1 M NaOH, and again with deionized water for 10 min each. The reservoirs were cleaned and the reservoir for sample solution was filled with sample solution, while all other reservoirs were filled with running buffer. Each of the corresponding pipette tips on the micro-channel chip was filled with their respective solution. Injection was carried out by applying the desired potential, 1200 V, between the sample reservoir and the grounded detection reservoir for 3 s, while all other reservoirs were allowed to float. Separation was performed by switching the high-voltage contacts and applying the corresponding separation voltages to the running buffer reservoir with the detection reservoir grounded. As soon as the voltage was switched to perform electrophoresis separation, the electrochemical analyzer was actuated to record signals.

2.5. Sample preparation

Sample solutions were blended for 300 s with a homogenizer. Two millilitre of sample solution was placed in capped centrifuge tubes and then centrifuged for 10 min at 3500 rpm. 0.5 mL of supernatant was then transferred to a centrifuge tube fitted with a filter membrane (0.45 μm Nylon membranes) and centrifuged for 5 min. The filtrate was placed in capped tubes. 0.5 mL of filtrate-sample solution was spiked with 50–100 μL of 2 mM mixed metal ion stock solution (lead(II), cadmium(II), and copper(II) ions) and further diluted with 25 mM MES and L-histidine buffer (pH 7.0) to give final concentrations of 100, 200, 400, 600, 800, and 1000 μM, respectively. Finally, the solutions were analyzed by microchip CE-ED.

3. Results and discussion

In general, the first step in using microchip CE for the determination of metal ions is the selection of the background electrolyte co-ion and subsequently, the optimization of the resolution and detection sensitivity of system. In this work, since electrochemical detection is used; the background electrolyte has a large effect on the signal sensitivity. To obtain a high signal-to-noise ratio, the conductivity of the background electrolyte co-ion, which is directly related to the electrophoretic mobility, should differ from those of analytes as much as possible. It is well known that carrier electrolytes with low-mobility co-ions are preferred for the analysis of small ions. 2-(*N*-Morpholino)ethanesulfonic acid (MES) + histidine is a typical carrier electrolyte with a low-mobility co-ion used for the separation of small ions because both compounds have relatively low mobilities. Moreover, their pK_a values are almost identical, which make them excellent components of buffer system. In the following parts, the influence of some experimental parameters such as the buffer pH, buffer concentration, the separation voltage and the detection potential on the separation efficiency and detection sensitivity are reported in detail.

3.1. Influence of the buffer pH

The running buffer pH is the first important parameter for optimization in microchip CE, the same as in conventional CE. Running buffer pH has effect on EOF rate, degree of ionization, mobility, and separation efficiency of analytes. Thus, the pH values of running buffer were examined in the pH range 6.0–8.5. All buffers contained 20 mM MES and 20 mM L-histidine. Table 1 shows the currents obtained and resolution of three metal ions (Cd(II), Pb(II), and Cu(II)). It can be seen that as buffer pH changed from 6.5 to 7.5, the three metal ions could be well separated. The highest current signal was obtained at buffer pH 7.0. Since the background noise increased relative to the signal intensity and took longer to stabilize between samples, a buffer pH of 7.0 was selected as the optimal pH for all subsequent work.

3.2. Influence of the buffer concentration

Buffer concentration is another important parameter that affects the separation efficiency and detection sensitivity. Electropherograms of 1.0 mM lead, cadmium and copper were performed in varying concentrations of pH 7.0 running buffer.

Table 1
Current and Resolution of three metal ions standards

pH of BGE	Current (nA)			Resolution	
	Pb(II)	Cd(II)	Cu(II)	$R_{Pb,Cd}$	$R_{Cd,Cu}$
6	7.35	7.35	1.87	–	7.75
6.5	1.98	14.81	7.88	2.58	2.51
7	13.49	25.71	17.09	1.91	3.33
7.5	13.25	18.48	10.99	2.18	2.31
8	14.69	20.42	13.69	1.45	1.18
8.5	11.38	11.89	10.35	1.79	1.05

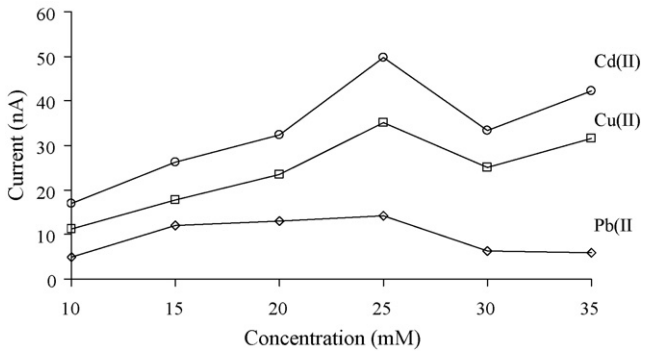

Fig. 1. The effects of the buffer concentration on peak currents. Experimental parameters: sample, 1.0 mM lead, cadmium and copper cations; running buffer, MES and L-His pH 7.0; separation voltage, 1000 V; detection potential, −0.8 V; sampling time, 3 s; working electrode, screen-printed carbon electrode.

