

## A Simple Method for Detection of Manganese in Marine Sediments\*

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Microparticles of sediment are mechanically transferred to the graphite electrode surface and the presence of manganese oxyhydroxides is detected by square-wave voltammetry in 0.1 M oxalic acid. After preelectrolysis at  $-2$  V vs. Ag/AgCl, a characteristic stripping peak appears at  $-0.60$  V. Following oxidation at 0.9 V, the response is dominated by a peak at 0.32 V.

### INTRODUCTION

Manganese is a ubiquitous, essential element. Its average concentration in the earth's crust is approximately 0.05%.<sup>1</sup> The concentration of dissolved  $\text{Mn}^{2+}$  ions decreases from about  $2 \times 10^{-7}$  M in rivers<sup>1,2</sup> to  $2 \times 10^{-8}$  M in estuaries<sup>3</sup> and near-shore seawater,<sup>4</sup> then to  $10^{-9}$  M in open-ocean surface waters<sup>5,6</sup> and  $10^{-10}$  M in deep oceanic waters.<sup>5,7,8</sup> Hydrothermal emanations may increase  $\text{Mn}^{2+}$  concentration near the ocean floor up to  $2 \times 10^{-9}$  M.<sup>6</sup> In seawater, manganese is oxidized to insoluble oxide  $\text{MnO}_2$  and oxyhydroxide  $\text{MnOOH}$  which form colloidal suspensions, coatings on other minerals and amorphous solid particles mixed with iron oxides.<sup>5,9,10</sup> The oxidation of  $\text{Mn}^{2+}$  can be bacterially mediated.<sup>11</sup> Ferro-manganese solid particles are covered by a film of organic compounds, adsorbed metal ions and attached microorganisms.<sup>12</sup> Thus, they are efficient scavenging agents. Besides, dissolved  $\text{Mn}^{2+}$  ions form strong ion pairs with bicarbonate and carbonate ions and co-

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precipitate with calcite.<sup>9</sup> In estuarine sediments there can be up to 0.03% of manganese,<sup>3,13</sup> and the concentration of  $Mn^{2+}$  ions in the pore water is about  $10^{-6}$  M as a consequence of reductive dissolution of manganese oxides.<sup>3</sup> In surface waters, suspended particles of manganese oxides undergo bacterially mediated photoreduction and this process is believed to largely control the solubility of manganese in seawater.<sup>14</sup>

In a previous paper, a method for direct electrochemical identification of manganese impurities in solid carbonate samples was described.<sup>15</sup> The method utilizes a procedure of abrasive stripping voltammetry.<sup>16</sup> This solid state electroanalytical technique is based on the mechanical transfer of microparticles of insoluble solid compounds to the circular surface of a graphite rod, which is then used as the working electrode in the classical voltammetric experiment.<sup>17,18</sup> It can be used to characterize various minerals.<sup>19,20</sup> In this communication, its application in detection of manganese in marine sediments is described.

A field study was performed in the Krka river estuary, which has been sedimentologically well investigated.<sup>21-23</sup> It is a karstic estuary, cut into the limestone erosional plane.<sup>21</sup> Carbonate sediments are covered with oxic seawater and consist predominantly of calcite with smaller amounts of aragonite, quartz, dolomite and clay minerals.<sup>22,23</sup> The content of manganese in the sediment increases downstream from 0.025% below the waterfalls to 0.1% in the Prokljan lake and to 0.3% in the lower estuary, opposite to the Šibenik Harbor, but decreases back to 0.035% at the sea-mouth.<sup>22</sup> However, in the harbor itself values higher than 1% were found in the vicinity of a ferromanganese factory.<sup>23</sup>

## EXPERIMENTAL

Analytical-grade  $KNO_3$  (Pliva, Zagreb),  $NH_4OH$ ,  $NH_4Cl$  (Kemika, Zagreb) and oxalic acid (Merck) were used as received. Water was double distilled. Supporting electrolytes were 0.1 M oxalic acid, 0.1 M  $NH_3/NH_4Cl$  buffer and 1 M  $KNO_3$ .

Electroanalytical experiments were performed with a spectral-grade paraffin-impregnated graphite rod (diameter 5 mm, length 50 mm) as working electrode, which was used in conjunction with a platinum gauze counter electrode and an  $Ag|AgCl|3M KCl$  (Metrohm) reference electrode ( $E = 0.208$  V vs SHE).<sup>24</sup> Before each voltammetric measurement, the circular surface of the graphite rod was rinsed with distilled water, polished on a wet polishing cloth, rinsed again, dried with a fine-grade paper tissue and carefully polished on a dry, white paper sheet. Then, it was pressed into a small pile of the fine grain fraction of the sediment sample on a highly glazed ceramic tile and moved circularly for about 10 seconds, as recommended.<sup>25</sup> By this procedure, the surface is contaminated by traces of silt fraction of the sample and can be used as a modified working electrode. The average size of attached solid particles was estimated at about 30  $\mu m$ . The samples were very wet and the poisoned electrode surface was left to dry in air for 5 minutes prior to voltammetric measurements. Only less than 1 mm of the graphite rod was immersed in the electrolyte, with the

objective of restricting its contact with the solution to the surface itself as much as possible.

