



## Electroanalytical determination of soluble Mn(II) species at high concentration levels



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### ABSTRACT

Glassy carbon electrodes have been successfully employed for the determination, by differential pulse voltammetry, of Mn(II) ions dissolved in aqueous solutions. In particular, a simple and fast procedure also suitable for on-line or at-line process control has been developed. Statistical analysis of the results obtained reveals that the procedure can be adopted in the range 0.59–57.30 mM Mn(II). The electrochemical responses are repeatable and reproducible. Repeatability is testified by the lack of variation of peak current values calculated from 20 subsequent scans carried out at the maximum explored concentration (relative standard deviation <1%). Reproducibility of the responses is supported by the data from the responses on three different electrodes. The proposed procedure does not require any pre-concentration of Mn species at the electrode surface or de-aeration of the solution. By adopting the developed procedure for the analysis, the GC electrode demonstrates to be suitable also for application in real matrices, namely solutions from spent battery recycling; in particular the results from the present electrochemical method are not significantly different from those obtained through inductively plasma coupled mass spectrometry. Interference from other metal species, such as Zn(II) and Fe(III), is negligible. This result is particularly meaningful, since the experimental conditions chosen, implying particularly high concentrations of heavy metals, are representative of those adopted in recovery and recycle processes of Mn species from batteries.

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### 1. Introduction

Dissolved Mn(II) ions are ubiquitous species that are present, for instance, in drinking water, foodstuff, plants, etc. [1,2]. Reasonably, most analytical methods developed so far focus the attention on the determination of traces of Mn species. In any case, the most widely diffused protocols for the quantitative evaluation of these species require the adoption of off-line procedures, implying sampling, transfer of samples to the laboratory equipped for the purpose and pre-treatment of the sample before the analysis. Methods, such as those based on atomic absorption or on emission spectroscopies, are well established [1]. Among few spectrophotometric methods in the UV–vis region for analyses in solution [3], the oxidation to Mn(VII) or the addition of formaldoxime or 1-(2-pyridylazo)-2-naphthol as complexing chromophores deserve citation. Unfortunately, a number of limitations have been reported in the cited Refs. [1,3]; as an example, methods

based on redox reactions suffer from the interference of other oxidisable species whilst those exploiting the formation of coloured complexes are adversely affected by the presence of heavy metals different from Mn.

Electroanalytical methods possess a number of advantages over other analytical techniques, such as simplicity, low cost, and possibility to operate in turbid solutions, which is quite a common situation encountered in real matrices, as it is the case examined here [1]. Once proper electrode systems and relevant procedures are developed, they are suitable for on-line and at-line analyses, i.e., using portable instrumentation, without the necessity to bring a sample to external laboratories [4]. At the moment, only few literature reports deal with the electrochemical determination of Mn(II) ions (see, for instance, Ref. [5] and a survey of the most significant papers reported in the Supplementary Materials). Many approaches make use of Hg-based electrodes; it is however well known that, despite the effectiveness of this electrode material in the determination of heavy metals at the trace level, it is progressively phased out from the laboratories and industrial plants, due to its toxicity. This forces to identify alternative

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electrode materials for effective electrochemical determination of a variety of chemicals; this is particularly urgent for heavy metal species.

Apart from trace analysis, a basically different, though comparably important, issue regards the quantification of Mn species present at high concentrations. These are conditions often encountered in a variety of industrial frames. In order to reduce the cost derived from the use of big instrumentation and the time required by transport and complex treatment of the sample, the use of sensing systems is essential. In situ continuous monitoring of Mn species is necessary in many cases, such as recycling of batteries, metal electrowinning, and production of fertilizers [6–10].

In principle, high dilution ratios could allow the use of the previously cited literature methods. However, such an approach is impractical for an effective at-line or on-line process control, due to the high dilution volumes that may be required. Additional points prevent from an effective application of established electroanalytical procedures: i) the necessity to remove dissolved oxygen by bubbling an inert gas, when anodic stripping analyses are performed [11,12]; ii) the low mechanical robustness of many electrode modifications, e.g. carbon pastes, potentially effective to the purpose [13,14]; iii) the high pH values required by the methods, that may lead to precipitation of Mn hydroxides at high Mn concentration level [15,16].

In the present paper, a procedure suitable for the determination of high concentrations of Mn(II) ions (0.59–57.30 mM) is presented. A simple glassy carbon (GC) electrode is used, once the conditions under which to obtain repeatable responses are set. It is worth noticing that this electrode material has been employed very rarely in the determination of Mn(II) ions, limitedly to the determination of traces (see, e.g., [17–19] and Table S-1 in Supplementary Materials). The method proposed here does not require any accumulation step. In addition, regeneration of the electrode surface between subsequent measurements, such as mechanical polishing, is unnecessary and even deaeration of the solution is not required: samples can be analysed without any specific pre-treatment.

Moreover, it should be emphasised that no literature report considers the concentration interval to which the present paper is devoted. Noteworthy, the electroanalytical determination of species, in particular of metal ions, at high concentrations requires to overcome a number of drawbacks, due to possible enhancement of the effect of poisoning adsorptions or enhancement of undesired side reactions, etc.