We found that the peak current of the three cations increased with increasing buffer concentrations from 10 to 25 mM, and then decreased with further increase of the buffer concentration as shown in Fig. 1. This phenomenon can be attributed to two reasons: (1) higher concentrations of running buffer result in high ionic strength, which will decrease the difference of conductivity between the sample zone and running buffer zone and result in low signal, and (2), higher concentrations of the running buffer makes for electrostacking, which results in relatively higher concentration of the sample zone and then a relatively high signal is obtained. A running buffer concentration of 25 mM was chosen for optimal detection sensitivity.

3.3. Influence of detection potential

Since the detection potential strongly affects the sensitivity and detection limits of microchip CE with an electrochemical system, the optimal detection potential was determined by investigating a hydrodynamic voltammogram. Fig. 2 shows the results which must draw a balance between low applied potentials and enough sensitivity for all the metal ions involved at screen-printed carbon electrode. We observed that the amperometric signal of heavy metals ions increased with the increase of detection potential from −0.70 to −0.85 V. However, the baseline current and the corresponding noise level become large at higher reduction potential. The sensitivity of the signal for the three ions with the change of detection potential was also different. In order to perform the simultaneous determination of lead, cadmium, and copper, the detection potential which most influences the measurement process was optimized. From the results, it can be seen that cadmium and copper have a similar change rate of the signal, while the relative peak current of lead has a lower change rate with changing the detection potential. This suppression of the lead signal could be explained by intermetallic effect of cupper [41]. There is the formation of intermetallic/solid between Cu–Pb. The phenomenon may result in low signal of Pb^{2+}, also resulting in possible calibration problem. To compromise between the sensitivity and signal-to-noise characteristics of three metals, especially Pb^{2+}, a detection potential of −0.8 V was chosen since it offered the most favorable results.

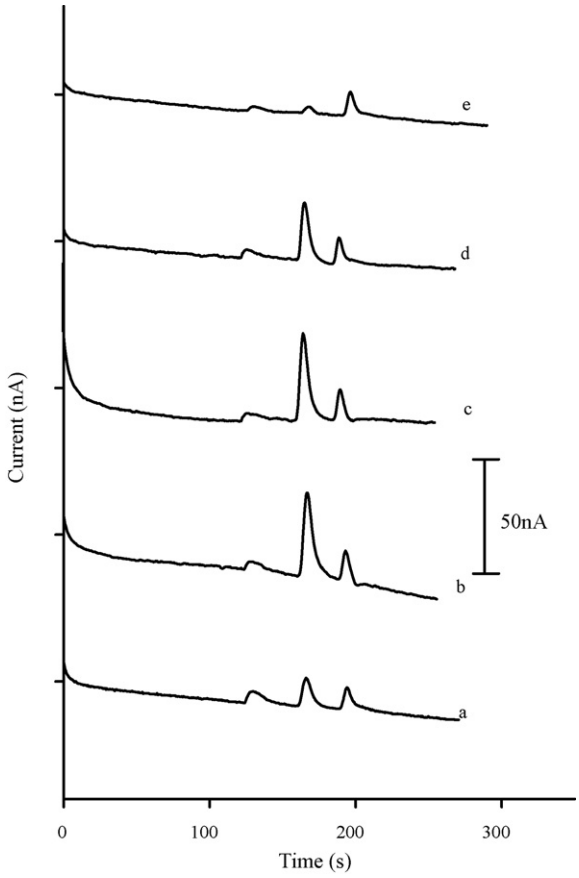

Fig. 2. Electropherograms of 1.0 mM lead, cadmium and copper cations at different detection potentials, −0.90 V (a), −0.85 V (b), −0.80 V (c), −0.75 V (d), −0.70 V (e). Experimental parameters: running buffer, 25 mM MES and L-His pH 7.0; separation voltage, 1000 V; sampling time, 3 s; working electrode, screen-printed carbon electrode.

