DENTAL AMALGAM, AN ALTERNATIVE ELECTRODE MATERIAL FOR VOLTAMMETRIC ANALYSES OF POLLUTANTS

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Liquid mercury and liquid mercury amalgams are superior electrode materials in voltammetry for analytical purposes. This is mainly due to the high overvoltage to hydrogen, which enables the detection of heavy metals with high negative half-wave potentials. Because of the toxicity of mercury and liquid mercury compounds, their use is increasingly restricted, and cannot be included in voltammetric devices for field and on-line applications. Authors have studied properties of dental amalgam as an electrode material in voltammetry. The results show that dental amalgam acts similarly to a silver electrode. Also, it has a high hydrogen overvoltage, allowing it to be used, *e.g.*, for detection of zinc. In addition, due to special properties of dental amalgam compared with mercury itself, it is not toxic. New in this paper is the determination of nickel and cobalt on the dental amalgam electrode using adsorptive cathodic stripping voltammetry (AdCSV). Also, some new data on detection of zinc, cadmium, lead and thallium are presented. The results show that this electrode can be used over a long period of time without any maintenance, which is important for on-line analyses of pollutants in soil and groundwater.

Keywords: Voltammetry; Non-toxic solid dental amalgam electrode; Heavy metals determination; Amalgams; Mercury.

Pure liquid mercury or liquid mercury amalgams are superior as electrode materials in voltammetry for analytical purposes[1–3]. This is mainly due to the high overvoltage of hydrogen, which renders possible a wide working potential range for the electrode.

There has been, however, a growing concern about the general use of mercury due to its toxicity. This includes the use of pure mercury as an electrode material in voltammetry. Even for the laboratory use, restrictions are expected to apply in the future. Therefore, it is of great interest to find alternative electrode materials to the liquid mercury and liquid amalgam

electrodes. The use of dilute amalgams, amalgam-film electrodes[4,5] or a mercury meniscus on silver electrode[6] may reduce greatly the amount of mercury used. However, even for these electrodes the risk due to the toxicity of mercury is not eliminated.

Among numerous papers dealing with alternative electrodes, the glassy carbon electrode[7–11], graphite electrode[12,13], gold electrode[14–16] and silver electrode[17–20] are important contributions. Also materials like iridium[21–23] and palladium[24] are interesting. But all these electrodes have a limited analytical value because they cannot operate below –900 mV. This is a great drawback since many important heavy metals have their half-wave potentials more negative, and therefore, they cannot be detected by use of these electrodes.

Although some work using mercury-free electrodes for, *e.g.*, zinc detection has been published[25,26], the procedure for making such electrode is often difficult and the reproducibility is often low. The bismuth-film electrode[27,28] is an interesting alternative, but it requires addition of bismuth ions to the solution to form the film, and therefore is not suitable for on-line analysis.

The present investigation describes the use of the solid dental amalgam electrode for zinc, cadmium, lead and thallium detection by differential pulse anodic stripping voltammetry (DPASV), and adsorptive cathodic stripping voltammetry (AdCSV) of nickel and cobalt in dimethylglyoxime (DMG) complexes. Such determinations are important for field and on-line analyses of pollutants in soil and groundwater, and the electrode may be used repeatedly. Further improvements may obviously be obtained by optimizing the composition of the alloy and electrolyte, and by application of sound to the electrode system[2,3]. The method may also be used with other voltammetric techniques. Preparation of solid amalgam electrodes is fast and simple, *e.g.* by using techniques well established in dental practice[29], and in addition they are non-toxic[30].

EXPERIMENTAL

Analyses of zinc, cadmium and lead were performed by differential pulse anodic stripping voltammetry in 0.05 M ammonium acetate solution. Nickel and cobalt were detected simultaneously as dimethylglyoxime complex by adsorptive cathodic stripping voltammetry in ammonium hydroxide–ammonium chloride buffer (pH 9.2) with $9.52 \cdot 10^{-4}$ M iminodiacetate added. Concentration of dimethylglyoxime was $4.75 \cdot 10^{-4}$ mol l^{-1}. The preparation of the dental amalgam electrode has been described in a previous paper[31]. A Metrohm voltammetric analyzer 746VA/747 was used with a solid dental amalgam working electrode

(6 mm in diameter), glassy carbon auxiliary electrode and a Ag/AgCl/3 M KCl reference electrode.

Standard solutions of zinc, cadmium, lead, nickel and cobalt were prepared from 1 000 ppm (Titrisol) analytical grade AAS-standard solutions purchased from Merck. From these solutions, a 10 ppm standard solution was made by diluting 10 ml to 1000 ml with distilled water and 1 ml of suprapure HNO_3. The water was purified with Millipore Elix and Millipore Milli-Q gradient system (Millipore Corporation, France). The analysis was performed with freshly prepared standard solutions in a 100 ml test cell. All reagents were of analytical grade. The solution was purged with nitrogen from AGA (6.0) under stirring for 10 min before the scan was started and 30 s between every standard addition.

The electrode was polished to a shiny surface with 0.25 mm diamond paste on a Struers polishing equipment, and then used without any other maintenance during a period of about two weeks. When the electrode was not in use, it was stored in distilled water, preferably at –400 mV.

