ELECTROCHEMICAL METHOD FOR LEAD DETECTION IN SOME MEDICINAL PLANTS

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\textbf{ABSTRACT}

The purpose of the paper is lead detection in lime and peppermint tea, both being collected from some different areas of our country. A sampling method for electrochemical analysis of lead content has been established.

\textbf{KEY WORDS:}

electrochemical techniques, specific electrodes, heavy metals

\section{1. INTRODUCTION}

The virtues of lime tea (\textit{Tilia} species) are already well known: the infusion of lime flowers is a good remedy against cold, flu and insomnia, being also a sedative of the nervous system. Yet the virtues of lime flowers and of the prepared from it have not been studied to the end (e.g. lime is merely unreplaceable in some renal diseases). Thus, in chronic pyelonephritis caused by a nephrolithiasis, the lime infusion decreases the body temperature from 37.3\degree C and sometimes even slops the inflammatory process in the kidneys. Thereby the chill sensation (hands, feet and even the whole body) associated with the disease can disappear. On the other hand, the lime infusion decreases the amount of blood urea. Associated with honey and lemon, the lime flowers infusion is a good remedy against the flu. These associations are also widely used, together with mint (\textit{Mentha} species) in cosmetics and toiletry.

Besides lime flowers, the wide variety of mint species (\textit{Mentha} piperita) known as with mint (spearmint) and black mint (peppermint) are used as infusions for centuries both as refreshing beverages and therapeutical remedies. The mint infusion is used against diarrhoea, rheumatic pain, nausea and skin diseases; in higher concentration (as mint oil) it is revulsive and tonic agent therefore largely used in cosmetics. Mint is usually associated with infusions or essential oils of salvia (\textit{Salvia officinalis}), rosemary (\textit{Rosmarinus officinalis}), hardhay (\textit{Hypericum perforatum}), parsley (\textit{Petroselinum officinalis}) and other in cosmetics and even as therapeutical aids (e.g. The Rudolf Breuss method of cancer treatment).

Both lime flowers and mint leaves are used in romanian traditional home care for hundreds of years. Their harvest and family use has reached an industrial scale.
In the recent years the increasing pollution of the environment put an emphases on poisons that can accumulate in herbal drugs. Lead is one of them. Therefore the control of lead content in these drugs is very important.

2. EXPERIMENTAL

a. Calibration curve

The calibration curve for lead was plotted using Thermo Orion Model 710A+ is a pH / ISE mV / Temperature Meter for general laboratory use. The work electrode was a Model 96-82-ionplus® Sure-Flow® lead electrode. The electrode is filled with solution Thermo Orion, Optimum ResultsTM B, no.900062. This model does not require a separate reference electrode.

The standard solution was 0.1 M Pb(ClO₄)₂ (Merck Co.) treated as follows:
- a mixture methanol-formaldehyde is prepared by adding 3 drops of 37% formaldehyde to 1 liter reagent grade methanol; this reagent is to be added in 50:50 ratio to all samples and standards to decrease solubility and retard oxidation of pellet;
- an ionic strength adjustor (ISA) is obtained by adding 80.25 g reagent grade NaClO₄·H₂O in 100 ml volumetric flask; add first 50 ml distilled water to dissolve solid and then dilute to mark;
- add 2 ml of ISA to 50 ml standard or sample and 50 ml mixture methanol-formaldehyde prepared as above; ISA was used for all lead measurements.

In the direct measurement procedure, a calibration curve is defined by the Nernst relation:

\[ E = E^0 + \frac{0.059}{n} \log [Pb^{2+}] \]  

(1)

The electrode potential of standard solutions were measured and plotted on the linear axis against their concentrations on the log axis (Fig.1.)

b. Sample preparation

At the beginning of this study, concentrated infusions of the above mentioned plants (lime flowers and mint leaves) have been taken in work. Since this infusions, containing proteins, oligosaccharides, saponines, hydrophobic compounds, et., showed an unusual behaviour (e.g. precipitation or development of colloidal structures) which leads to suppose a complexation of the small amounts of existing lead and thus the possible clogging of the electrode, the further runs have been made on dry drugs.