3.4. Influence of separation voltage

The separation voltage affects the electric field strength, which in turn affects the EOF and the migration velocity of charged particles, which determine the migration times of the analytes. Moreover, higher separation voltages may result in higher Joule heating. The effect of separation voltage on the migration time of the analytes is shown in Fig. 3A. As expected, increasing the voltage gives shorter migration times but also increases the background noise, resulting in a higher detection limit. The migration times were dramatically decreased for all three metal ions, from 120 to 90 s for lead, 150 to 110 s for cadmium, and 175 to 140 s for copper. Although the resolution of analytes can be improved to some extent, too low a separation voltage will increase the analytical time considerably, which in turn causes severe peak broadening (Fig. 3B). Based on experiments, 1200 V was chosen as the optimum voltage to strike a good compromise.

3.5. Effect of oxygen

The effect of oxygen using batch system by screen-printed carbon electrode compared to that by glassy carbon electrode

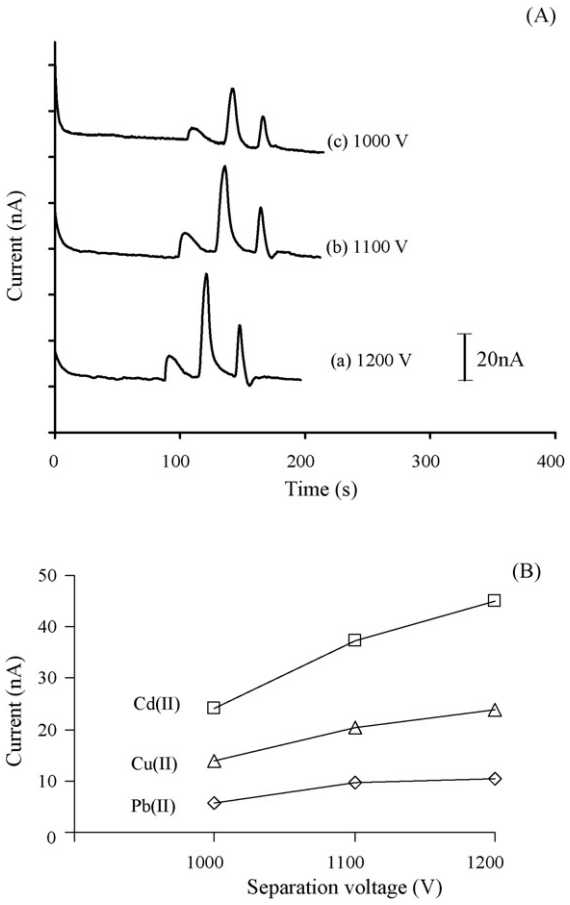

Fig. 3. Electropherograms of 1.0 mM lead, cadmium and copper cations at different separation voltages. The relationship between the peak currents and the separation voltage (A), 1200 V (a), 1100 V (b), 1000 V (c). The relationship between the peak current and the separation time (B). Other parameters same as in Fig. 2.

was studied. It was found that there was a little effect of oxygen on the background signal using screen-printed carbon electrode whereas the high effect of oxygen on the background signal using glassy carbon was obtained. It indicates that screen-printed carbon electrode is less sensitive to oxygen. We also investigated the effect of oxygen of three metals using normal and degas solutions. It was found that the peak current decreased around 11% for $Cd^{2+}$and 21% for Pb^{2+}, respectively. For Cu^{2+}, very small change of the peak current was obtained (data not shown). For the microchip separation system, the experiment was performed in a very small system. Therefore, the effect of oxygen on the determination of these metals can be negligible. From this point, it should be an advantage of this proposed method that it does not need to perform the experiment under the oxygen-free condition.

3.6. Linear range and detection limits

According to the previous studies on pH value and concentration of the running buffer, as well as the separation voltage and the detection potential; optimized conditions of 1200 V separation voltage, −0.8 V detection potential, with 25 mM (pH 7.0) of MES + L-histidine as running buffer were obtained. Under

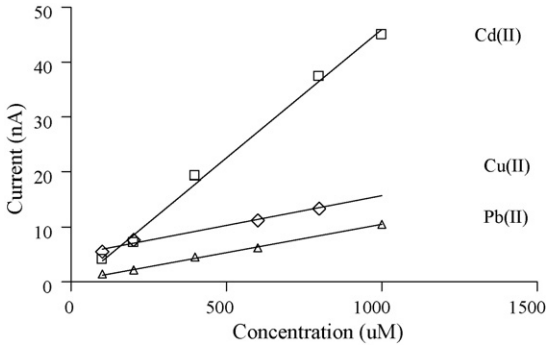

Fig. 4. The relationship between the peak currents and the concentrations. Experimental parameters: running buffer, 25 mM MES and L-His pH 7.0; separation voltage, 1200 V; detection potential, −0.8 V; sampling time, 3 s; working electrode, screen-printed carbon electrode.

