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## Polarographic Studies of Metal-Ion Complexes

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**ABSTRACT:** Metal-ligand models and complex stability constants of newly synthesised chelating ligands, N,N'-bis(2-hydroxycyclopentyl)-ethylenediamine (Cyp2EN) and N,N'-bis(2-hydroxycyclohexyl)-ethylenediamine (Cy2EN), with metal ions Cd<sup>2+</sup>, Cu<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup> and Zn<sup>2+</sup> were established in this work. Stability constants were determined by Glass Electrode Potentiometry (GEP) and polarography as electrochemical techniques. A new concept, termed Virtual Potentiometry (VP), was also used for the evaluation of stability constants. In this concept, polarographic or polarographic + potentiometric data were evaluated using potentiometric computer software (ESTA). This concept assisted in obtaining a final model for Cd–Cyp2EN and Pb–Cyp2EN systems. It could refine M(HL) complex inaccessible via polarographic study of Pb–Cyp2EN system and refined the hydroxo–complex ML<sub>2</sub>(OH) that in turn was inaccessible using GEP for Cd–Cyp2EN system. For all metals studied, the complexes ML formed with the ligand Cy2EN were found more stable than the complexes ML formed with the ligand Cyp2EN. The complex M(HL) was obtained for all systems studied, but it seemed to be a minor species. The complex ML<sub>2</sub> was obtained in different systems studied with the ligand Cy2EN while this complex was only found in Cd–Cyp2EN system. In several systems potentiometric (ESTA) and voltammetric (3D–CFC) software could not distinguish which hydroxo–complexes were present as these species were formed in the pH range where the ligand was fully deprotonated. Selectivity trends for Cyp2EN and Cy2EN were compared and related to DHEEN as a function of metal ion radius. It was observed that the large metal ions were favoured by the addition of cyclopentyl bridges in DHEEN while the small metal ions were favoured when cyclohexyl bridges were added.

**KEYWORDS:** polarography, metal-ion, potentiometric, cyclo-hexyl bridges, stability, techniques, constants

### I. INTRODUCTION

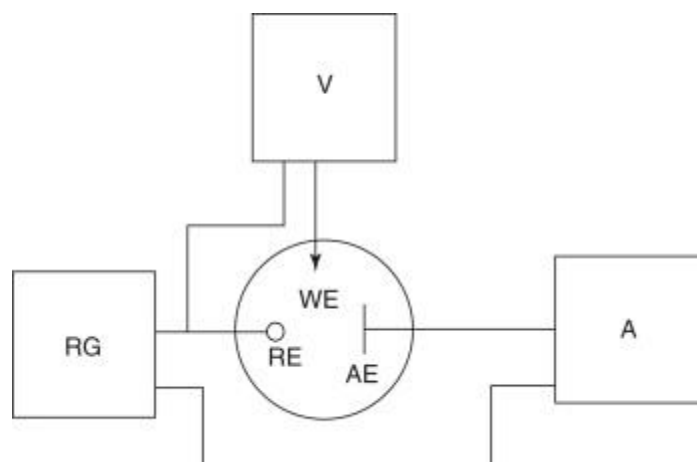
Polarography was first developed by Heyrovsky in 1922. The polarographic method was defined by the inventor as electrolysis with a polarizable dropping mercury electrode (DME) and it gained rapid acceptance not only in the investigation of electrode processes but, particularly, as a very important analytical technique. In 1925, Heyrovsky and Shikata constructed the polarograph, a device that automatically records current–potential curves. The polarograph was probably the first automatic apparatus to be applied in analytical chemistry. The theoretical basis of the method was laid by Ilkovič in 1934 (the value of the diffusion current) and by Heyrovsky and Ilkovič in 1935 (the shape of the current–potential curve, i.e., the so-called polarogram).

