STRIPPING ANALYSIS USING ION-TRANSFER VOLTAMMETRY AT LIQUID/LIQUID INTERFACE

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Principles and theory of stripping ion-transfer voltammetry at the organic solvent (O)/water (W) interface are described, in which a thin O-film is used to preconcentrate an ionic substance by electroextraction followed by stripping analysis using linear sweep voltammetry or normal pulse voltammetry. For ease of handling, the thin O-film was gelled by adding poly(vinyl chloride) to make an O-gel electrode. Lead(II), cadmium(II) and zinc(II) ions behave reversibly or quasi-reversibly in voltammetric transfer at the O/W interface assisted by 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (DPT) present in the O-phase. Thus, these ions at trace levels can be determined using stripping ion-transfer voltammetry with the O(DPT)-gel electrode. The detection limit was as low as a few tens of nmol/l of these ions. Simultaneous determination of two or more ions is possible when their half-wave potentials of ion transfer are reasonably separated.

Keywords: Extraction; Ion transfer; Liquid/liquid interface; Trace analysis; Voltammetry; Gel electrodes.

Stripping analysis[1,2] is an electrochemical method of trace determination that utilizes a bulk electrolysis step (pre-electrolysis) to preconcentrate a substance from solution in the small volume of an electrode, *e.g.*, a thin mercury film, or on the surface of an electrode. After this pre-electrolysis step, the material is redissolved (stripped) from the electrode using some voltammetric techniques. Recent electrochemical or voltammetric studies of ion transfer across the interfaces of two immiscible electrolyte solutions (ITIES) or, in short, organic solvent or oil (O)/water (W) interface have revealed that the ion transfer at the O/W interface, with or without assistance of ionophors or extracting reagents, is of voltammetric-reversible nature in many cases[3–5]. Therefore, the ion-transfer voltammetry at the O/W interface could be combined with the method of stripping analysis to allow

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trace determination of ionic substances. In previous papers, it has been shown that the voltammetric transfer of heavy metal ions, such as mercury(II) and lead(II), assisted by 1,4,7,10,13,16-hexathiacyclooctadecane (HTCO) present in the O-phase, takes place reversibly at the O/W interface[6,7] and that these ions at trace levels as low as nmol/l can be determined using the stripping ion-transfer voltammetry at the O(HTCO)/W interface[8], in which the ions are preconcentrated in a thin O-film in the pre-electrolysis. Strictly speaking, this is not the electrolysis but electrochemical or electro-assisted liquid/liquid extraction or, in short, electroextraction[9,10] followed by stripping linear sweep ion-transfer voltammetry. For ease of handling, the thin O-film was gelled to make the O-gel electrode. Heavy metal ions, such as zinc(II), lead(II) and cadmium(II), also give reversible or quasi-reversible wave in ion-transfer voltammetry at the O/W interface assisted by 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (DPT) present in O-phase[11]. In this paper, the stripping analysis of the metal ions with the O(DPT)-gel electrode, using normal pulse voltammetry (NPV) as well as linear sweep voltammetry (LSV), will be described.

An advantage of the stripping ion-transfer voltammetry at the O/W interface is that the stripping analysis can be applied to the determination of non-redox ionic species. Thus, nonionic, poly(oxyethylene) alkyl and alkylphenyl ether surfactants at trace levels can be determined by the stripping ion-transfer voltammetry based on the transfer of the surfactant–metal ion complex at the O/W interface[10,12]. Ionizable drugs have also been a research subject of ion-transfer voltammetry at the O/W interface[13]. Mareček and Samec[14] studied the stripping differential pulse voltammetry (DPV) of acetylcholine at the nitrobenzene (NB)/W interface with a hanging NB drop electrode. Senda and his coworkers[15,16] have studied electrochemical-analytical property of a glass micropipette O/W interface electrode designed for *in vivo* voltammetry and stripping voltammetry of acetylcholine and choline. Recently, Gitrault and his coworkers[17] have shown applicability of the micro-fabricated composite membrane O/W electrode for stripping voltammetric determination of choline and a choline-related enzyme. Some basic problems in stripping ion-transfer voltammetry with a thin film O-gel electrode and a micropipette O/W interface electrode will also be discussed in this paper.