the selected conditions, a series of the standard mixture solutions of lead, cadmium, and copper with a concentration range of 100–1000 μM was tested to determine the linearity for all analytes at the screen-printed carbon electrode in this system. The data are shown in Fig. 4. The results of regression analysis on calibration curves are 0.9977, 0.9902, and 0.9958 for lead, cadmium, and copper, respectively. The detection limits were evaluated on the basis of a minimum signal-to-noise ratio of 3. The calibration curves exhibit excellent linear behavior over the concentration range of about micromolar orders of magnitude, with detection limits ranging from 0.13 to 1.74 μM for all the metal ions (data shown in Table 2).

A standard mixture solution of lead, cadmium, and copper (1 mM each) was analyzed ten times to determine the reproducibility of the peak current and migration time for all analytes under the optimal conditions in this experiment. The relative standard deviations (R.S.D.s) of peak current and migration time are 4.20% and 1.47% for lead, 5.27% and 1.40% for cadmium, 3.92% and 1.20% for copper, respectively. It is indicated that the proposed system exhibited an excellent performance on both separation and detection for prolonged operation.

3.7. Sample analysis

The analytical potential of screen-printed carbon electrodes in constant EC detection coupled with microchip CE for the separation of lead, cadmium, and copper in juice samples were investigated. By applying the optimum conditions described above, the injection of three metal ions were analyzed by standard addition method. We studied the metal ions of three different juice samples obtained from a local market. The results are

Table 2
The reproducibility of peak current, retention time and limit of detection of metals

Metal ions	%R.S.D. of peak current	%R.S.D. of retention time	LOD (μM)
Cu(II)	3.92	1.20	0.13
Cd(II)	5.27	1.40	0.73
Pb(II)	4.20	1.47	1.74

Table 3
Determination of Pb(II), Cd(II), and Cu(II) in different samples by means of microchip CE-ED using screen-printed carbon electrode

Sample	Amount added (μM)			Amount found (μM)			%Recovery ($n=3$)			%R.S.D. ($n=3$)		
	Pb	Cd	Cu	Pb	Cd	Cu	Pb	Cd	Cu	Pb	Cd	Cu
Green vegetable juice	1000	750	750	1032	791.85	784.35	103.20	105.58	104.58	2.93	2.10	2.11
	750	500	500	757.95	477.15	459.65	101.06	95.43	91.93	2.37	2.39	2.67
	500	250	250	486.95	269.75	250.08	97.39	107.90	100.03	3.40	2.13	3.75
Tomato juice	1000	800	800	1012.8	775.44	781.84	101.28	96.93	97.73	2.65	0.90	2.68
	800	600	400	791.12	603.06	389.80	98.89	100.51	97.45	4.25	1.63	4.76
	400	200	200	399.92	200.50	191.18	99.98	100.25	95.59	6.48	6.07	6.23
Pine apple juice	800	800	800	819.12	803.84	810.96	102.39	100.48	101.37	3.56	2.87	2.28
	600	600	600	586.26	639.66	621.66	97.71	106.61	103.61	1.57	2.71	2.25
	400	200	500	396.56	214.62	490.05	99.14	107.31	98.01	2.13	1.87	2.57

shown in Table 3. Recoveries ranged from 91.93 to 107.90 with ten replicate each, giving %R.S.D.s of 0.90–6.48. The results show that the proposed methods can be efficiently used for the determination of metal ions in practical samples. Such the high speed of analysis and efficiency of proposed method, it should be possible to separate and detect other metals in different kinds of food by simply varying the detection potential.

4. Conclusions

This work presents the first application of microchip CE-ED in direct mode for the simultaneous determination of lead, cadmium, and copper in vegetable juices. It has been demonstrated that microchip CE-ED is characterized by its simplicity, quickness, higher resolution and sensitivity, excellent reproducibility, low expense of operation and minor amounts of samples and reagent. The reproducibility of quantitative analysis by this method is satisfactory. Electrochemical detection coupled with microchip CE enables selective and sensitive detection of the electroactive constituents and simplification of the electropherograms. We conclude that microchip CE-ED is a powerful technique for the study of heavy metal ions and has become an alternate, competitive and supplementary method for HPLC, because of its special attributes. In particular, microchip CE-ED provides an attractive approach for a portable analytical device for rapid screening and the analysis of complex systems simultaneously containing metals and heavy metals. Such a microchip CE-ED system may have wide applications, particularly in food analysis.

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