Voltammetric measurements were performed using a multimode polarograph  $\mu$ -Autolab (EcoChemie, Utrecht), which was connected to a lap-top computer P5-486 (IPC) and printer BJ-10 sx (Canon).

Solutions were degassed with high-purity nitrogen for 30 minutes prior to the measurements. A nitrogen blanket was maintained thereafter. The cell was thermostated at 25 °C.

Marine sediment samples were collected in July 1996 from a depth of 15 meters in the vicinity of the ferromanganese factory in Šibenik. A simple acrylic glass tube (20 cm long and 7 cm internal diameter) was used for the sampling by scuba-diving. The total length of the tube was inserted into the seabed and plugged with a polyethylene stopper. Using a quartz spatula, a few grams (wet weight) of the finest sand and silt were collected from the top of the sediment core and transferred to the ceramic tile. The electroanalytical measurement was performed immediately after the sampling.

## RESULTS AND DISCUSSION

The proposed method is based on the electroreduction of manganese ions at  $-2$  V and the subsequent reoxidation by square-wave voltammetry. A typical net response is shown in Figure 1A. The characteristic peak at

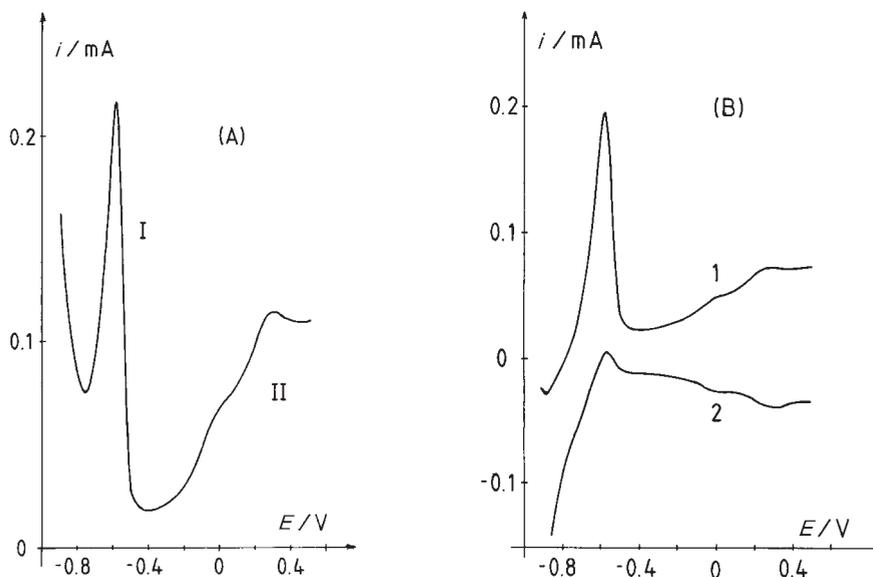


Figure 1. Square-wave voltammogram of sediment microparticles. A net response (A) and its forward (1) and backward (2) components (B). Electrolyte is 0.1 M oxalic acid.  $E_{acc} = -2$  V,  $t_{acc} = 30$  s,  $f = 100$  Hz,  $E_{SW} = 50$  mV and  $dE = 2$  mV.

$-0.60 \pm 0.02$  V, which is marked by (I), is a consequence of totally irreversible oxidation, as it can be concluded from the forward and backward components of the square-wave voltammetric response shown in Figure 1B. They also indicate that the second peak of the nett response, marked by (II) in Figure 1A, corresponds to a quasireversible redox reaction. The relationships between peak currents (I) and (II) and the duration and the potential of preliminary electroreduction are shown in Figure 2. Peak (I) is well developed if the reduction potential is negative to  $-1.5$  V. Also, if the preelectrolysis is shorter than 10 seconds, the response is dominated by peak (II) appearing at  $0.28 \pm 0.02$  V, as can be seen in Figure 3.

