Original Article

Determination of total lead (II) in commercial kohl by cyclic voltammetry at a glassy carbon electrode

T. Lanez¹, A. Rebiai¹, M. A. Saha² and M. Alia²

¹VTRS Laboratory, University Centre of El-Oued, P.O. Box 789, 39000, El-Oued, Algeria
²Chemical engineering department, University of Biskra, P.O. Box 145, 07000, Biskra, Algeria

Email: lanezt@gmail.com

Received 03 May 2011; accepted 23 May 2011

Abstract

Since no studies were carried out on kohl (surma) pollution with lead using voltammetry techniques, the present work aimed at measuring lead contamination in several kohl samples purchased from Algeria retail stores. Twelve commercial samples of kohl were analyzed for their contents of lead using cyclic voltammetry techniques. The results showed up to 35% of lead present in kohl, this concentration was over the safe limits of lead set by the world health organization standards. However; only five commercial samples of kohl tested contained less than 0.05% lead. Complete recovery of lead from the kohl was obtained by simple nitric acid digestion.

Key words: kohl, surma, lead, cyclic voltammetry.

1. Introduction

Kohl is widely used traditional eyeliner in all Islamic countries because its use is encouraged within the “sauna”, the religious behavioral guidelines of the Islamic belief. Undoubtedly the “sauna” identifies kohl as a free lead substance. However, analysis consistently revealed that the main composition of kohl is lead [1-2]. However Kohl that contains lead may be a pervasive source of lead poisoning, which usually occurs from repeated exposure to small amounts of lead. Contamination of kohl by lead may originate from leaded paint in production equipment or from contaminated dust. Kohl also may be contaminated with lead if they are manufactured with ingredients that naturally contain lead or are produced under conditions that could introduce lead into the ingredients. Lead is a toxic metal that can be harmful to a human health. Once absorbed by the body, lead can damage the brain, nervous system, reproductive system, kidneys and other parts of the body [3]. The high toxicity of lead is due to its stability and accumulation in human body.

Recent reports showed that lead poisoning in childhood can cause a lifetime negative effect on intelligence and learning abilities, the effects of which persist long after the initial exposure to lead [4]. Kohl contaminated with lead could be the cause of countless unexplained third-world infant deaths, and a significant contributory factor to early mortality? Several methods have been reported for the analysis of lead, such as atomic absorption spectrometry [5, 6], atomic emission spectrometry [7] high performance liquid chromatography [8], inductively coupled plasma-mass spectrometry [9] and neutron activation analysis [10]. However, these techniques have some disadvantages such as complicated operation, high cost of maintenance expensive apparatus and requiring well-controlled experimental conditions. However, the electrochemical methods for the determination of lead are of the most favorable methods because of their low cost and easy operation [11]. The aim of this study is to investigate the possibility of using cyclic voltammetry techniques for quantifying lead in commercial kohl.
In cyclic voltammetry techniques the potential is varied in some systematic manner to cause electroactive chemical species to be reduced or oxidized at the electrode surface. The peak current, is proportional to the chemical species concentration over a given concentration range, and is given by the Randles-Sevcik equation,

$$i_p = 0.269 \times 10^5 \times A \times n^{\frac{3}{2}} \times D^{\frac{1}{2}} \times C \times \nu^{\frac{1}{2}}$$

where

- $A$, electrode area in cm$^2$
- $n$, number of electrons transferred in the electrochemical reaction
- $D$, diffusion coefficient in cm$^2$/s
- $C$, concentration in mol/cm$^3$
- $\nu$, scan rate in V/s

2. Material and methods
2.1. Chemicals
All reagents were of analytical grade. Lead biacetate (99.5%), sodium nitrate (99%), nitric acid (99%), acetic acid (99%), were all purchased from biochem chemopharma Co.

2.2. Kohl simples
Samples of kohl were purchased from Algeria retail stores, most of these samples originated from Pakistan, India, and Saudi Arabia.

2.3. Instrumentation and software
Cyclic voltammetry measurements were performed using PGZ301 potentiostat (radiometer analytical SAS) and a voltammetric cell with a volumetric capacity of 50 mL containing a glassy carbon electrode working electrode (radiometer analytical SAS), a Pt wire counter electrode, and an Hg/HgCl$_2$ reference electrode (saturated with KCl). The potential was swept in inverse scanning mode starting from 900 to 0 mV with a scanning rate of 100 mV/s. To avoid reducing the sensitivity of the working electrode, the latter was polished after each cycle by rubbing its surface using alumina oxide (particle size 0.3µm) before every electrochemical assay. After polishing it was rinsed thoroughly with bidistilled water for 30 s. In order to reduce adsorption on glassware, the electrochemical cell, calibrated flasks and pipettes were previously soaked in 30% nitric acid for 24 hours and rinsed with deionized water [12].

The recorded cyclic voltammograms of lead solutions in the range of concentrations 4, 2, 1, 0.5, 0.25 mM are represented in (Fig.1).

