

Antivibration Electrode Support for Shipboard Stripping Voltammetry

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Abstract

Cathodic stripping voltammetry (CSV) is subject to interference by engine vibrations when used on-board ship. Scanning wave-forms utilizing high-frequency potential modulations can to some extent overcome this problem, but these cannot be used for catalytic CSV without major loss of sensitivity. To minimize the effects of vibrations an antivibration electrode support was developed based on a PVC plate suspended from elastic bands. The support was compared to the more simple expedient of placing the electrode on large rubber ("Hi-Fi") feet. Successful damping was evaluated from ship-board determinations of iron in seawater by catalytic CSV. The rubber feet were found to lower the relative standard deviation (RSD) of these measurements to 34 % from 70 % without damping. The antivibration support was found to lower the RSD to an acceptable 10 % and was used extensively for voltammetry on-board ship.

Keywords: Cathodic stripping voltammetry, Vibration suppression

Cathodic stripping voltammetry (CSV) is sufficiently sensitive to determine low concentrations of trace metals in seawater. Important advantages of voltammetry are that it can be used to determine the chemical speciation as well as the concentration of dissolved species, and does not require pretreatment of the water, which is usually time-consuming and may lead to contamination. These characteristics and the portability of the instrumentation make the technique well suited for the determination of trace metals on-board ship. CSV can be used to determine some twenty elements directly in seawater, and has been adapted for flow-analysis enabling shipboard analysis with on-line detection [1, 2].

Each voltammetric scan is preceded by adsorptive deposition of complexes of the metal with a ligand, which is added for this purpose. During the potential scan all the metal in the adsorbed layer is reduced, producing a reduction current, which is directly related to the dissolved metal concentration.

Vibrations cause interference in the current during the potential scan due to variations in the diffusion layer thickness surrounding the electrode during the scan (caused by variations in the physical shear) causing variations in the concentrations of the oxidant (bromate), and of the oxidation product (Fe(III)), in the diffusion layer surrounding the electrode, both leading to "noisy" scans; a second effect is due to variations in the capacitance of the double-layer due the liquid movement. One way to minimize these problems is to use high-frequency square-wave scans, or fast linear-sweep scans [3]. The fast scans tend to lead to increased peak currents, which might then become greater than the interfering capacitance currents, albeit at a loss of resolution for poorly reversible reactions. However, this is not suitable for catalytic CSV as the fast scans negate the catalytic effect, which depends on diffusion of the oxidant to the electrode surface during the scan. The catalytic effect is important to detect iron, cobalt, and other metals, in seawater [4, 5]. These techniques show a high sensitivity due to the catalytic effect and thus, require short deposition times even for low metal concentrations. For these reasons, it is important to minimize the effect of vibrations.

Shipboard work is subject to two types of motion. One is a relatively slow, rocking, motion due to the ship moving with the waves; the other is due to high-frequency vibrations due to the engine or propulsion system [6]. The ship's motion due to waves causes a gentle swaying of the solution in the voltammetric cell, which causes the diffusion layer thickness to vary. This effect is negligible during the deposition step as the solution is stirred which swamps the swaying movement. During the scan the solution is not stirred to prevent turbulence in the diffusion layer surrounding the electrode. Variations in the diffusion layer thickness would affect the concentration of oxidant (as well as in the oxidation products) at the electrode surface in catalytic CSV, causing poorly reproducible measurements of the reduction current. This effect can be minimized by using a linear sweep mode, or a fast square-wave modulation. At higher wind force the rocking motion becomes unpredictable, and all equipment (including the electrode support, but not the electrode itself) has to be fixed with ropes and elastic bands to the workbench in order to avoid damage to the equipment.

The second type of motion, due to vibration, was found to be very serious without precautions. The vibrations affect the reduction current by superimposing noise from variable capacitance currents, as well as causing variations in the reduction current in modulated techniques because the reoxidized ions are transported away, and in catalytic methods by causing variations in the oxidant concentration.

Initially it was attempted to alleviate the vibration problem by mounting the electrode on thick rubber feet, or by suspending the electrode from elasticized ropes, which did not prove sufficient, and was inconvenient. Attempts to mount the electrode on a special antivibration support consisting of a plate suspended from short, elasticized bands, were successful, and are described here, along with the tests to evaluate the support on-board ship in the determination of iron in seawater by catalytic CSV (Fig. 1)

The effects of varying the degree of damping on the voltammetric scans was tested as follows under constant vibration and wave conditions: a) no damping, b) by placing the electrode on rubber feet, and c) by placing the electrode on the antivibration

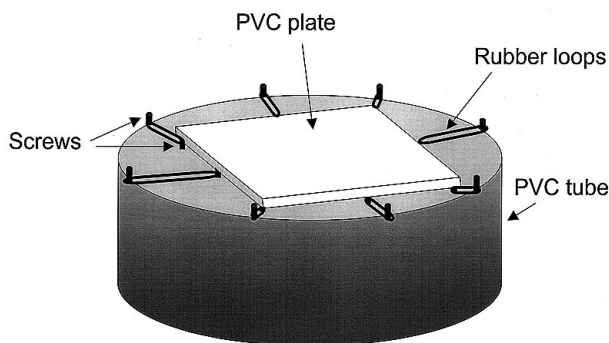


Fig.1. Antivibration support for the electrode stand. (PVC tube: \varnothing 38 cm, 15 cm \times 2 cm; PVC plate: 25.5 \times 25.65 \times 2 cm; rubber loops: 0.35 \times 0.45 \times 7.5 cm.

stand. Example scans obtained in the three experimental conditions can be compared in Figure 2. Without vibration damping (Fig. 2a) the scans of the sample were “noisy” with irregular peaks and poor reproducibility: the relative standard deviation (RSD) of the repeated scans was nearly 70% ($n = 5$). The scans were improved by positioning the electrode on rubber feet, giving a RSD of 34% for repeated scans ($n = 5$) (Fig. 2b). The standard deviation decreased with increasing iron concentration, in line with expectation, as the contribution of the varying capacitance current would be smaller with the increased Faradic current.