Thus, samples of about 2 g of dry drugs, harvested in different sites of Romania, have been treated two times with 4 ml of HNO₃ 65% (Merck Co., lead free) while
burned to ash in order to oxidise all organic matter and recover all metals as nitrates. Thorough burning to ash requires about 30 min. Dry ash has been extracted several times with distilled water, filtered through Filtrax 389 paper and volume has been corrected to 100 ml mark. The aqueous samples thus obtained were treated in the same manner as the Pb(ClO$_4$)$_2$ standards, as above.

The results obtained are shown in Table 1 and Table 2 for samples of lime flowers and peppermint, respectively.

Table 1. Lead concentration in lime flowers

<table>
<thead>
<tr>
<th>Sample/Source</th>
<th>Weight, g</th>
<th>E, mV</th>
<th>Conc. Pb(ClO$_4$)$_2$, mol/l</th>
<th>ppm Pb$^{2+}$/ g lime flowers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rm.Vâlcea</td>
<td>1.6614</td>
<td>-314.5</td>
<td>$3.89 \cdot 10^{-6}$</td>
<td>1.1967</td>
</tr>
<tr>
<td>Botoşani</td>
<td>1.8991</td>
<td>-336.6</td>
<td>$6.15 \cdot 10^{-7}$</td>
<td>0.1655</td>
</tr>
<tr>
<td>Orăştie</td>
<td>2.2617</td>
<td>-346.5</td>
<td>$2.69 \cdot 10^{-7}$</td>
<td>0.0608</td>
</tr>
<tr>
<td>Timişoara</td>
<td>1.9329</td>
<td>-332.3</td>
<td>$9.03 \cdot 10^{-7}$</td>
<td>0.2329</td>
</tr>
<tr>
<td>Cluj-Napoca</td>
<td>1.9028</td>
<td>-337.0</td>
<td>$5.95 \cdot 10^{-7}$</td>
<td>0.1598</td>
</tr>
<tr>
<td>P.Neamţ</td>
<td>1.8911</td>
<td>-324.4</td>
<td>$1.7 \cdot 10^{-6}$</td>
<td>0.4594</td>
</tr>
</tbody>
</table>

Table 2. Lead concentration in peppermint leaves

<table>
<thead>
<tr>
<th>Sample/Source</th>
<th>Weight, g</th>
<th>E, mV</th>
<th>Conc. Pb(ClO$_4$)$_2$, mol/l</th>
<th>ppm Pb$^{2+}$/ g peppermint</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rm.Vâlcea</td>
<td>2.1134</td>
<td>-330.6</td>
<td>$1.015 \cdot 10^{-6}$</td>
<td>0.2455</td>
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<tr>
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<td>$7.27 \cdot 10^{-7}$</td>
<td>0.2187</td>
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<tr>
<td>Orăştie</td>
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<td>-340.4</td>
<td>$4.48 \cdot 10^{-7}$</td>
<td>0.1086</td>
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<tr>
<td>Timişoara</td>
<td>1.8129</td>
<td>-332.5</td>
<td>$8.66 \cdot 10^{-7}$</td>
<td>0.2442</td>
</tr>
<tr>
<td>Cluj-Napoca</td>
<td>2.7294</td>
<td>-337.4</td>
<td>$5.75 \cdot 10^{-7}$</td>
<td>0.1078</td>
</tr>
<tr>
<td>P.Neamţ</td>
<td>1.9981</td>
<td>-328.9</td>
<td>$1.17 \cdot 10^{-6}$</td>
<td>0.2993</td>
</tr>
</tbody>
</table>

Lead accumulation in lime flowers and peppermint leaves is better represented in Fig. 2.

3. CONCLUSION

An effective and easy-to-use electrochemical method of lead content in herbal drugs has been established by using a portable Thermo Orion Model 710A+. The values obtained in these experiments for lime flowers and peppermint leaves are allowable by FAO/OMS standards in food chemistry.

This method may be successfully used in other fields: medicine, chemistry, environment (waste water and soil quality analyses) for lead detection and can be easy adapted for continuous monitoring of many particular processes.
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