Finally, the interference of different heavy metals and of oxygen is negligible, at variance with a number of literature reports. The effectiveness of the analytical procedure has been also checked by us, operating on an untreated and particularly challenging real matrix, namely the leachate from the recycling process of spent alkaline batteries [9]. The results from the present method are not significantly different from those obtained through inductively plasma coupled mass spectrometry.

## 2. Experimental

### 2.1. Chemicals and sample preparation

Chemicals, namely  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ,  $\text{PbCl}_2$  and 96% w/w  $\text{H}_2\text{SO}_4$ , were from Sigma. In addition, Cd(II), Hg(II) and Co(II) standard solutions (1000 ppm from Peak Performance) have been employed. All solutions were prepared using ultrapure water (18 M $\Omega$  cm resistivity, MILLIQ plus by MILLIPORE). A multistandard from Inorganic Venture (IV-ICPMS-71A) has been employed for the calibration of the ICP instrument.

$\text{MnO}_2$ -carbon powder mixture from commercial spent alkaline batteries (Energizer E93 LR14 AM2 1.5 V) has been employed as the real matrix [9]; the powder was obtained dismantling the batteries and crushing the cathode in a mortar. The industrial recycling process [9] requires the leaching of the powder with  $\text{H}_2\text{SO}_4$ . This procedure leads to a partial reduction and dissolution of  $\text{MnO}_2$  to Mn(II) ions; the residual solid, containing carbon and  $\text{MnO}_2$  powder, is recovered to undergo a further leaching process, after the addition of fresh powder from battery crushing. We selected typical experimental conditions adopted in the industrial process: the battery powder (0.5 g) has been leached at room temperature using  $\text{H}_2\text{SO}_4$  solutions (50 ml) at different concentration, namely 0.1, 0.5, 1 and 2 M. After 15 h contact time,  $\text{MnO}_2$  has been partially reduced to soluble Mn(II) salts; the final concentration of Mn(II) ions was 18.3, 20.4, 23.0, 19.8 mM, respectively, as determined using an Inductively Coupled Plasma (ICP) system equipped with a mass spectrometer detector (XSeriesII from Thermo). The leachate also contained Zn(II) ions (19.0, 21.3, 21.0, 19.6 mM for 0.1, 0.5, 1, 2 M  $\text{H}_2\text{SO}_4$ , respectively); its influence on the electrochemical response has been investigated in Section 3.2. The concentration values of other metals are negligible ( $< 2 \times 10^{-6}$  M). Before the execution of the analysis the samples have been filtered using a 0.45  $\mu\text{m}$  cellulose nitrate filter (Albet NC-045-47-BL) and diluted to ca.  $9 \times 10^{-6}$  M Mn(II) ions concentration, using ultrapure  $\text{HNO}_3$  4% w/w.

### 2.2. Electrochemical investigations

The electrochemical measurements were performed with an Autolab PGSTAT12 (Ecochemie) potentiostat/galvanostat, in a single-compartment three-electrode cell, at room temperature. 3 mm diameter GC disks (CH Instruments CHI104) constituted the working electrodes. They were polished subsequently with 6, 3, and 1  $\mu\text{m}$  monocrystalline diamond spray (Remet Arfex) on polishing cloth (Remet Microlap Mic-200). An aqueous Ag/AgCl, 3.0 M KCl (Metrohm) electrode was the reference electrode; all the potential values given are referred to it. A 4 mm diameter graphite rod (Graphitestore NC001300) was the auxiliary electrode.

Cyclic voltammetric (CV) tests have been performed at 50 mV  $\text{s}^{-1}$  potential scan rate. Either in the absence or in the presence of Mn(II) ions, the solution was stirred for one minute between two subsequent runs, the working electrode being at open circuit potential.

It is worth noticing that GC surfaces can suffer from a progressive modification during potential sweeps in 1 M  $\text{H}_2\text{SO}_4$ , due to the occurrence of oxidation processes of the surface carbon atoms [20,21]. In our experimental conditions we verified that steady state voltammetric responses, diagnostic of a stable status of the electrode surface, were achieved after 6 potential cycles from  $-0.70$  to  $+1.80$  V, in solutions containing only 1 M  $\text{H}_2\text{SO}_4$ . Solvent oxidation is observed at potentials higher than  $+1.80$  V.

Calibration curves, constructed from background-subtracted voltammograms, have been computed by linear least squares regression, using data from differential pulse voltammetric (DPV) measurements. The adopted parameters of the potential waveform were as follows: 20 mV pulse amplitude, 150 ms pulse time, 5 mV step potential, 150 ms step time. Complete removal from the electrode surface of Mn-based coating generated by anodic oxidation of Mn(II) ions was achieved, even in the cases of the highest concentrations, by fixing the potential at  $-0.70$  V for 10 s under stirring of the solution, after that the analysis was completed. The  $-0.70$  V value was chosen due to poor sensitivity of the calibration plots obtained employing less negative cleaning potentials; deposition of interfering metal species, e.g. Zn, are observed at more negative potentials.

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