![Cyclic voltammograms referring to different Pb(II) concentrations at 100 mV/s on 3 mm-diameter glassy carbon working electrode, in aqueous NaNO$_3$ (0.01 M)](image)

3. Results and discussion
3.1. Cyclic voltammetry measurements
Cyclic voltammetry measurements were performed in an electrochemical cell with a volumetric capacity of 50 mL containing a glassy carbon electrode working electrode (radiometer analytical SAS), a Pt wire counter electrode, and an Hg/HgCl$_2$ reference electrode (saturated with KCl). The potential was swept in inverse scanning mode starting from 900 to 0 mV with a scanning rate of 100 mV/s. To avoid reducing the sensitivity of the working electrode, the latter was polished after each cycle by rubbing its surface using alumina oxide (particle size 0.3µm) before every electrochemical assay. After polishing it was rinsed thoroughly with bidistilled water for 30 s. In order to reduce adsorption on glassware, the electrochemical cell, calibrated flasks and pipettes were previously soaked in 30% nitric acid for 24 hours and rinsed with deionized water [12].

The recorded cyclic voltammograms of lead solutions in the range of concentrations 4, 2, 1, 0.5, 0.25 mM are represented in (Fig.1).

The calibration graph is obtained by plotting the peak current of the anodic curve of the voltammogram of each sample of the standard versus its concentration. Lead diacetate was used as a standard in the calculation of the concentration of studied kohl samples because its anodic peak current displays excellent linearity toward lead concentrations.

As it can be seen from figure (1) there is an increase in oxidation peaks current with the increase in lead concentrations which leads to a linear relation between these two parameters.

The oxidation peaks current are summarized in (Table 1).
Table 1. Oxidation peaks current obtained from cyclic voltammograms of lead

<table>
<thead>
<tr>
<th>C (mM)</th>
<th>( i_{Pb} ) (mA.cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.84</td>
</tr>
<tr>
<td>2</td>
<td>0.45</td>
</tr>
<tr>
<td>1</td>
<td>0.23</td>
</tr>
<tr>
<td>0.5</td>
<td>0.11</td>
</tr>
<tr>
<td>0.25</td>
<td>0.044</td>
</tr>
</tbody>
</table>

The equation obtained from the linear calibration graph in the studied concentration range for lead (II) in aqueous NaNO\(_3\) is \( y = 0.007 + 0.421x \) (where \( y \) represents the value of oxidation current and \( x \), the value of lead (II) concentrations, expressed as mM) with a correlation coefficient of \( R^2 = 0.9969 \). Results obtained are shown in (Fig.2).

Fig.2: Calibration curve obtained by cyclic voltammograms for different Pb(II) concentrations at 100 mV/s on 3 mm-diameter glassy carbon working electrode in aqueous NaNO\(_3\) (0.01 M).

3.2. Voltammetric lead determination
50 mL of the digested kohl solution was introduced into the electrochemical cell and the oxidation peak current of the voltammogram was recorded. The above procedure was repeated for all samples. The concentration of lead in kohl samples was obtained using the density of the oxidation peak current of the corresponding voltammogram. (Fig.3) shows different voltammograms of the twelve studied kohl samples.

In order to get a better reading of peak current density, the voltammograms are retraced in the range of potential: -0.50 to -0.40 V as shown on (Fig.4). The potential shift is probably due to the increase of the resistance solution.

Table 2 shows kohl samples, their origin and level of contamination of lead, all samples were tested in replicates.

Table 2. Lead content of kohl samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Origin</th>
<th>( i_{Pb} ) (mA/cm(^2))</th>
<th>Lead %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Unknown</td>
<td>1.29</td>
<td>31.65</td>
</tr>
<tr>
<td>2</td>
<td>Saudi Arabia</td>
<td>1.46</td>
<td>35.84</td>
</tr>
<tr>
<td>3</td>
<td>Unknown</td>
<td>0.69</td>
<td>33.69</td>
</tr>
<tr>
<td>4</td>
<td>Unknown</td>
<td>0.73</td>
<td>35.67</td>
</tr>
<tr>
<td>5</td>
<td>Unknown</td>
<td>0.64</td>
<td>31.23</td>
</tr>
<tr>
<td>6</td>
<td>India</td>
<td>*</td>
<td>&lt; 0.05*</td>
</tr>
<tr>
<td>7</td>
<td>Unknown</td>
<td>*</td>
<td>&lt; 0.05*</td>
</tr>
<tr>
<td>8</td>
<td>Pakistan</td>
<td>*</td>
<td>&lt; 0.05*</td>
</tr>
<tr>
<td>9</td>
<td>Saudi Arabia</td>
<td>*</td>
<td>&lt; 0.05*</td>
</tr>
<tr>
<td>10</td>
<td>Unknown</td>
<td>0.65</td>
<td>31.72</td>
</tr>
<tr>
<td>11</td>
<td>Saudi Arabia</td>
<td>*</td>
<td>&lt; 0.05*</td>
</tr>
<tr>
<td>12</td>
<td>Saudi Arabia</td>
<td>0.62</td>
<td>15.12</td>
</tr>
</tbody>
</table>

*Value below the detection limit.
4. Conclusion
Seven of the twelve kohl samples analyzed in this work contained high detectable amounts of lead when digested with HNO$_3$. The concentration of lead in six studied samples was found to contain in excess of 30% lead, one contained 15% lead, and this level is considered to be over the safe limits according to the world health organization standards. The remaining five samples were found to be below the detection limit of lead by voltammetry cyclic which is less than 0.05%.

5. References

Source of support: Nil; Conflict of interest: None declared