Published in final edited form as:

Electroanalysis. 2009 August 12; 21(17-18): 1939–1943. doi:10.1002/elan.200904613.

Comparison Between Potentiometric and Stripping Voltammetric Detection of Trace Metals: Measurements of Cadmium and Lead in the Presence of Thallium, Indium, and Tin

Karin Y. Chumbimuni-Torres, Percy Calvo-Marzal, and Joseph Wang^{*}

Department of Nanoengineering, University of California San Diego, La Jolla, CA 92122, USA

Abstract

Recent advances in ion-selective electrodes have pushed the detection limits of direct potentiometry to the nanomolar concentration range. Here we present a direct comparison of the sensitivity and selectivity of potentiometric and stripping-voltammetric measurements of cadmium and lead. While both techniques offer a similar sensitivity, the potentiometric method offers higher selectivity in the presence of excess of metal ions (e.g., thallium, tin) that commonly interfere in the stripping-voltammetric operation. Because of the complementary nature of the potentiometric and stripping-voltammetric methods, it is recommended that these techniques will be selected based on the specific analytical problem or used in parallel to provide additional analytical information.

Keywords

Stripping voltammetry; Potentiometry; Sensitivity; Selectivity; Trace analysis; Cadmium; Lead

1. Introduction

Over the past 5 decades, anodic stripping voltammetry (ASV) has been the electrochemical technique of choice for trace and ultratrace measurements of metal ions [1–3]. The inherent sensitivity of ASV reflects its built-in preconcentration step during which the target metal ions are electro-deposited onto the working electrode. Recent research efforts in the field of ion-selective electrodes (ISEs) have led to dramatic improvements in the detection limits of direct potentiometric measurements [4–6]. Currently, ISEs achieve detection limits in the nanomolar range (or even lower) without any accumulation step, with good selectivity, and with essentially no sample perturbation. Reaching such low detection limits with ISEs requires the minimization of diffusional ion fluxes from the ionophore-containing membrane into the sample [7]. Such dramatic improvements in the sensitivity of potentiometric measurements have made modern ISEs very attractive for trace metal measurements and competitive to stripping voltammetry, and to other trace-metal techniques, in general. However, the literature to date contains no direct comparison of ASV and ISE measurements under identical conditions.

This paper reports for the first time on a direct comparison of stripping-voltammetric and direct potentiometric measurements of trace metals. In particular, it critically compares trace measurements of cadmium and lead in the presence of high concentrations of thallium, indium

^{*}josephwang@ucsd.edu.

Presented at the International Conference on Electrochemical Sensors Matráfűred 2008

and tin (that commonly interfere in ASV analysis of cadmium and lead) [1]. Our findings illustrate that while both techniques offer a similar sensitivity, the ISEs offer higher selectivity in the presence of an excess of these interfering metal ions. It should be pointed out that this limited comparative study focuses on a specific analytical scenario, and does not represent a comprehensive comparison of the two techniques. Both methods have their own merits and limitations, along with different scopes of analytes and matrix effects, that make them suitable or advantageous for a specific analytical problem. We also hope that such comparative work will bring together scientists involved in voltammetry and potentiometry and will stimulate joint efforts toward hybrid ASV-ISE systems [8] and/or for parallel information-rich ASV/ISE operations.

2. Experimental

2.1. Reagents

The ionophores *N,N,N',N'*-tetradodecyl-3,6-dioxaoctane-dithioamide (ETH 5435), *tert*-butylcalix[4]arene-tetra-kis(*N,N*-dimethylthioacetamide) (lead ionophore IV), the lipophilic cation exchanger sodium tetrakis[3,5-bis(trifluoromethyl) phenyl]borate (Na-TFPB), and the lipophilic salt tetradodecylammonium tetrakis(4-chlorophenyl)borate (ETH 500), were purchased in Selectophore or Puriss grades from Fluka (Milwaukee, WI). Methylene chloride was obtained from Fisher (Pittsburgh, PA). Poly(3-octylthiophene) (POT) was synthesized following the procedure of Jarvinen et al. [9] and was purified according to a recent patent application [10]. The synthesis of methyl methacrylate-decyl methacrylate (MMA-DMA) copolymer matrix was based on Qin et al. [11]. The cadmium nitrate, lead nitrate, thallium nitrate and tin chloride solutions were purchased from Fluka while the bismuth and indium nitrate solutions and the acetate buffer were obtained from Sigma-Aldrich (St. Louis, MO). All stock solutions were prepared using double deionized water (18.2 MΩ cm).