EXPERIMENTAL

Electrochemical cell. In this study, a two-electrode system was employed. The electrochemical cell used in the stripping ion-transfer voltammetry of heavy metal ions with the thin film O-gel electrode described below is

$$\begin{array}{l|l|l|l|l}
 & & & {}^{*} & \\
\mathrm{Ag|AgCl|0.1\,M\ LiCl} & \mathrm{0.1\,M\ LiCl} & \mathrm{0.02\,M\ DPT} & x\ \mathrm{nM\ MCl_2} & \mathrm{0.1\,M\ LiCl|AgCl|Ag} \\
 & \mathrm{0.02\,M\ LiTPB} & \mathrm{0.02\,M\ THATPB} & \mathrm{0.04\,M\ MOPS\text{-}LiOH} & \\
 & & \mathrm{0.1\,M\ BTPPATFPB} & \mathrm{(pH\ 7)} & \\
\mathrm{(W)} & \mathrm{(W)} & \mathrm{(FNDPE\text{-}PVC\text{-}gel)} & \mathrm{(W,\ test\ soln)} & \mathrm{(W)}
\end{array}$$

cell I

where LiTPB, THATPB, BTPPATFPB and MOPS stand for lithium tetraphenylborate, tetrahexylammonium tetraphenylborate, bis(triphenylphosphoranylidene)ammonium tetrakis(4-fluorophenyl)borate and 3-morpholinopropane-1-sulfonic acid, respectively, (FNDPE-PVC-gel) denotes the organic solvent phase consisting of 2-fluoro-2′-nitrodiphenyl ether (FNDPE) solution gelled by adding poly(vinyl chloride) (PVC). The test solution (W, test soln) contains zinc(II), cadmium(II) or/and lead(II) chloride (MCl_2) usually at nmol/l levels in buffer solution of pH 7.0. The polarized O/W interface is indicated by an asterisk. The left-hand half-cell, Ag/AgCl/0.1 M LiCl(W)/0.1 M LiCl, 0.02 M LiTPB(W)/0.02 M DPT, 0.02 M THATPB, 0.1 M BTPPATFPB(FNDPE-PVC-gel), constitutes the O-gel electrode as described below. The right-hand half-cell, Ag/AgCl/0.1 M LiCl(W), constitutes the external reference electrode which was separated froM the test solution by a sintered glass. The applied potential, E, is defined by the terminal potential of the right-hand Ag/AgCl reference electrode referred to that of the left-hand Ag/AgCl electrode. The interfacial potential difference across the polarized O/W interface, *i.e.*, the O-gel/W(test soln) interface, $\Delta_{\mathrm{O-gel}}^{\mathrm{W,\,test}}\phi$ (= $\phi^{\mathrm{W,\ test\ soln}} - \phi^{\mathrm{O\text{-}gel}}$), ϕ^{α} being the Galvani potential of α (W, test soln or O-gel) phase, is related with E by

$$E = \Delta_{\mathrm{O}}^{\mathrm{W}}\,\phi + \Delta E_{\mathrm{ref}}\ , \tag{1}$$

where ΔE_{ref} is determined by the reference electrode system employed. The reversible half-wave potential of the transfer of tetraethylammonium (TEA^+) ion at the FNDPE-PVC-gel/W interface, ${}_{\mathrm{r}}E_{1/2,\mathrm{TEA}}$, as determined from the midpoint potential of cyclic voltammogram of TEA^+ ion, was found to be ${}_{\mathrm{r}}E_{1/2,\mathrm{TEA}} = 0.308 \pm 0.005$ V with cell I, in which the test solution was replaced with 50 μM TEABr and 0.1 M LiCl(W). In the following, the E values are reported *versus* ${}_{\mathrm{r}}E_{1/2,\mathrm{TEA}}$. The solution resistance between the two reference electrodes was about 10 kΩ. A laboratory-made potentiostat furnished with a positive-feedback Ohmic potential drop compensation circuit was used to control the applied potential. All measurements were carried out at 25 ± 1 °C.

