

Determination of heavy metals (Cd, Pb, Cu) in some herbal drops by Polarography

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ABSTRACT

Herbs are considered as effective remedies to heal diseases worldwide. As a result of given increasing trend of air, water and soil pollutions, health and quality of these herbs have now become a quite serious and important issue to be attention to. One of the main concerns is the presence of heavy metals in herbal drugs. In this study, the amount of lead, cadmium, and copper in edible herbal dribbles present in Iranian drug market have been measured with the aid of a polarography technique, Differential Pulse Stripping Voltammetry (DPSV). The simultaneous determination of the target elements was done in samples obtained from herbal drops present in citywide drugstores was performed. It was observed that the mean values of measured ions in the samples were beneath WHO and FDA's standards and the concentration of cadmium in most samples was beneath the applied technique detection limit and consequently could not be traced.

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Keywords

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INTRODUCTION

Herbs have been long used as practical remedies to cure diseases. In recent years, acceptability and reception of herbs have received a considerable share of remedy in a way that different herbal drugs have been provisioned and their usage is increasing on a daily basis [1-3]. One of the reasons of an increased consumption of these drugs is their relatively inexpensive price compared to chemical drugs beside their treatment efficacy and less side effects. [4-5].

Unfortunately the increasing flow of air, water and soil pollutions has doubted health and quality of the herbs

apply for medicinal use. Concerning the fact that the consumption of herbs is increasing and little information is available regarding the effect of the pollutants they encounter with, measurement of this harmful chemical contaminants in final herbal products is of great importance.

One of the major chemical pollutants is not degradable toxic metals that mainly enter the environment by sewages industries. As metallurgy, foundry, oil refineries, mines, etc [6, 7]. Since plants absorb chemical compounds

dissolved in water through roots, these hazardous elements can be transferred to human through plants. Further, pollutants in the air, fertilizers, and pesticide poisons can also be absorbed via leaves, which have by themselves toxic metals [8]. Heavy metals remain during a plant's growth in it and after collection and transformation to a drug form, they could be transferred to man and cause problems [9,10]. Studies are being performed in China, Brazil and Egypt to measure the presence of heavy metals in herbal drugs [11-13]. The measurements can be done with different methods such as gold nanoparticle based sensing of spectroscopically silent treatment ions [14], electrothermal atomic absorption spectrometry (ETAAS), ultrasonic nebulization system coupled to inductively coupled plasma optical emission spectrometry (USN-ICP-OES) [15], inductively coupled plasma-mass spectroscopy (ICP-MS) [16], and reversed-phase high-performance liquid chromatography (RP-HPLC) [17]. Beside these techniques, voltammetry is an advantages alternative because of its high sensitivity to heavy metals, good accuracy, and possibility of determination of a group of metals with little cost [18, 19]. Here in this study, polarography technique was applied for the simultaneous determination of lead, cadmium, and copper in edible herbal dribbles present in current Iranian drug market [20].

MATERIALS AND METHODS

Apparatus

Analysis was conducted by Polarography device (797 VA Computrace, Metrohm, Switzerland) with a three electrode systems, consisting of a dropping mercury electrode (DME) as the working electrode, platinum counter electrode and an Ag/AgCl reference electrode. The device was outfitted in the following conditions: measurement mode DP, purge time 300 s, equilibration time 10 s, pulse amplitude 0.05 V, start potential -0.88 V, end potential 0.05 V, voltage step 0.006 V, voltage step time 0.3 s, sweep rate 0.020 V/s. The methodology used is according to application note V035-CdPbCu [21].

Reagents

All chemicals used were of analytical reagent grade from Merck (Germany). Standard solutions used included 0.02 mL from standard 1 mg/L cadmium solution, 0.02 mL

from standard 1 mg/L lead solution and 0.025 mL from standard 1 mg/L copper solution. The ammonium acetate buffer solution was prepared by dissolving of 74.9 mL of nitric acid (25%) and 118 mL of acetic acid and then adding ultrapure water in 1000 mL. The buffer solution pH was then adjusted to 4.6.