Good results were obtained when the electrode was placed on the anti-vibration support, leading to smooth scans, even in rough weather and when the ship was travelling at high speeds (i.e., when returning to port) (Fig. 2c). Repeated scans after 60 s deposition time had a relative standard deviation of less than 10% ($n = 5$) when the ship was travelling at 10 knots (close to its maximum speed).

The reactive iron concentration determined in the seawater (Fig. 2) was 0.5 nM. In view of the 10% standard deviation the analytical, ship-board, analytical, limit of detection would be around 0.15 nM ($3 \times$ SD) at the 60 s adsorption time used; this limit of detection can be lowered by increasing the adsorption time. The limit of detection is about twice that obtained in the land-based laboratory using the same adsorption time [5] but is still sufficiently low to determine iron in uncontaminated seawater; using a 3 min adsorption time it compares well to the

sensitivity achieved by FIA with luminescence detection [7] which can also be used on-board ship.

The CSV measurements were carried out without prior UV-digestion of the seawater, and the detected iron concentrations therefore represent reactive rather than total dissolved iron. The ligand concentration (20 μ M NN) was much higher than used normally to determine organic complexation of iron in seawater (5–8 μ M NN) [8] and would tend to lead to dissociation of most organically complexed iron.

Although this antivibration support was chiefly developed to improve the ship-board detection of iron in seawater, the same support could also be used to improve the detection of other metals, and in other environments (other field-based measurements or in industrial environments) subject to engine vibrations.

Experimental

Apparatus: The voltammetric apparatus consisted of a μ Autolab voltammeter (Ecochemie, Netherlands) and a static mercury drop electrode (SMDE) (Metrohm Model 663VA) with integral stand. In addition to the SMDE the electrodes include a double-junction, Ag/saturated AgCl, reference electrode with a salt bridge filled with 3 M KCl, and a glassy carbon counter electrode. The Metrohm electrode stand weighs about 11 kg, and is normally supported by four small (ca 1 cm diameter) rubber feet.

The concentration of reactive iron was determined by CSV using 20 μ M 1-nitroso-2-naphthol (NN), which forms adsorptive complexes with iron at pH 8 (0.01 M HEPPS) [5]. The reactive iron is all the iron that reacts with the NN and is comprised of all inorganic iron(II) and iron(III), and the major part of the organically complexed iron due to the strong complex formation by the 20 μ M NN. Bromate (40 mM) was added to improve the sensitivity through the creation of a catalytic cycle. The potential scan was carried out from -0.2 to -0.7 V using sampled DC at a frequency of 10 Hz.

Antivibration support: The antivibration support consisted of a 38 cm diameter PVC tube with a height of 15 cm and a wall thickness of 2 cm (Fig.1), and an electrode support consisting of a PVC plate (25.5 \times 25.5 \times 2 cm), which was suspended by eight rubber loops (designed to connect tent-herrings to a tent; 0.35 \times 0.45 \times 7.5 cm, Mountaincraft Outdoor Essentials) attached to the tube. The rubber loops stretched by 2.5 cm when subjected to a weight of 2.3 kg. The antivibration support was fixed to the workbench with ropes to prevent it from sliding, and the electrode stand was tightly fixed to the support with elastic rope.

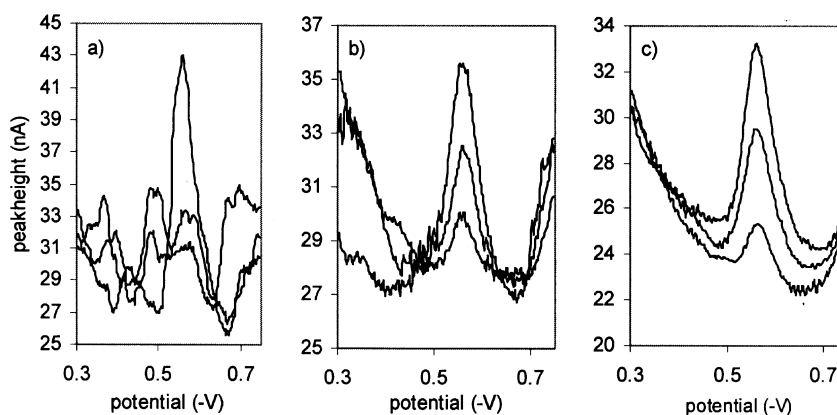


Fig. 2. Comparison of voltammetric scans on-board ship for the determination of iron in seawater. The ship (RV Pelagia) was steaming at around 10 knots in the North Atlantic. An adsorption time of 60 s was used; the sensitivity ($3.8 \text{ nA min}^{-1} \text{ nM}^{-1}$) was calibrated by two standard iron additions to the sample, and the scans shown are for 0.5 nM Fe. a) without vibration damping, b) electrode placed on rubber feet, and c) on the special antivibration support.

Rubber feet (4) in the shape of a half sphere (2.5 cm thick) were placed underneath the electrode stand for use as an alternative, more simple, electrode support with improved damping properties.

The antivibration apparatus was tested during a cruise on the North Atlantic on board the research vessel Pelagia (Netherlands).

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