Determination of lead and cadmium in tap water and soils by stripping analysis using mercury-free graphite–epoxy composite electrodes

Arben Merkoçi, Ulku Anik-Kirgoz and Salvador Alegret

7.1 OBJECTIVES

(a) To construct a graphite–epoxy composite electrode (GECE). (b) To test the GECE in standard solutions of heavy metals. (c) Analysis of lead and cadmium in contaminated soils. (d) Analysis of lead and cadmium in water samples.

7.2 MATERIALS AND INSTRUMENTS

Graphite powder (BDH, England), Epo-Tek (H77) and hardener (Epoxy Technology, USA). PVC tube (6 mm i.d.), 12 cm long; flexible PVC tubing (6 mm o.d.) and copper disk (6 mm o.d. and 0.5 mm thickness).

Bismuth nitrate (analytical grade); 1 ppm high-purity standard solutions of the nitrate salts of Pb and Cd prepared using supporting electrolyte solutions and acetate buffer (0.1 M, pH 4.5) as supporting electrolyte prepared in Milli-Q water.

Platinum auxiliary electrode (model 52–67 1, Crison, Spain); double junction Ag/AgCl reference electrode (Orion 900200) with 0.1 M KCl as external reference solution and GECE as working electrode.

Autolab PGSTAT 20 System (Eco-chemie, The Netherlands) for stripping measurements.

All the other reagents not mentioned here are of analytical grade.
7.3 CONSTRUCTION OF THE GRAPHITE–EPOXY COMPOSITE ELECTRODES

- Obtain a 12 cm long PVC tube (6 mm i.d.). Fit inside this tube a flexible PVC o-ring (6 mm o.d.) and set it about 3 mm from one end of the tube.
- Clean a copper disk with a diameter of 6 mm by dipping it in HNO₃ solution (1:1) (to remove copper oxide) and rinsing it well with bi-distilled water. Then, solder a 6 cm long shielded wire to the middle of the disk.
- Insert the wire into the PVC tube from the end near which the flexible PVC o-ring was set. Pull the wire inside the tube until the copper disk rests on the PVC ring. Figure 7.1 shows the configuration of the GECE.
- Meanwhile, prepare the non-conducting epoxy resin by mixing well Epo-Tek H77 (epoxy resin) and its hardener (both from Epoxy Technology, USA) at a ratio 20:3 (w/w). When the resin and hardener are well mixed, add the graphite powder (particle size 50 μm, BDH, UK) in the ratio 20:80 (w/w) and mix the paste thoroughly for 30 min until it becomes homogenous. This step will produce the graphite–epoxy composite paste.
- Apply the conductive composite paste on the copper disk. Allow the resin to cure at 40°C for about 1 week.
- After the resin has hardened, polish the surface of the composite first with abrasive paper, and then with alumina paper (polishing strips 301044-001, Orion). Wash the polished surface well with

![Diagram of the GECE configuration](image)

Fig. 7.1. Configuration of the GECE.
Milli-Q water. When not in use, store the sensor in a dried place at room temperature.

7.4 STRIPPING ANALYSIS OF STANDARD SOLUTIONS

- The square-wave voltammetric (SWV) analysis mode is chosen in the Autolab software program. The parameters are conditioning potential, +0.6V; conditioning time, 60 s; quiescent time, 15 s; accumulation potential (\(E_{\text{acc}}\)), −1.3V; accumulation time (\(\tau_{\text{acc}}\)), 120 s; stripping range from −1.3 to −0.3V; frequency, 50 Hz; amplitude, 20 mV and potential step, 20 mV.

- The three electrodes: GECE as working electrode, the Ag/AgCl as reference electrode and the platinum as auxiliary electrode, are immersed in a 25 ml electrochemical cell containing 0.1 M acetate buffer (pH 4.5) and 400 µg/l of bismuth. During the stripping step, the current is recorded in quiescent solution.