Bilinski *et al.*<sup>23</sup> have shown previously that the investigated sediments contain between 1% and 9% of manganese, partly in the form of amorphous oxyhydroxides. They identified the minerals kutnahorite calcian ( $\text{Ca}_{0.74}(\text{Mn},\text{Mg})_{0.26}\text{CO}_3$ ) and takanelite ( $\text{Mn}^{2+}_{2/3}\text{Ca}^{2+}_{1/3}\text{Mn}_4\text{O}_9 \times 3 \text{H}_2\text{O}$ ) as minor components of the sediments. The main sources of manganese were industrial slag and dust containing the minerals calcium manganate ( $\text{CaMnO}_3$ ) and manganosite ( $\text{MnO}$ ), respectively.

Microparticles of manganese oxyhydroxides attached to the electrode surface are both electronically and ionically conductive.<sup>26</sup> By changing the electrode potential, manganese ions in the particles can be reduced, or oxidized, and these redox reactions are accompanied by the exchange of protons with the electrolyte.<sup>27</sup> The pseudopolarogram (I) shown in Figure 2B corresponds to the electrogeneration of metallic manganese.<sup>28</sup> Thus, the characteristic stripping peak (I) at  $-0.60$  V was most probably caused by the oxidation of

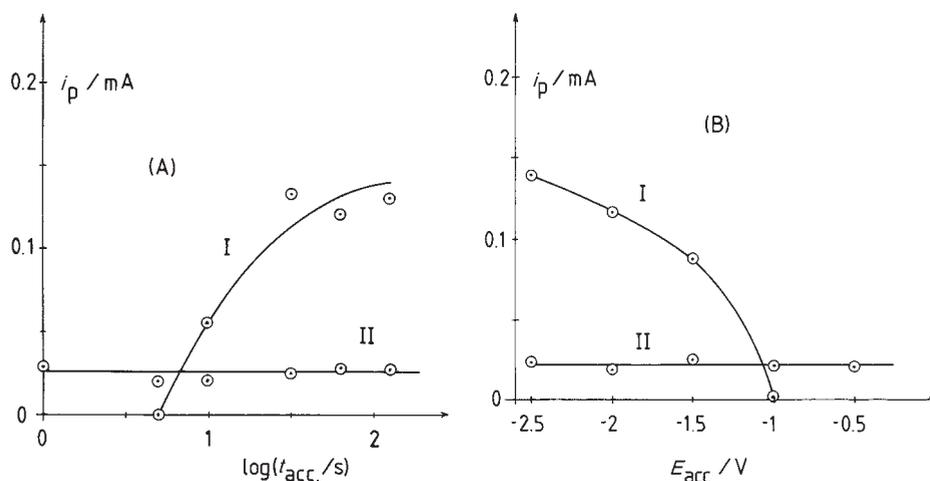


Figure 2. Dependence of stripping peak currents (I) and (II) on the logarithm of the accumulation time (A) and the potential of the accumulation (B).  $E_{\text{acc}} = -2$  V (A) and  $t_{\text{acc}} = 30$  s (B). All other data as in Figure 1.

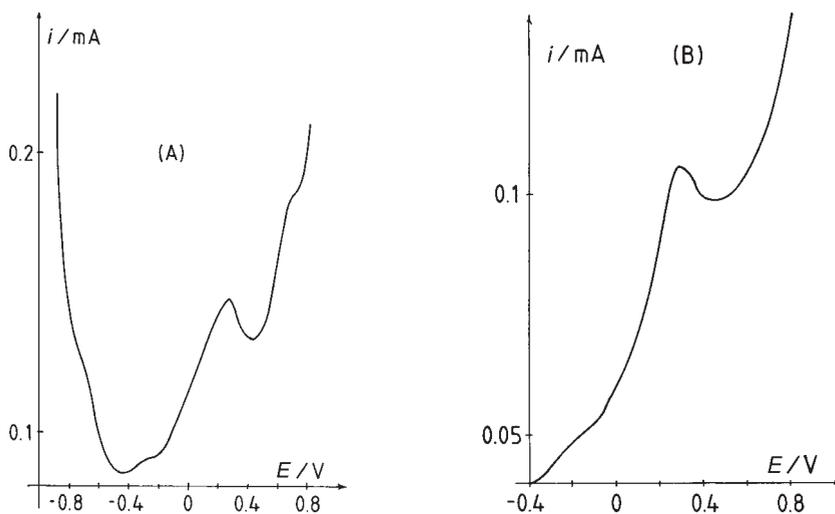


Figure 3. Square-wave voltammograms of the sediment. (A)  $E_{\text{acc}} = -2$  V and  $t_{\text{acc}} = 5$  s. (B)  $E_{\text{acc}} = -0.4$  V and  $t_{\text{acc}} = 30$  s. All other data as in Figure 1.

metallic manganese to dissolved  $\text{Mn}^{2+}$  ions. Peak (II) at 0.28 V is independent of the preelectrolysis potential. It can be attributed to the oxidation of Mn(II) ions to the Mn(III) redox state:  $\text{Mn}(\text{OH})_2 \rightarrow \text{MnOOH} + e^- + \text{H}^+$ .<sup>15,29</sup> In carbonate minerals, these redox reactions may occur at the three-phase boundary where the crystal, the electrolyte and the electrode meet. From there, the reactions may be propagated over the particle surface by a series of electron hoppings between the neighbouring manganese ions of different redox states.<sup>30</sup> Penetration of electrons into the crystal lattice depends on the ionic conductivity of the mineral.