2.2. Instrumentation

Potentiometric measurements were performed with a 779026-01 USB-6009 14 Bit Multifunction data acquisition board (National Instruments, Austin, TX), connected to a six-channel high impedance interface. For stripping voltammetric measurements, an electrochemical Analyzer (CH 1232A Instruments, TX), interfaced to a desktop computer, was used.

2.3. Stripping Voltammetric Measurements

Stripping voltammetric measurements were performed in a 5 mL cell containing a three-electrode system with a bismuth-coated glassy carbon (GC) working electrode, a platinum wire counter electrode, along with a Ag/AgCl reference electrode. For the preparation of bismuth film, the GC electrode was first mechanically polished with alumina slurry (0.5 μm), rinsed with deionized water, and further cleaned ultrasonically in 1 M HNO₃ in water and in ethanol. The bismuth film was then preplated by immersing the polished glassy carbon electrode in a 5 mL cell containing 100 ppm of bismuth in 0.1 M acetate buffer (pH 4.6). A deposition potential (−0.6 V) was applied to the glassy carbon electrode for 10 minutes, while the solution was stirred slowly. Measurements were performed in the same acetate buffer medium using deposition potentials of −0.9 V (Pb) and −1.2 V (Cd) for 5 min (with stirring) followed by a square-wave voltammetric scan to −0.45 V (in a quiescent solution), and holding the potential at this final potential for 15 s.

2.4. Potentiometric Measurements

The potentiometric measurements were carried out at room temperature (22°C), using a 100 mL sample and a commercial double junction reference electrode (type 6.0729.100, Metrohm AG, 9101 Herisau, Switzerland).

2.5. Preparation of the Ion-Selective Electrodes

The Cd²⁺-ISE membrane was prepared by dissolving 60 mg of the following components in 0.8 mL CH₂Cl₂: ETH 5435 (15 mmol kg⁻¹), NaTFPB (5 mmol kg⁻¹), ETH 500 (10 mmol kg⁻¹), and the copolymer MMA-DMA (58.26 mg, 97.1%). The Pb²⁺-ISE membrane was prepared by dissolving 60 mg of the following components in 0.8 mL CH₂Cl₂: Lead ionophore IV (10 mmol kg⁻¹), NaTFPB (5 mmol kg⁻¹), ETH 500 (10 mmol kg⁻¹), and the copolymer MMA-DMA (58.42 mg, 97.36%). The membrane solution was degassed by purging it with N₂ before coating the microelectrodes.

The solid-contact Cd²⁺ and Pb²⁺-selective microelectrodes were prepared following an earlier procedure [8]. These microelectrodes were conditioned first in 10⁻³ M Cd(NO₃)₂ and subsequently in 10⁻⁹ M Cd(NO₃)₂ containing 10⁻³ M Ca(NO₃)₂ (1 day each) for the Cd²⁺-ISE, and in 10⁻³ M Pb(NO₃)₂ and subsequently in 10⁻⁹ M Pb(NO₃)₂ containing 10⁻⁴ M HNO₃ (1 day each) for the Pb²⁺-ISE.

2.6. Selectivity Measurements

Separate calibration curves for the different interfering ions on ISEs conditioned in a 1 mM solution of the most discriminated ion (Ca²⁺) were used to evaluate the selectivity of both electrodes. Such protocol allows to obtain unbiased selectivity coefficients [12]. The interfering ions of primary interest for the present study were thallium and indium for the Cd²⁺-ISE and tin for the Pb²⁺-ISE. Additional ions tested included calcium, sodium, and hydrogen.