Collection of samples

Seven types of common herbal drops with different curing effects were obtained from Tehran drugstores. Some therapeutic effects of these herbal drops are represented in Table 1.

Sample preparation

0.5 mL of each sample was poured into the flask and to it 100 mL of 65% nitric acid was added. The reflux was performed for an hour in oil bath with the temperature of 200 °C and speed of 250 revolutions per minute (rpm). After cooling, the solution was filtered with filter paper. Although all items used had high degree of purity, it was taken blank for high integrity.

Measurement

For 10 mL of the obtained solution; 15 mL of deionized water and one mL of ammonium acetate buffer (pH = 4.6) were placed in apparatus cell. Repetition was adjusted on three. Measurement was done by the standard addition method. All stages were conducted for every sample the corresponding polarograms were obtained.

RESULTS

Average of the concentrations measured in herbal drops under examination are reported in Table 2. The differential puls polarograms of cadmium, lead and copper in herbal medicine sample can be seen in Fig. 1. Mean concentration of cadmium, lead, and copper in the samples were 0.004µg/L, 0.503µg/L and 3.187µg/L, respectively. Also, the maximum concentrations of cadmium, lead and copper were obtained to be 0.02µg/L, 2.559µg/L and 9.941µg/L respectively. Cadmium was only observed in two samples of *T. vulgaris* and *P. incarnate*, which had 0.012µg/L and 0.02µg/L concentrations of cadmium, respectively. Lead was measured in all samples, with the least value being associated with *H. perforatum* (0.078µg/L) and the highest associated with *M. recutita* (2.559µg/L). Copper was also

Table 1. Some remedying effects of these herbal drops

| <i>Botanical name of herbal drops</i> | <i>Indication</i> | <i>Max Dose^a (mL/day)</i> |
|---------------------------------------|--------------------------|--------------------------------------|
| Thymus Vulgaris | Antitussive, Expectorant | 3 |
| Matricaria recutita | Peptic ulcer, Gastritis | 3 |
| Vitex agnus castus | Menstrual disorder | 3 |
| Crataegus oxyacantha | Heartthrob, Hypertension | 10 |
| Hypericum perforatum | Depression, Migraine | 4 |
| Urtica dioica | Urinary problems | 6 |
| Passiflora incarnate | Anxiety, Insomnia | 3 |

^a Daily usage of these drugs was calculated according to the instructions of their manufacturers