RESULTS

Electrode Background

In order to establish the working range of the electrode, a background scan in ammonium acetate buffer was performed. This is illustrated in Fig. 1.

At –1 200 mV, hydrogen gas evolution was observed at the electrode surface. At –200 mV rising of an anodic current was observed, most likely due to decomposition of the dental amalgam in the electrode. In order to avoid

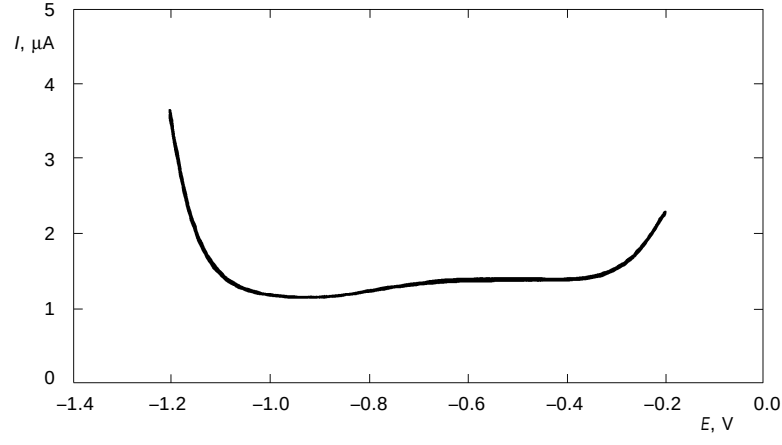

FIG. 1
Background signal of the dental amalgam electrode in NH_4Ac at pH 6.4. Deposition 60 s at –1 200 mV is followed by a scanning to –200 mV. Three successive scans are shown

changes in the electrode response, the rest potential of the electrode was set to –400 mV.

Analyses of Zinc, Cadmium, Lead and Thallium

Analysis of cadmium was performed in ammonium acetate at pH 6.4. The standard addition technique was utilized for quantification.

The electrode response to cadmium is shown in Fig. 2, which reports three individual analyses. Even after 14 days of operation without polishing the electrode surface, the relative standard deviation of determination was within 5%.

Under the same conditions as described for cadmium, determination of thallium was performed as shown in Fig. 3.

A series of multielement analyses were performed in ammonium acetate at pH 6.4. A sample solution containing 25 ppb of nickel, zinc, cadmium, lead and copper was analyzed. Nickel and copper were outside the potential range applicable in this media. The results are shown in Fig. 4.

The electrode shows good response to metals. Apparently the response to zinc was suppressed by copper, which can be explained by formation of an intermetallic compound. However, a linear response to the zinc concentration was obtained without addition of trivalent gallium[32] to the solution.

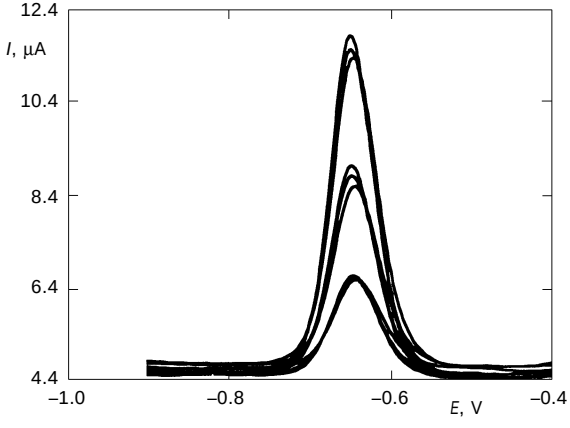

FIG. 2

Cadmium detection by anodic stripping voltammetry. Deposition at –900 mV for 60 s is followed by scanning to –400 mV. The scan rate is 30 mV s^{-1}, a standard modulation of 50 mV is applied. Cadmium concentration is 25, 50 and 75 ppb, respectively, with three repeated measurements at each concentration level

The dental amalgam electrode differs from the mercury drop electrode by showing a higher response to lead than to cadmium. As known, the solubility of cadmium in mercury is greater then that of lead and, consequently, a

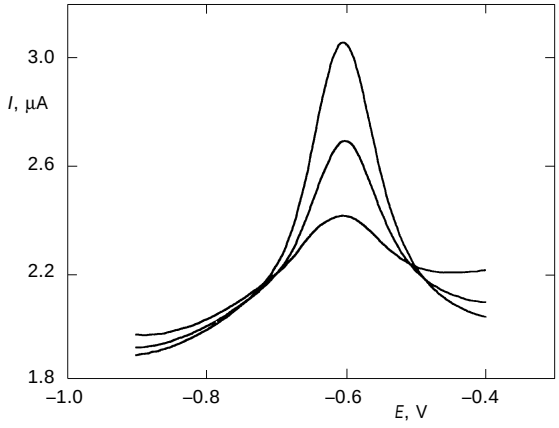

FIG. 3
Thallium detection by anodic stripping voltammetry. Conditions as described in Fig 2. Thallium concentrations are 25, 50 and 75 ppb. Half-wave potential is slightly more positive than that of cadmium