O-gel electrode. The O-gel electrode is schematically illustrated in Fig. 1. The thin membrane of FNDPE-PVC-gel at the open end of a tapered poly(propylene) tube was made by casting a mixture of 0.1 ml of an FNDPE solution containing 0.02 M DPT, 0.02 M THATPB and 0.1 M BTPPATFPB, 50 mg of PVC and 1 ml of tetrahydrofuran (THF). An aliquot, usually

0.04 ml, of the mixture was dropped on the narrower open end (6.5 mm outer and 5.0 mm inner diameters), temporarily packed by the flat end of a glass rod of 5.0 mm diameter, of the poly(propylene) tube. The THF was allowed to evaporate for 15 min while the poly(propylene) tube was rotated around its axis at 300 rpm. The glass rod was removed and the poly(propylene) tube with the FNDPE-PVC-gel membrane was stored in the dark at least overnight before use. The thickness of the O-gel membrane was about 50 μm as determined using a microscope with a scale. The area of the O-gel membrane was 0.33 cm^2. The poly(propylene) tube with the FNDPE-PVC-gel membrane was filled with an internal aqueous solution containing 0.1 M LiCl and 0.02 M LiTPB, and the reference electrode Ag/AgCl/0.1 M LiCl(W) with a Vycor glass separator was immersed into the internal solution to make the O-gel electrode, as illustrated in Fig. 1. DPT was obtained from Dojindo Lab. Other chemicals are described elsewhere[12].

Stripping voltammetry with the O-gel electrode. First, in the preconcentration step, a constant potential, E_e, is applied to cell I to electroextract the analyte ion into the O-gel membrane from the test solution for pre-electroextraction time, t_e (180 s, unless otherwise stated in this study), while the O-gel electrode is rotated around its axis (usually at 300 rpm), followed by the rotation-off period (30 s, in this study) to recover the stationary state while the applied potential E_e is sustained. Second, in the determination step, the applied potential is changed according to the stripping voltammetry scheme used to back-electroextract the preconcentrated ions from the O-gel membrane into the bulk solution. In this study, linear sweep voltammetry (LSV) or normal pulse voltammetry (NPV) was used in the determination step. When LSV was used, the applied potential was scanned from E_e in cathodic (minus) direction at the scan rate, ν (10 mV/s in this study, unless otherwise stated). When NPV was used, the voltage pulses of increasing amplitude were superimposed on E_e in the cathodic direction; in this study, the duration of the voltage pulse was 0.5 s, the interval 5 s and the voltage increment 25 mV. The current was sampled at the end of the voltage pulse to obtain the cathodic stripping current *vs* potential, I_s–E, curve. In analytical applications, pulse amperometry[10,18] (PA) can be used for stripping analysis, in which a cathodic constant-height pulse potential, E_s, *i.e.*, a constant-height voltage pulse superimposed on E_e usually corresponding to the limiting current of the I_s–E curve, was applied to the O-gel electrode.

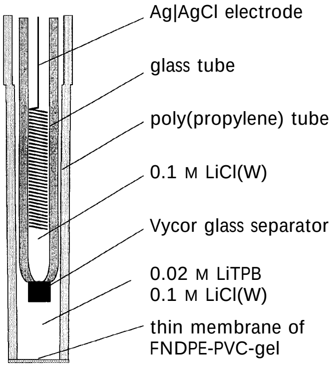

FIG. 1
Scheme of the O-gel electrode

PRINCIPLE AND THEORY OF STRIPPING ION-TRANSFER VOLTAMMETRY

Preconcentration in the O-gel electrode. In the preconcentration step the metal ion is transferred, *i.e.*, electroextracted under the applied potential E_e into the O-gel phase from the test solution (across the O-gel/W(test soln) interface in cell I) to form the metal-DPT complex ion[11] in the O-gel phase. On the other hand, the transfer of the ion from the O-gel phase into the left-hand aqueous solution, *i.e.*, 0.1 M LiCl, 0.02 M LiTPB(W) in cell I across the left-hand W/O-gel interface is controlled to be negligibly small since the potential difference across the left-hand W/O-gel interface, $\Delta^{\text{W, test}}_{\text{O-gel}}\phi$ ($= \phi^{\text{W, left-hand}} - \phi^{\text{O-gel}}$), is kept at a sufficiently positive value, which is realized by adding a hydrophobic anion, such as TFPB^- in cell I in ref.[8] or TPB^- in cell I above, as a common ion in both the left-hand W and O-gel phases at relatively high concentration. Note that, in cell I above, 0.1 M BTPPATFPB was added to the O-gel phase to reduced the solution resistance; the TFPB^- ion (and possibly the Li^+(W) ion[19]) may cause certain uncertainty in the potential difference across the left-hand W/O-gel interface in the present experiments.