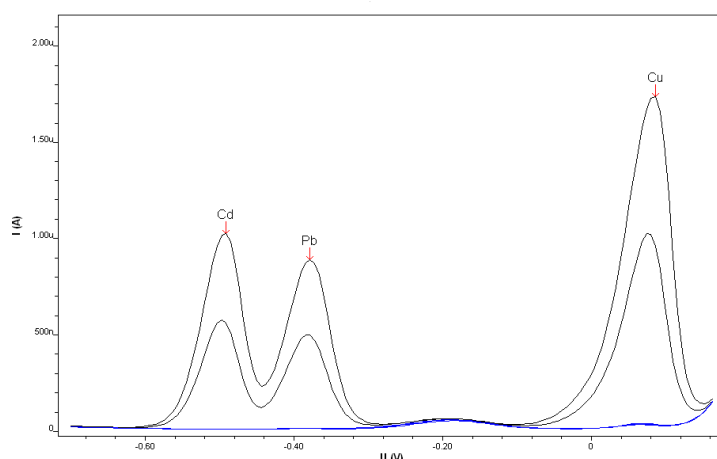


Figure 1. The differential pulsed polarogram of heavy metals in herbal

Table 2. The result of Cadmium, Lead and copper determination by polarography

| Herbal drops name | Cd | | | Pb | | | Cu | |
|------------------------|--|---------------------------------|----------------------------------|--|---------------------------------|----------------------------------|--|---------------------------------|
| | Mean Cons. ($\mu\text{g/L}$) \pm SD | Max Intake $\mu\text{g/day}$ | Max Intake $\mu\text{g/week}$ | Mean Cons. ($\mu\text{g/L}$) \pm SD | Max Intake $\mu\text{g/day}$ | Max Intake $\mu\text{g/week}$ | Mean Cons. ($\mu\text{g/L}$) \pm SD | Max Intake $\mu\text{g/day}$ |
| 1 <i>T. vulgaris</i> | 0.012 ± 3.388 | 0.383×10^{-4} | 2.681×10^{-4} | 0.264 ± 0.071 | 7.92×10^{-4} | 55.44×10^{-4} | 0.782 ± 0.057 | 23.35×10^{-4} |
| 2 <i>M. recutita</i> | - | - | - | 2.559 ± 0.589 | 76.77×10^{-4} | 537.39×10^{-4} | 9.941 ± 1.001 | 298.23×10^{-4} |
| 3 <i>V. castus</i> | - | - | - | 0.110 ± 0.024 | 3.3×10^{-4} | 23.1×10^{-4} | 1.646 ± 0.178 | 49.38×10^{-4} |
| 4 <i>C. oxyacanta</i> | - | - | - | 0.206 ± 0.118 | 20.6×10^{-4} | 144.2×10^{-4} | 1.880 ± 0.495 | 188×10^{-4} |
| 5 <i>H. perforatum</i> | - | - | - | 0.078 ± 0.033 | 3.12×10^{-4} | 21.84×10^{-4} | 1.817 ± 0.134 | 72.68×10^{-4} |
| 6 <i>U. dioica</i> | - | - | - | 0.081 ± 0.046 | 4.86×10^{-4} | 34.02×10^{-4} | 1.886 ± 0.149 | 113.16×10^{-4} |
| 7 <i>P. incarnate</i> | 0.02 ± 3.261 | 0.604×10^{-4} | 4.228×10^{-4} | 0.228 ± 0.073 | 6.84×10^{-4} | 47.88×10^{-4} | 4.362 ± 0.845 | 130.86×10^{-4} |

observed in all samples, with the least value being associated with *T. vulgaris* ($0.782 \mu\text{g/L}$) and the highest associated with *M. recutita* ($9.941 \mu\text{g/L}$).

DISCUSSION

Samples analysis showed that all the studied herbal drops were polluted with lead and copper. Further, cadmium pollution was witnessed in thymus and passiflora drops as well.

Maximum amount of non-announced lead in the finish product is $20 \mu\text{g/day}$ according to the NSF/ANSI criterion. According to US FDA, limit for total daily consumption is $75 \mu\text{g/day}$ for adults and $25 \mu\text{g/day}$ for pregnant women, and according to WHO criteria, lead's provisional tolerable weekly intakes (PTWI) for adults is $25 \mu\text{g/kg/week}$ that is $1750 \mu\text{g/week}$ in a person with the average weight of 70kg [22]. As a matter of fact, the obtained results imply that lead concentration in the analyzed samples poses no threat to consumers' health.

Maximum amount of non-announced cadmium in the finish product is $6 \mu\text{g/day}$ according to the NSF/ANSI criterion. According to US FDA, limit for total daily consumption is $55 \mu\text{g/day}$ for adults, according to ATSDR minimal risk level of cadmium is $14 \mu\text{g/day}$, and according to WHO criteria, cadmium's PTWI for adults is $7 \mu\text{g/kg/week}$ that is $490 \mu\text{g/week}$ in a person with the

average weight of 70kg . Cadmium is congregated in plants by cadmium infected water especially in Irrigating plants [23]. The low cadmium pollution in the studied products shows that the employed plants have presumably been irrigated with low-pollution waters.

WHO guideline has announced a $70 \mu\text{g/day}$ limit for high-level copper up takes [24]. Copper-containing pesticides and fungicides are one of the main causes of copper accumulations of this metal in plants. Although copper is an essential element for plants, because of its serious effects on health, its concentrations need to be controlled.

To conclude, none of the analyzed samples contained unacceptable concentrations of these metals.

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CONFLICT OF INTEREST

The authors declare that this research does not have any conflict of interest with anyone or any institute.

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