Polarography uses potentiostatic control (Figure 1) of the working electrode polarized under conditions of convective diffusion; the current response  $i$  of the electrode system is measured depending on the polarizing voltage  $E$  whose time rate of change,  $dE/dt$ , is negligible with respect to the time constant of the mass transport toward the electrode surface. This means that measurable  $i$  is independent from the time rate of change of the polarizing voltage. The International Union of Pure and Applied Chemists definition limits polarography to the use of liquid electrodes whose surfaces are periodically or continuously renewed (e.g., dropping and streaming mercury electrodes).[1]

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**Figure 1. Fundamental scheme of a three-electrode polarographic circuit for iR drop correction**

RG, ramp generator; A, current measurement device; V, voltmeter; WE, working electrode; RE, reference electrode; AE, auxiliary electrode.

Methods derived from polarography increase analytical sensitivity (or yield new information concerning the mechanism of the electrode process). Pulse polarographic techniques apply discontinuous polarization potential and measure the current response in given time intervals. The alternating current (AC) polarographic techniques are derived from direct current (DC) polarography as described above by imposing a small perturbation voltage of various frequencies upon the main DC polarizing voltage. These methods chiefly detect the adsorption of the participants of the electrode processes.

Polarography is probably the only dynamic (electrolytic) electroanalytical technique that can be conveniently and reliably applied for the determination of a wide spectrum of organic compounds. Candidate analytes must typically contain at least one electroactive functional group, which can participate in electrode reactions at potentials within the polarization range of the dropping-mercury electrode (DME). The  $E_{1/2}$  values depend mainly on the nature of the particular electroactive functional group(s), while the rest of the molecule (the size and/or the overall conformation) has only a minor effect on  $E_{1/2}$ . Therefore, it should be stressed that as polarography cannot discriminate between similar organic compounds, such as members of the same homologous series, chromatographic techniques are the methods of choice in these cases. Organic polarographic analysis is primarily used for the microdetermination of small amounts of a particular electroactive compound in the presence of excess of other nonelectroactive compounds and matrices. It can also be used for the simultaneous determination of mixtures of electroactive compounds with different electroactive groups, under conditions (carrier electrolyte, solvent, and appropriate pH) ensuring wide separation of the corresponding polarographic waves. In the latter case, there must also be no interaction between the product(s) of the electrode reaction of one analyte with the other analyte(s). [2] The methods of polarography can be used to follow the progress of a titration that produces or consumes some electroactive species. The voltage applied to the working electrode is constant and sufficient to provide the diffusion-limited current for the observable analyte. The current is then recorded as a function of the volume of titrant added to the sample solution. Since the working electrode is a microelectrode with an area of only a few square millimeters, and the current that flows is usually of the order of microamperes or less, only an insignificant amount of analyte ion is removed from the sample solution. This implies that the redox process involved at the working electrode has a negligible effect on the chemical titration reaction and does not introduce significant error in most instances. Scientists have used differential pulse polarography for the direct determination of aluminum in natural waters. If the pH is carefully controlled to  $4.00 \pm 0.01$ , there is a linear relationship between the peak height of the polarographic wave and the aluminum concentration up to  $600 \mu\text{g L}^{-1}$  aluminum. The coefficient of variation is about 4% at the  $250 \mu\text{g L}^{-1}$  level. With increasing aluminum concentrations, the relationship ceases to be linear, and above  $300 \mu\text{g L}^{-1}$ , the peak splits, probably because of hydrolysis and polymerization. Sodium, ammonium, magnesium, and calcium interfere at levels 100 times greater than

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that of aluminum, whereas iron(III), iron(II), copper(II), zinc(II), nickel(II), nitrate, perchlorate, chloride, and sulfate do not interfere.[3]

## II. DISCUSSION

Polarography is a voltammetric technique in which chemical species (ions or molecules) undergo oxidation (lose electrons) or reduction (gain electrons) at the surface of a dropping mercury electrode (DME) at an applied potential. Polarography only applies to the DME. The resultant reduction or oxidation current is recorded against the applied potential to yield the analytical parameter. Polarography may be used simply as an analytical tool or as a diagnostic method to interpret mechanisms and rates of electrode chemical reactions. Electrode surface redox reactions may occur with both inorganic and organic chemical species, although this article will deal solely with the inorganic applications of polarography.