- Run the first stripping cycle so as to obtain the SWV peak of the background response.

- After running the background stripping, add in the same electrochemical cell few microlitres from stock solutions of lead and cadmium so as to obtain a solution with a determined concentration. Run the stripping analysis and repeat it without removal of the electrodes for different concentrations.

- All experiments will be carried out without removal of oxygen.

Figure 7.2 shows a typical response of the GECE for standard solutions with increasing concentrations of Cd and Pb.

7.5 ANALYSIS OF LEAD AND CADMIUM IN REAL SAMPLES

The detection of heavy metals in contaminated soil samples as well as the recoveries in tap water samples have been studied.

7.5.1 Soil samples

- The soil samples were grounded to 200 µm and then 1 g was weighed. The soil sample was first extracted with water and then centrifuged, and the residue was extracted with 0.11 M acetic acid following standard procedures.
A three-electrode system (based on a GECE) along with conditions as described in Section 7.4 have been established. The volume of the electrolyte solution was 24 mL. The bismuth concentration was adjusted to be 400 mg/L.

- Multiple standard addition method (three additions of 50 ppb of Cd and Pb solution) is used to detect Cd and Pb in the sample.
- The concentration of each metal is estimated from \(x\)-axis interception of the corresponding linear plots (current vs. added concentration of the metal; not shown).

### 7.5.2 Water samples

- Tap water was taken from our laboratory and used as it is.
- A three-electrode system as described in Section 7.5.1 has been established. The volume of the electrolyte solution was 24 mL. The bismuth concentration was adjusted to be 400 mg/L.
- Multiple standard addition method (three additions of 50 ppb of Cd and Pb solution) was utilised to recover two concentration levels of 40 and 80 mg/L of spiked metals into the solution composed of 1 mL tap water and 24 mL electrolytic cell (0.1 M acetate buffer, pH 4.5).
- The concentration of each metal is estimated from \(x\)-axis interception of the corresponding linear plots (current vs. added concentration of the metal; not shown). The recoveries were then calculated.
TABLE 7.1
The recoveries from tap water and the amounts of metals from soil extract samples obtained by using SWV with GECE and AAS technique (printed with permission from Ref. [1])

<table>
<thead>
<tr>
<th>Metal</th>
<th>Spiked concentration (µg/L)</th>
<th>Found concentration (µg/L)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>40.0</td>
<td>34.0 ± 3.1</td>
<td>85.0 ± 7.6</td>
</tr>
<tr>
<td></td>
<td>80.0</td>
<td>95.0 ± 2.1</td>
<td>118.8 ± 2.7</td>
</tr>
<tr>
<td>Cd</td>
<td>40.0</td>
<td>43.3 ± 1.2</td>
<td>108.3 ± 3.0</td>
</tr>
<tr>
<td></td>
<td>80.0</td>
<td>85.0 ± 5.1</td>
<td>106.6 ± 6.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal</th>
<th>AAS concentration (µg/L)</th>
<th>Found concentration (µg/L)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>88.0</td>
<td>80.0 ± 4.7</td>
<td>90.9 ± 5.4</td>
</tr>
<tr>
<td>Cd</td>
<td>24.8</td>
<td>19.0 ± 1.1</td>
<td>80.0 ± 3.5</td>
</tr>
</tbody>
</table>

7.6 DISCUSSION

Table 7.1 shows the results obtained along with those given by using the graphite furnace atomic absorption spectrophotometry (AAS).

One of the key points in the preparation of the GECE is the well homogenisation of all the components before curing of the composite pastes. The homogenised distribution will ensure a good reproducibility of the electrodes after each renewing surface procedure (mechanical polishing as described in the procedures). The same graphite epoxy composite pastes can be used to prepare thick-film electrodes by using screen-printed technology. By this way, a better reproducibility of the electrodes will be achieved.

SELECTED LITERATURE

FURTHER READING