3. Results and Discussion

Advanced working electrodes were used in the present work for conducting the comparison between the stripping voltammetric and potentiometric measurements. The former involved a bismuth-coated glassy-carbon electrode shown recently to be an attractive alternative to common mercury-film electrodes [2]. Potentiometric measurements were performed using recently developed solid-contact cadmium and lead ion selective electrodes (Cd²⁺-ISE and Pb²⁺-ISE) that offer low detection limits of 0.2 and 2.0 nM, respectively [13,14]. Such low detection limits reflect their highly selective ionophores used, and the low diffusion coefficients in the copolymeric (MMA-DMA) matrix support [15,16]. Overall, the low detection limits and high selectivity of these ISEs make them attractive for detecting nanomolar concentrations in the presence of higher background interferences.

We evaluated the selectivity of the Cd²⁺-ISE and Pb²⁺-ISE against metal ions that commonly interfere in ASV measurements, including indium, thallium, or tin, using the new unbiased method [12]. For this purpose, the ISEs were first conditioned in the presence of the most discriminated ion, then calibration plots for each interfering ion were obtained, followed by calibration for the target ion (cadmium or lead). Both membranes exhibit good selectivities against the relevant interfering ions, Ca²⁺, In³⁺, Tl²⁺ and H⁺, with logarithmic selectivity coefficients, log K_{Cd,J}^{POT}, of -7.3, -4.8, -5.2 and -3.2, respectively, for the Cd²⁺-ISE, and log K_{Pb,J}^{POT} values of -3.3, -5.8 and -4.2 for Ca²⁺, Sn²⁺ and H⁺, respectively, for the Pb²⁺-ISE. These data indicate that the cadmium and lead ISEs offer high selectivity against the thallium, indium and tin ions which are the major interferences in analogous ASV measurements of cadmium and lead [1]. Note that the selectivity of the Cd²⁺-ISE over hydrogen ions is inferior relative to that of a recently reported liquid inner contact cadmium ISE based

on the same ionophore [17]. This might be attributed to intermixing of POT and the membrane during the casting.

For example, Figure 1 compares the stripping voltam-metric (a) and potentiometric (b) signals for trace levels of lead (A) and cadmium (B) in the presence of increasing levels of thallium and tin (from 10^{-7} to 4×10^{-7} M), respectively (2 – 5). A well-defined stripping response is observed for the 10^{-7} M lead or cadmium solutions (A, a1 and B, a1, respectively). However, the additions of tin and thallium resulted in the appearance of new peaks that severely overlap with the lead or cadmium stripping signals, respectively. As a result of the similarity of the peak potentials and the distortion of the analyte peak, convenient quantitation of the target lead and cadmium ions is not possible even when the Pb/Sn or Cd/Tl concentration ratio is 1:1 (A, a2 and B, a2). With a large (4-fold) excess of these interferences the target lead or cadmium stripping peaks appear only as small shoulders of the tin and thallium peaks (A, a5 and B, a5).

The potentiometric ISEs also display well-defined lead and cadmium signals (A, b1 and B, b1, respectively), with similar signal-to-noise characteristics as the ASV runs. Unlike the stripping measurements, such potentiometric signals are not affected by the increasing levels of tin or thallium (A, b2 – 5 and B, b2 – 5, respectively). Even a 10-fold excess of tin or thallium does not affect the response of the lead or cadmium ISEs, respectively (not shown). Such effective discrimination against the interfering ions is expected from the low $\log K_{\text{Cd,Tl}}^{\text{POT}}$ and $\log K_{\text{Pb,Sn}}^{\text{POT}}$ values obtained in the selectivity studies (described earlier). Overall, the data of Figure 1 indicate that while the Pb^{2+} -ISE and Cd^{2+} -ISE offer similar sensitivity as the bismuth-coated stripping electrode, they offer a superior selectivity over the voltammetric route in the presence of the interfering tin and thallium, respectively. The potentiometric method offered also similar improvements in the selectivity of cadmium measurements in the presence of increasing indium concentrations (not shown). Note also that the stripping operation requires a time-consuming accumulation step (e.g., 5 min in Fig. 1), as compared to the nearly instantaneous potentiometric readout.