Polarography was first introduced in 1922 by Heyrovsky; however, by the mid-1950s its usefulness as an analytical technique was superseded by spectroscopic techniques such as atomic absorption spectroscopy (AAS). For example their popularity for dissolved trace metal analysis was due to their greater sensitivities (ca.  $<0.1 \text{ mmol l}^{-1}$  compared to typically  $>0.1 \text{ mmol l}^{-1}$  for polarography), elemental diversity, flexibility, and ease of use. However, during the 1970s and 1980s polarographic techniques were more widely adopted owing to advances in instrumental design, particularly in enhancement in solid-state electronic circuitry, which led to enhanced sensitivities. In addition, the applications of polarography widened, along with the technique's relatively low capital and running costs. More recently advances in the technique may be attributed to the design of the DME and interfacing with information technology (enabling quicker analyses; the electrode has minimum interference, consuming very little mercury and is sealed and simple to handle, as well as economical to use).[4]

Polarographic analysis has been applied to a wide variety of samples including natural waters, biological, mineral, and environmental samples. A summary of the applications is shown in Table 1. In addition, Table 1 illustrates the typical detection limits encountered for each element, although this will vary depending upon the sample solution conditions. All the applications quoted in Table 1 are for differential pulse polarography (DPP; discussed later). Lower detection limits may be achieved using techniques such as stripping voltammetry. Stripping voltammetry, both anodic and cathodic, has advanced over the last decade enabling the detection of trace levels of organic and inorganic chemical species in aqueous solutions (typical limits of detection  $<10^{-9} \text{ mol l}^{-1}$ ), surpassing the detection limits of polarography for certain analyte determinations, and indeed advanced spectroscopic techniques.

**Table 1 . Summary of DP polarographic inorganic applications**

Element	Application	DL ( $\mu\text{mol l}^{-1}$ )	Comments <sup>a</sup>
Ti	j, k, o	0.05	
V	m, i	0.6	Catalytic enhancement of sensitivity
Cr	e, c, i, j, o, r	1	Discrimination between Cr(III) and Cr(VI)
Mo	d, e, j, k, o, p	0.1	Catalytic enhancement of sensitivity
W	k, o	5	
Mn	a, b, h, o, p	0.1	
Fe	c, b, h, i, j, k, n, o, p	1	Discrimination between Fe(III) and Fe(II)

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Element	Application	DL ( $\mu\text{mol l}^{-1}$ )	Comments <sup>a</sup>
			possible
Co	c, g, i, j, o, p	0.1	Adsorptive process
Ni	c, g, i, k, m, o, p	0.1	Adsorptive process
Cu	a, g, h, i, j, l, m, n, o, p, r	0.1	
Zn	g, h, i, j, o, p	0.5	
Cd	a, c, g, h, i, j, k, l, p	0.01	
Al	i, o	0.1	Derivatization followed by adsorption onto the DME
In		1	Determination after complex preconcentration
CN <sup>-</sup>	c	0.04	
Si	b, d,	0.1	Derivatization followed by adsorption
Sn	a, c, g, i, o	1	
Pb	a, c, g, h, i, j, l, m, o, p	0.1	
NO <sub>3</sub> <sup>-</sup>	a, b, c, e, j, p	1	
NO <sub>2</sub> <sup>-</sup>	a, b, c, e, j, p	0.1	Derivatization followed by adsorption
P (as PO <sub>4</sub> <sup>3-</sup> )	a, b, c, d, e	0.05	Derivatization followed by adsorption
As	c, h, n, o	0.1	Differentiation between As(V) and As(III) possible
Sb	a, p	0.1	Differentiation between Sb(V) and Sb(III) possible
Bi	o	0.5	
O <sub>2</sub>	a, b, c, d, e, f		
S	b, c, h, i, l, m, s		
Se	a	0.01	Catalytic enhancement of sensitivity
Br (as BrO <sub>4</sub> <sup>-</sup> )	c, f	1	
Cl (ClO <sub>4</sub> <sup>-</sup> )	c, f	1000	Catalytic enhancement of sensitivity
I (as IO <sub>4</sub> <sup>-</sup> )	a, d	0.02	
Ce, Pr, Nd, Sm,		0.1	

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Element	Application	DL ( $\mu\text{mol l}^{-1}$ )	Comments <sup>a</sup>
Eu			
U(VI)	a, c, k, o	1.2	After adsorption of ion-associated complex

a, biological fluids; b, freshwater; c, wastewater; d, seawater; DL, detection limit; e, drinking water; f, groundwater; g, foods; h, beverages; i, ceramics and glass; j, soil; k, minerals; l, aerosol; m, fuel and mineral oils; n, electronics; o, alloys, steel, bronzes; p, plant material; q, sediments; r, cements.