When the thickness of the O-gel membrane, l, is so small that l is of the order of or less than $(2D^{\text{O}}t_e)^{1/2}$, D^{O} being the diffusion coefficient of the ion in the O-gel phase, the concentration of the ion in the O-gel membrane at the start of the stripping voltammetry may be considered to be uniform in the first approximation. Then, the uniform concentration of the ion, c^{O}_{M}, is expressed by

$$c^{\text{O}}_{\text{M}} = i_e t_e / zFAl \qquad (2)$$

when the current intensity in the pre-electroexraction step, i_e, is constant for the pre-electroextraction period, t_e. In Eq. (*2*), z is the charge number of the analyte ion, F the Faraday constant and A the surface area of the O-gel membrane electrode. Generally, i_e is proportional to the bulk concentration of the metal ion in W(test soln), $^*c^{\text{W}}_{\text{M}}$, so that we have

$$c^{\text{O}}_{\text{M}} = k_e \, {}^*c^{\text{W}}_{\text{M}} \,, \qquad (3)$$

where k_e is a parameter which depends on the experimental conditions of pre-electroextraction. Thus, for example, provided E_e is sufficiently large and i_e is controlled by the limiting diffusion flux of metal ion onto the O-gel membrane electrode which is rotated around its axis, k_e should be given by $k_e = (D^W/\delta^W)t_e/l$ since $i_e = zFA(D^W/\delta^W){}^*c_M^W$, D^W and δ^W being the diffusion coefficient of the metal ion in W(test soln) phase and the thickness of diffusion layer on the surface of the O-gel membrane, respectively. On the other hand, when E_e is not sufficiently large, we have $i_e = zFA(D^W/\delta^W)({}^*c_M^W - {}^Oc_M^W)$, in which the surface concentration of the metal ion, ${}^Oc_M^W$, should increase as c_M^O increases with time so that i_e should decrease gradually with time. This should result in increasing k_e with increasing t_e but the increment gradually decreases with t_e, which has been actually observed in stripping ion-transfer voltammetry of metal ions and nonionic surfactants with an O-gel membrane electrode[8,10,12]. Usually, since the surface area of the O-gel membrane is so small, and t_e is much smaller than the time needed for exhaustive electroextraction, ${}^*c_M^W$ may remain essentially constant during the preconcentration step.

Preconcentration in microelectrode. When a microelectrode, in which the polarized O/W interface is formed at the tip of a micropipette with the O phase inside the micropipette[16], is used instead of a O-gel membrane electrode, the current intensity in the pre-electroextraction step, i_e, is given with good approximation by $i_e = 2zF\pi(a/2)D^W{}^*c_M^W$, a being the diameter of the tip[20]. Therefore, k_e in Eq. (*3*) is expressed in first approximation by $k_e = (4D^W/a)t_e/l$ for the microelectrode, l being the thickness of the O phase inside the micropipette.

Stripping current. The stripping-voltammetric current, i_s, is generally expressed by

$$i_s = zFAk_{\mathrm{amp}}\, c_M^O \;, \tag{4}$$

where k_{amp} is a constant which depends on the kind of voltammetry used for the determination. The theory of the stripping current when LSV with a plane, thin-(mercury)layer electrode is used has been discussed by de Vries[21,22] and is therefore not given in detail here. It can be shown that the semi-infinite linear diffusion behavior predominates for large values of $l^2(zF/RT)v/D^O$ (approximately, >15)[23], then the stripping current *vs* potential curve becomes identical to that of LSV. This condition is likely satisfied in the present experiment (see Fig. 3 below).