To further assess the relative selectivities of these stripping-voltammetric and potentiometric analyses we examined their response to different concentrations of the target cadmium ion in the presence of a large (100-fold) excess of the thallium interferent (Fig. 2A and B, respectively). In stripping voltammetry, the presence of 10^{-7} M thallium leads to a well defined peak (A, a). No cadmium stripping signals are observed upon additions of 10^{-9} M and 10^{-8} M cadmium into this thallium solution (A, b, c). Only an additional 10^{-7} M cadmium increment resulted in the appearance of a small shoulder on the large thallium peak (A, d). Analogous potentiometric measurements with the Cd^{2+} -ISE are not susceptible to such large thallium interference (B), reflecting the ability to detect nanomolar cadmium concentrations in the presence of higher background interferences. While no potentiometric response is observed for the 10^{-7} M thallium addition (a), adding a 100-fold lower level of cadmium leads to a defined signal (b). Similarly, well-defined cadmium signals are observed for subsequent additions of 10^{-8} M and 10^{-7} M cadmium (c and d, respectively). Clearly, the potentiometric technique offers a significantly better performance than the stripping voltammetric method when low concentrations of cadmium need to be detected in the presence of a high level of thallium.

Figure 3 demonstrates the ability to perform quantitative potentiometric measurements of cadmium in the presence of excess thallium. It compares the response of the Cd^{2+} ISE to increasing cadmium concentrations over the 1×10^{-9} M – 5×10^{-7} M range (b – e) in the presence (A) and absence (B) of an excess thallium. While a negligible response is observed for the 1×10^{-7} M thallium addition (A, a), well defined signals are observed for the different cadmium concentrations in the presence of such high thallium level (A, b – e). Such potentiometric signals are identical to those observed in the absence of thallium (compare A

vs. B). Identical cadmium calibration plots are thus obtained in the presence or absence of 1×10^{-7} M thallium (see inset for such plots; A vs. B), confirming the lack of thallium interference.

4. Conclusions

We demonstrated for the first time a direct comparison of stripping-voltammetric and potentiometric measurements of trace level metals, in connection to measurements of cadmium and lead in the presence of thallium, indium and tin. While both techniques offer a similar sensitivity, the potentiometric technique displays higher selectivity in the presence of excess of metal ions that commonly interfere in the stripping-voltammetric operation. Our data further support the suitability of direct potentiometry for trace measurements of heavy metals and its advantage over stripping voltammetry for specific analytical problems. For example, trace measurements of copper could benefit from the discrimination of the Cu ISE against antimony or bismuth ions that commonly affect analogous ASV measurements. In contrast, the present Cd^{2+} -ISE and Pb^{2+} -ISE are expected to display large interferences from lead and copper or mercury and silver ions, respectively [18], while these ions are unlikely to interfere in ASV measurements of cadmium and lead [1]. ASV will thus be advantageous in the presence of these interfering ions. The selection of an ISE (over ASV) for a particular analytical problem would thus depend largely upon its selectivity coefficients for the expected coexisting metal ions, and upon additional considerations (discussed below).

Our goal, however, is not to generate competition between voltammetry and potentiometry, but rather to encourage joint activities, coupling the attractive properties of ASV and ISEs, and to guide the selection of the proper electroanalytical technique for specific analytical challenges. One successful joint endeavor has been the development of stripping potentiometry, thus couples the preconcentration feature of stripping measurements with the inherent advantages of potentiometric measurements [1,19]. A recent hybrid ASV-ISE system, coupling an electrolytic preconcentration with ISE detection, was shown extremely attractive for minimizing matrix (salt) effects in potentiometric measurements [8]. The two electroanalytical trace techniques complement each other with respect to the scope of analytes or the type of sample (owing to different matrix effects), and have their own merits and limitations. Because of the complementary nature of the ASV and ISE data, it is recommended that the two techniques will be used in parallel or be selected based on the specific analytical problem. For example, parallel speciation measurements will benefit from the ability of ISE and ASV to measure the free-metal ion and labile fractions of the metals, respectively. Unlike potentiometry, ASV offers a distinct multi-analyte capability, with simultaneous measurements of up to 5 – 6 metals, including Pb and Cd tested here (down to the sub-nanomolar range) on a single electrode. The two methods are also prone to different types of interferences. For example, potentiometric measurements are not susceptible to intermetallic or surfactant effects, common in stripping voltammetry [1]. Both techniques are highly suitable for in-situ continuous monitoring, are well suited for a wide range of additional field operations, and are amenable to miniaturization, integration and automation. Joint efforts to combine the power of stripping-voltammetry and potentiometry are thus highly encouraged.