Essentially, direct current (DC) polarography yields detection limits in the orders of  $10^{-5}$ – $10^{-6}$  mol  $\text{l}^{-1}$ . However, if the applied potential scan is either in the DPP or the alternating current (AC) mode then the detection limits may be enhanced to  $10^{-7}$ – $10^{-8}$  mol  $\text{l}^{-1}$ , widening their analytical applications.

The major advantages using polarography for inorganic analysis may be summarized: (1) comparatively inexpensive equipment is required, (2) ability of the technique to distinguish between elemental oxidation states (i.e., Cr, As), (3) ability of the technique to establish the chemical form of elements (e.g., characterization and quantification of metal–organic complexation in natural waters), (4) simultaneous elemental analysis (e.g., Cu, Pb, Cd, Zn), and (5) sensitivity (down to  $10^{-8}$  mol  $\text{l}^{-1}$ ).[5]

As with all analytical techniques polarography has a number of limitations; these are (1) technique is not sensitive enough for direct ultratrace elemental analysis (in these circumstances the use of stripping voltammetry may be considered), (2) long analysis times (minutes compared to seconds for other analytical techniques such as AAS, ICP-AES) are required, (3) operator experience more critical (understanding of electrode processes is essential), in data interpretation, (4) limited elemental range owing to the constraints of the voltage window of the DME, and (5) toxic nature of mercury has recently limited its use.

However, the present discussion is to highlight the extensive capabilities of polarography for inorganic analysis. The discussion is by no means complete in both analytes detectable and sample application. However, it does serve to indicate the range of elements, which may be determined, along with the approximate detection limits for each application.

Ever since the development of direct current (DC) polarography, much efforts have been undertaken to compensate for the following three main limitations:

The drawback of DC polarography with regards to sensitivity is the current required to change the potential of the dropping mercury electrode (DME) to the required value: at a depolarizer concentration of  $10^{-5}$  mol  $\text{l}^{-1}$ , this time-averaged charging current is comparable to the Faradaic current.

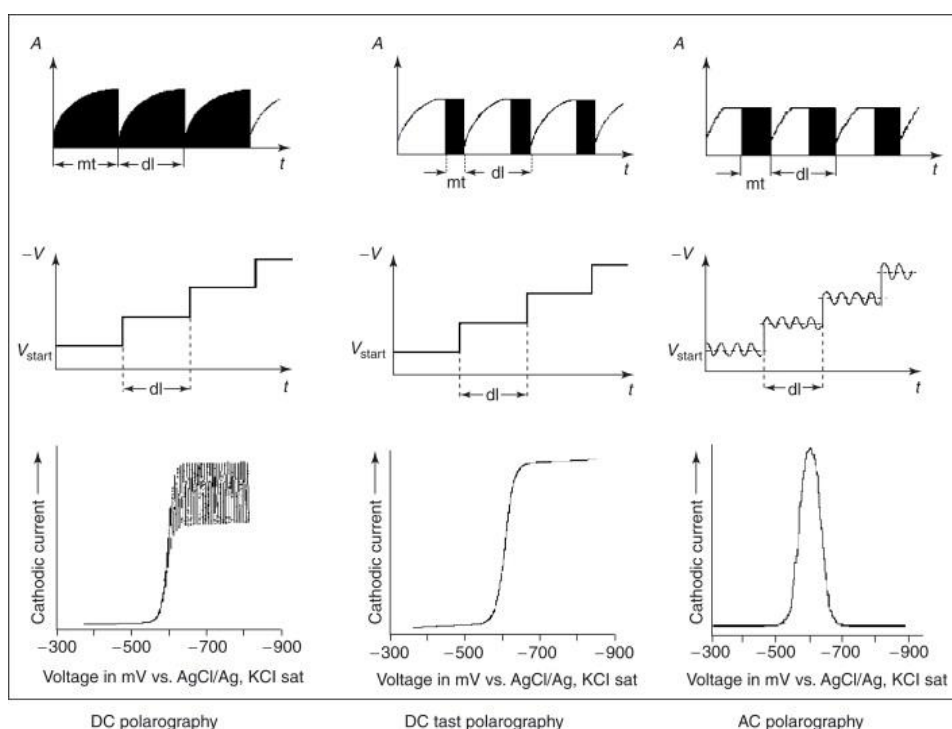
Lack of resolution of the sigmoid-shaped waves (e.g., DC polarography, normal pulse polarography (NPP)). In order to sufficiently distinguish two polarographic waves so as to be able to measure their corresponding half-wave potentials and limiting current values, it is necessary that the former half-wave potentials should differ in more than 200 mV. All subsequent polarographic techniques, in which the obtained response is in the form of a peak (derivative polarography, square-wave polarography (SWP), alternating current (AC) polarography, differential pulse polarography (DPP), etc.) present a higher resolution, a difference of only  $\sim 50$  mV being sufficient to be able to discriminate two substances presenting close half-wave potentials.