Previous measurements have shown that the presence of separate  $\text{MnO}_2$  and  $\text{MnOOH}$  phases can be detected if their average content in the solid carbonate sample is about 0.01%.<sup>15</sup> However, such samples are not strictly homogeneous and the voltammetric responses depend on the size and the number of manganese microparticles which are mechanically transferred to the electrode surface. The same problem appears if  $\text{MnO}_2$  is added to the natural sample to calibrate the voltammetric responses. By this procedure, the assignation of peaks can be confirmed, but quantitative estimations can be only approximative.

The presence of manganese in the sediments can be detected also by an alternative procedure in which the cathodic square-wave voltammetric scan is preceded by electrooxidation at 0.9 V. The response is shown in Figure 4. The main peak appears at 0.32 V. It is reversible, as indicated by its forward and backward components. The peak is attributed to the reduction of Mn(IV) to Mn(III) redox state:  $\text{MnO}_2 + e^- + \text{H}^+ \rightleftharpoons \text{MnOOH}$ .<sup>15,31,32</sup> The second peak at -0.45 V probably corresponds to the reduction of  $\text{MnOOH}$  to

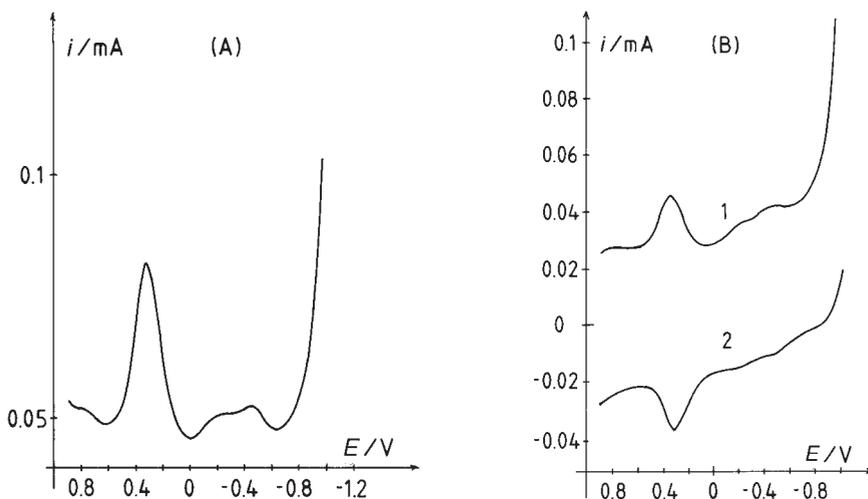


Figure 4. Square-wave voltamogram of the sediment (A) and its forward (1) and backward (2) components (B).  $E_{acc} = 0.9$  V and  $t_{acc} = 30$  s. All other data as in Figure 1.

$Mn^{2+}$  ions.<sup>15</sup> A similar response was obtained in 1 M  $KNO_3$ , but in 0.1 M  $NH_3/NH_4Cl$  the peak current was ten times smaller than in the oxalic acid. After the preelectrolysis at  $-2$  V, the single stripping peak appeared at  $-0.28$  V in 1 M  $KNO_3$ , and at  $-0.08$  V in 0.1 M  $NH_3/NH_4Cl$ . Peak currents in both electrolytes were five times smaller than in the acidic medium under the same conditions. Hence, the use of 0.1 M oxalic acid as the electrolyte is recommended.

The proposed method can be used for fast, qualitative detection of manganese in marine sediments. By this preliminary test, samples can be selected for a more elaborate, quantitative determination. The instrumentation used in this work can be battery powered and the analyses may be performed on the spot, either in a boat, or on the shore near sampling locations.

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## SAŽETAK

### Jednostavna metoda za određivanje mangana u morskim sedimentima

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Mikročestice sedimenta mehanički su nanosene na površinu grafitne elektrode, a postojanje iona mangana utvrđeno je voltametrijom s pravokutnim valovima potencijala u 0,1 M oksalnoj kiselini. Poslije predelektrolize kod –2 V prema Ag/AgCl, voltamogram je karakteriziran maksimumom kod –0,60 V. Ako je čestica oksidirana kod 0,9 V, odzivom dominira maksimum kod 0,32 V.