Acknowledgments

The authors thank the National Institutes of Health (RO1 EB002189) for financial support of this research.

References

1. Wang, J. Stripping Analysis: Principles, Instrumentation, and Applications. VHC ; Deerfield Beach, FL: 1985.

2. Wang J. *Electroanalysis* 2005;17:1341.
3. Buffle J, Tercier-Waeber ML. *Trends Anal Chem* 2005;24:172.
4. Sokalski T, Ceresa A, Zwickl T, Pretsch E. *J Am Chem Soc* 1997;119:11347.
5. Bakker E, Buhlmann P, Pretsch E. *Electroanalysis* 1999;11:915.
6. Bakker E, Pretsch E. *Anal Chem* 2002;74:420A. [PubMed: 11811417]
7. Sokalski T, Zwickl T, Bakker E, Pretsch E. *Anal Chem* 1999;71:1204.
8. Chumbimuni-Torres K, Calvo-Marzal P, Wang J, Bakker E. *Anal Chem* 2008;80:6114. [PubMed: 18570385]
9. Jarvinen H, Lahtinen L, Nasman J, Hormi O, Tammi A. *Synth Met* 1995;69:299.
10. Xiao, S.; Qui, C.; Qui, CX. US Patent Application. 20040254336. 2004.
11. Qin Y, Peper S, Bakker E. *Electroanalysis* 2002;14:1375.
12. Bakker E. *Anal Chem* 1997;69:1061.
13. Numnuam A, Chumbimuni-Torres K, Xiang Y, Bash R, Thavarungkul P, Kanatharana P, Pretsch E, Wang J, Bakker E. *Anal Chem* 2008;80:707. [PubMed: 18184015]
14. Chumbimuni-Torres K, Rubinova N, Radu A, Kubota L, Bakker E. *Anal Chem* 2006;78:1318. [PubMed: 16478128]
15. Heng L, Toth K, Hall EA. *Talanta* 2004;63:73. [PubMed: 18969405]
16. Long R, Bakker E. *Anal Chim Acta* 2004;511:91.
17. Thurer R, Vigassy T, Hirayama M, Wang J, Bakker E, Pretsch E. *Anal Chem* 2007;79:5107. [PubMed: 17530777]
18. http://www.sigmaaldrich.com/etc/medialib/docs/Sigma-Aldrich/Bulletin/pb_lead.Par.0001.File.tmp/pb_lead.pdf
19. Serrano N, Diaz-Cruz M, Arino C, Estaben M. *Electroanalysis* 2007;19:2039.

Fig. 1. Stripping voltammetric (a) and potentiometric (b) measurements of lead (A) and cadmium (B) in the presence of increasing levels of tin (A) and thallium (B) in 10^{-7} M increments. Concentrations of lead (A, 1 – 5), 10^{-7} M; cadmium (B, 1 – 5), 10^{-7} M, tin, 0 to 4×10^{-7} M (A, 1 – 5) and thallium, 0 to 4×10^{-7} M (B, 1 – 5). Stripping voltammetric measurements were made at a bismuth-coated GC electrode in acetate buffer (0.1 M, pH 4.6) using deposition potentials of -0.9 V (A) and -1.2 V (B) for 5 min followed by a square-wave scan to -0.45 V. Potentiometric measurements were performed in a 10^{-5} M $\text{Ca}(\text{NO}_3)_2$ background solution.

Fig. 2. Voltammetric (A) and potentiometric (B) measurements of cadmium in the presence of thallium. Successive additions of cadmium: 1 nM (b), 10 nM (c) and 100 nM (d) to a 100 nM thallium solution (a). Conditions, as in Fig. 1.

Fig. 3. Potentiometric measurements and calibration plots (inset) of trace cadmium in the presence (A) and absence (B) of excess of thallium. Thallium concentration (A), 10^{-7} M (a–e); cadmium concentrations (A, B), 10^{-9} (b), 10^{-8} (c), 10^{-7} (d) and 5×10^{-7} M (e).