When PA (or NPV) is used, the stripping current, $I_{s,PA}$, is given by

$$I_{s,PA} = zFA(D^{O}/\pi t_{s})^{1/2} c_{M}^{O} \{1 - 2\Sigma(-1)^{n} \exp[-(n+1)^{2} l^{2} / D^{O} t_{s}]\}, \qquad (5)$$

where t_s is the sampling time and the summation Σ extends from $n = 0$ to ∞. Equation (5) is readily derived from the equation representing the concentration distribution of diffusing species in a plane sheet[24]. In Eq. (5), the second, summation terms in parentheses on the right-hand side represent the correction for the depletion effect caused by the thin-layer (not semi-infinite) diffusion behavior, indicating that the effect could be practically insignificant when $t_s < l^2/4D^O$. This condition is satisfied in the present experiment. Table I shows calculated values of $I_{s,PA}/zFA(D^O/\pi t_s)^{1/2}k_e{}^*c_M^W$ for several values of $D^O t_s/l^2$.

Essentially the same equations and reasoning could be applied to the stripping current with the micropipette O/W electrode[16].

RESULTS AND DISCUSSION

Figure 2 shows cyclic voltammograms of Pb^{2+}, Cd^{2+} and Zn^{2+} ions and the base current obtained with an laboratory-made O-gel electrode (see Fig. 1) in the stationary state. These ions gave reversible or quasi-reversible waves attributable to DPT-assisted transfer at the O-gel/W interface. The voltammograms can be compared with those in Figs 1, 4 and 5 in ref.[11]. Figure 3 shows stripping voltammograms of 250 nM Zn^{2+} in a test solution when $E_e = 0.10$ V was applied to the O-gel electrode under rotation for t_e = 60, 180 or 300 s, followed by stripping LSV. The peak current height was proportional to the bulk concentration of Zn^{2+} in the test solution for a constant pre-electroextraction time. The result together with those of Cd^{2+} and Pb^{2+} ions are illustrated in Fig. 4. The detection limits were calculated to be a few tens of nmol/l for the ions. These experimental results obtained with the O-gel electrode are likely in harmony with the general prediction of Principle and Theory stated above. In Fig. 4, the peak current height of

TABLE I

Stripping pulse amperometric current as a function of $D^O t_s/l^2$

$D^O t_s/l^2$	0.0	0.2	0.4	0.6	0.8	1.0	1.5	2.0
$I_{s,PA}/zFA(D^O/\pi t_s)^{1/2}\ {}^*c_M^{W\,a}$	1.000	0.986	0.836	0.622	0.440	0.298	0.110	0.035

[a] See Eq. (5).

Pb^{2+} is relatively low compared with those of the other ions under the same voltammetric conditions. This could be explained by the fact that E_e is not large enough to attain i_e of the limiting diffusion current for Pb^{2+} but is large enough to attain i_e of the limiting diffusion current for Cd^{2+} and Zn^{2+}. Further discussion on the experimental results in terms of the experimental parameters stated above will be premature. Effect of the structure of

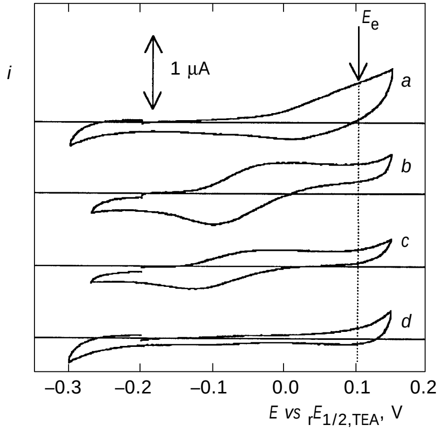

FIG. 2
Cyclic voltammograms of 25 μM Pb^{2+} (*a*), Cd^{2+} (*b*) and Zn^{2+} (*c*) in 0.04 M MOPS–LiOH buffer (W, test soln, pH 7.0) at the stationary O(DPT)-gel electrode and the base current (*d*)

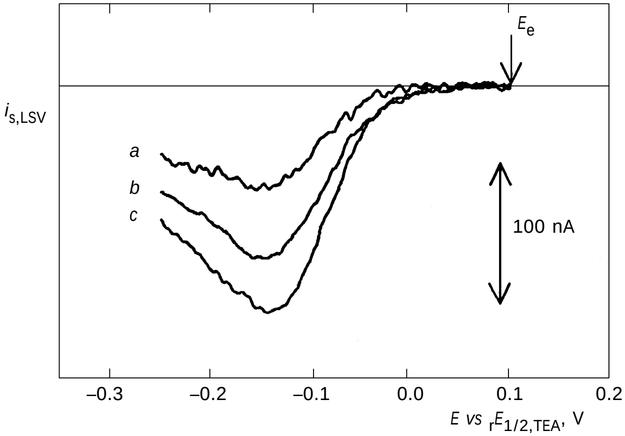

FIG. 3
Stripping voltammograms, corrected for the base current, of 250 nM Zn^{2+} at the O(DPT)-gel electrode after pre-electroextraction at E_e = 0.1 0 V for t_e = 60 (*a*), 180 (*b*) and 300 s (*c*)

O-PVC-gel on the diffusion process of ions at and near the O/W interface[25] should be considered in advanced theory.