As observed in Figure 1 (DC polarography), the noise of the oscillations increases considerably after the reduction of a substance. Thus, making the calculation of the limiting current of any other compound, which is being reduced after the first substance, is difficult, especially when this compound is present at low concentrations. This difficulty decreases when peak-shaped polarograms are attained, for which the signal returns to the baseline.[6]

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**Fig. 2. Several polarographic techniques obtained using a digital polarograph. The DC technique has been obtained with a dynamic mercury electrode, whereas those of DC tast and AC have been attained with a static electrode and current integration. mt=measuring time, dl=drop life, t=time, A=electrode surface, V=voltage applied to the working electrode. The scanning are cathodic, i.e., toward more negative voltages, giving rise to cathodic currents.**

### III. RESULTS

Scientists revolutionized electroanalytical chemistry with his invention of polarography, which employed a dropping mercury electrode; At their suggestion, scientists pursued the anomaly in the maximum of the electrocapillary curve. Originally, a constant voltage was applied to a dropping mercury electrode, and some 50 drops of mercury were collected, dried, and weighed. Scientists measured the current flowing through the cell instead of recording the drop time. On 10 February 1922, scientists recorded the first current–voltage curve for a 1 mol L<sup>-1</sup> solution of sodium hydroxide, and interpreted the current increase between -1.9 and -2.0 V as being due to the deposit of Na<sup>+</sup> ions, forming an amalgam. Together with his coworker scientist constructed the first automatic polarograph in 1925 and demonstrated the new technique of amperometry (1927).

The interpretation of limiting currents and half-wave potentials was simplified by the equation of Dionyz Ilkovič (1934), assistant of Heyrovský. Ralph H. Müller and John F. Petras (New York, 1938), as well as Bruno Breyer (Sidney, after 1945), established finally ac polarography.

In 1928, Ernst Baars (later Marburg), Frank Bowden, and Erik Rideal (later Cambridge) performed the first relaxation measurements at electrodes. In 1940, Dolin, Ershler, and Frumkin investigated electrode reactions by impedance measurements – which got state-of-the-art in the 1980s.

Arne Tiselius (Uppsala, Sweden) developed his electrophoretic apparatus in 1937. The movement of an electrically charged substance under the influence of an electric field, due to the coulomb force, has become most important in biochemistry.[7]

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Laszlo Szebelledy and Laszlo Somogyi, in Budapest in 1938, established coulometric titration – although Faraday's theory was known since 1833, the tube amplifier could be developed only in the 1920s. The first potentiostat was built by Archie Hickling (Leicester, Liverpool) in 1942.