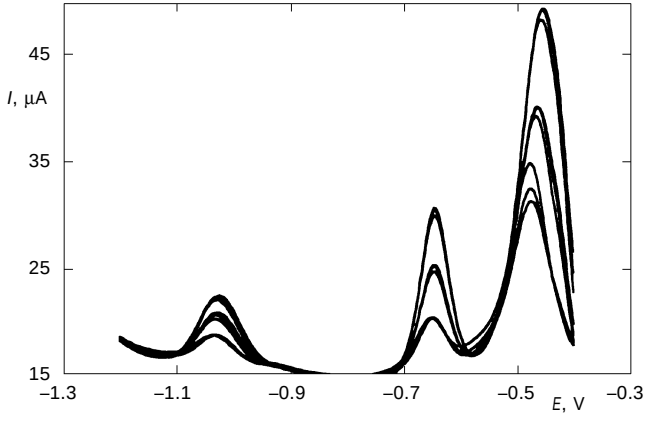

FIG. 4
Detection of Zn, Cd and Pb by anodic stripping voltammetry. The original 25 ppb sample was spiked to 50 and 75 ppb with a mix-standard of Ni, Zn, Cd, Pb and Cu. Deposition at –1 200 mV for 60 s was followed by scanning to –400 mV. Scan rate and pulse height are described in the text

higher response for cadmium is observed at the mercury drop electrode[33]. At the solid amalgam electrode however, metal ions form solid deposits. These observations show good agreement with experiments on silver electrode[19].

Analyses of Nickel and Cobalt

Analyses of nickel and cobalt were performed as adsorptive cathodic stripping voltammetry of their dimethylglyoxime complexes in ammonium buffer solutions as described above. The nickel and cobalt alone yielded well-defined peaks resolved from hydrogen evolution.

Interference problems however, occurred when both nickel and cobalt were present in the solution. The response for nickel was much higher than that for cobalt, and at nickel concentration two to three times higher than that of cobalt, only a small cobalt shoulder appeared on the nickel peak. Thus the quantification of cobalt concentration was impossible.

The use of iminodiacetate for a better complexation of cobalt was tried out as a solution to this problem. Simultaneous detection of nickel and cobalt at different concentrations in the presence of iminodiacetate is shown in Fig. 5.

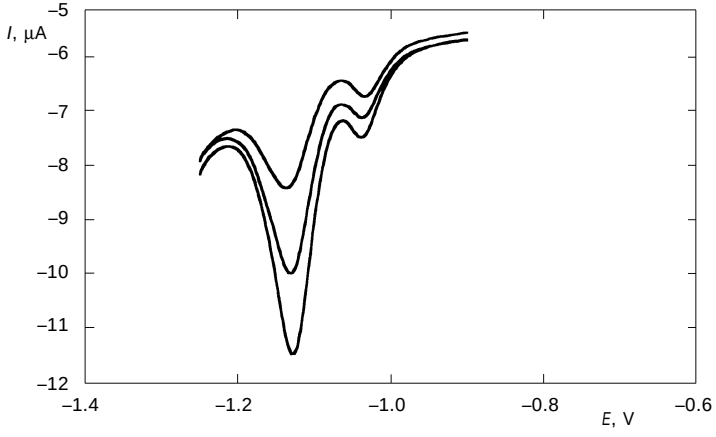

FIG. 5

Adsorptive cathodic stripping voltammetry detection of Ni(II) and Co(II) (10, 20, 30 ppb) as dimethylglyoxime complex in NH_4Cl buffer solution. Iminodiacetate was added to enhance the cobalt response. Deposition times 30 s at –0.7 V, scan from –0.7 to –1.25 V, pulse height –50 mV

Addition of iminodiacetate caused a considerable enhancement of the cobalt response and quantification of both cobalt and nickel could be done without problems.

CONCLUSIONS

Results presented in this paper further support findings from former work[31], indicating that dental amalgam represents promising electrode material for use in electroanalysis due to its high hydrogen overvoltage and low toxicity.

It can be used as an electrode for detection of heavy metals, such as nickel, cobalt, zinc, cadmium, lead and thallium which has its importance in environmental analysis.

Dental amalgam electrodes combine properties of both mercury and silver electrodes. For instance, dental amalgam material Ag_2Hg_3 exhibits high hydrogen overvoltage, similar to mercury, while metal deposition differs significantly from pure mercury electrode. The addition of copper in a zinc solution decreases the response for zinc substantially, indicating thus the formation of an intermetallic compound with copper and zinc. The response for lead is significantly better than for cadmium, which otherwise is typical for the silver electrode[17–20]. At the potential of –200 mV, an anodic current is observed, most likely due to decomposition of the dental amalgam.

As solid, non-toxic material, the dental amalgam can be used in on-line analyses in the field. The detection limits for the metals presented in this paper are in the same range as for the mercury-film electrode. Dental amalgam electrodes can be used repeatedly over a long period of time without any maintenance, which is essential for an on-line and field apparatus.

Finally, such electrodes are cheap and easy to manufacture, using techniques well established in dental praxis.

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