When two or more ion species that will be electroextracted at the O-gel electrode are present in a test solution and if their half-wave potentials are

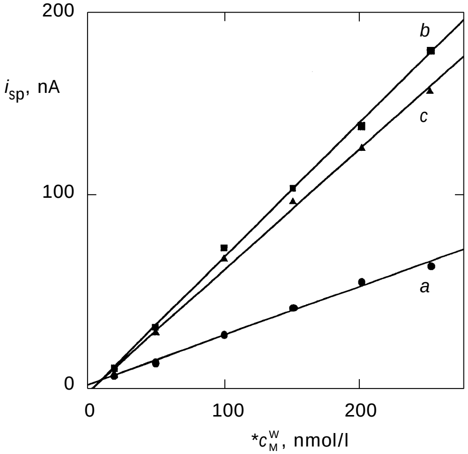

FIG. 4
Plots of the stripping peak currents of Pb^{2+} (*a*), Cd^{2+} (*b*) and Zn^{2+} (*c*) *vs* the ion concentration in test solution after the pre-electroextraction at E_e = 0.10 V for t_e = 180 s

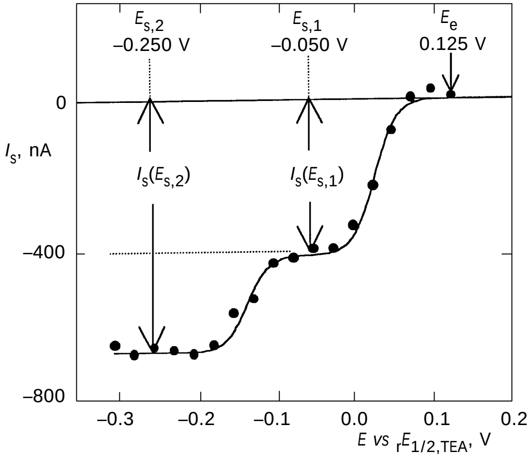

FIG. 5
Plot of the stripping NPV currents *vs* the stripping applied pulse potential of 500 nM Pb^{2+} and 250 nM Zn^{2+} in 5 mM $(CH_3COO)_2Mg$ (W, test soln) at the O(DPT)-gel electrode after pre-electroextraction at E_e = 0.125 V for t_e = 180 s

reasonably separated, simultaneous determination of the ions is possible with one and the same electrode. For this purpose, NPV or PA (ref.[26]) and probably DPV (ref.[14]) can conveniently be used. Figure 5 shows a stripping NPV plot obtained with a test solution containing Pb^{2+} and Zn^{2+} under the condition given in the figure caption, where 0.01 M acetate ion was added to the test solution to accelerate the separation of the half-wave potentials of the two ions[6] ($E_{1/2,Pb} - E_{1/2,Zn} = 0.17$ V). The experimental points represent each the sampled current intensity averaged for five pulses. Thus, we can simultaneously determine the concentration of two ions using PA with two applied potentials $E_{s,1} = -0.050$ V and $E_{s,2} = -0.250$ V, as illustrated in Fig. 5. The current response of the first pulse, $I_s(E_{s,1})$, should give the concentration of Pb^{2+}, whereas that of the second pulse minus the first one, $I_s(E_{s,2}) - I_s(E_{s,1})$, should give the concentration of Zn^{2+}. When 0.5 mM *N*-(dithiocarboxy)sarcosine, diammonium salt as a masking agent[27] is added to a test solution containing Pb^{2+}, Cd^{2+} and Zn^{2+}, Pb^{2+} and Cd^{2+} ions gave no stripping voltammograms, whereas Zn^{2+} ions gave a well-defined stripping voltammogram at an O-gel electrode (data not shown).

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