The polarographic current-potential wave that is illustrated by Fig. 3 conforms to the Nernst equation for reversible electrochemical processes. However, it is more convenient to express the concentrations at the electrode surface in terms of the current,  $i$ , and diffusion current,  $i_d$ . Because  $i_d$  is directly proportional to the concentration of the electroactive species in the bulk and  $i$  at any point on the curve is proportional to the amount of material produced by the electrolysis reaction, these quantities can be directly related to the concentration of the species at the electrode surface. For a generic reduction process [Eq. (45)], the potential of the electrode is given by the Nernst equation

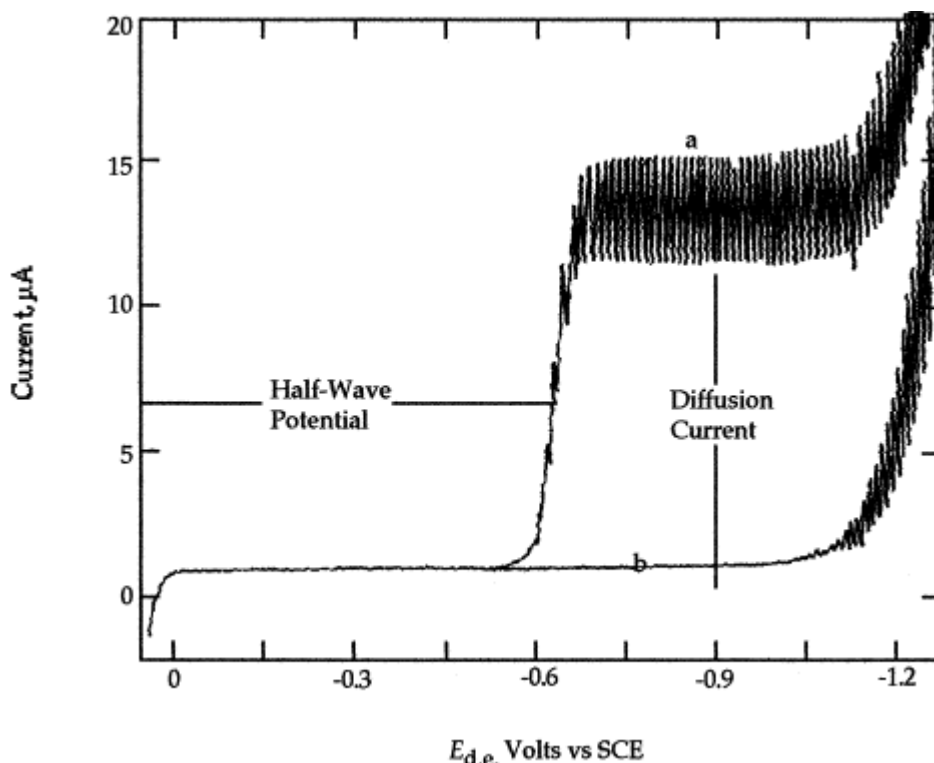


FIGURE 3. Polarograms for (a) 0.5 mM  $Cd^{II}(OH)_2^{2+}$  in 1 M HCl and (b) 1 M HCl.

Henry and Thorpe [120,121] separated monomethylarsenic acid, dimethylarsinic acid, As(III) and As(IV) on an ion-exchange column from samples of pond water receiving ash from a coal-fired power station. They then determined these substances by differential pulse polarography. The above four arsenic species were present in natural water systems. Moreover, a dynamic relationship exists whereby oxidation-reduction and biological methylation–dimethylation reactions provide the pathways for the inter-conversions of the arsenicals. Recoveries ranged from 4.4% (AsIII) to -2.4% (AsV) and between -2% and -3% for the organoarsenic compounds.

Henry et al. [121] reported a method for the determination of As(III), As(V) and total inorganic arsenic by different pulse polarography. As(III) was measured directly in 1 M perchloric acid or 1 M hydrochloric acid. Total inorganic arsenic was determined in either of these supporting electrolytes after the reduction of electroinactive As(V) with aqueous sulphur dioxide. As(V) was evaluated by difference.

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## IV. CONCLUSIONS

Anodic stripping voltammetry, potentiometric stripping voltammetry, and differential pulse polarography are used for the simultaneous determination of up to 10 analytes at extremely low concentrations (detection limits  $< 0.01 \text{ mg}^{-1}$ ). Electroanalytical techniques are applicable for  $\sim 30$  elements. Stripping analysis allows differentiation between chemical forms but is subject to interference from adsorption and poisoning by organic compounds onto the mercury electrode. Additional interferences include peak overlapping due to similarity of redox potentials and the formation of intermetallic compounds between the deposited metals.[7]

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