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REAGENT PURIFICATION BY MERCURY CATHODE ELECTROLYSIS I: A PRACTICAL GUIDE

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INTRODUCTION

Mercury cathode electrolysis has been recognized for decades as having the potential for being extremely effective for purifying aqueous solutions of various reagents.[1] However, practical use of the method for reagent purification has been largely restricted to the preparation of purified electrolytes for electrochemical studies, for electroanalytical separations, or for polarographic analyses. Although much information on the use of the mercury cathode for analyses has been reviewed,[2,3] information on its general application for preparing pure analytical reagents is relatively sparse and scattered throughout the literature. During the present investigators' quest to apply this principle on a general basis, no manuscript was found that comprehensively covered the basic aspects of the method with emphasis on purification. This manuscript was prepared as a practical guide for the general analytical chemist who critically needs ultrapure chemicals particularly amenable to purification by the mercury cathode process.

The electroanalytical chemist will also find practical information important for preparing ultrapure reagent chemicals. In addition to this general review experimental results of examinations of the efficiency of the process for purifying several buffer reagents are reported. Purification efficiencies have been determinted by simultaneously monitoring the electro-reduction of several cations by gamma ray spectroscopy of radioisotopes.

EXPERIMENTAL

Reagents

Solutions of the buffer reagents KH_2PO_4, Na_2HPO_4, $NaOOCCH_3$, and Na_2CO_3 were prepared by dissolving appropriately weighed amounts of the reagent grade chemicals in demineralized water. Where possible a concentrated stock solution was first prepared. The solutions eventually processed by mercury cathode electrolysis were prepared by placing the necessary aliquot of the stock solution and measured quantities of trace element carrier solution into volumetric flasks and diluting to a final volume corresponding to 100 ng/mL of the impurity element. A 100 mL quantity of the buffer solution containing carrier was doped with a sufficient quantity of the carrier-free or high specific activity isotopes of ^{60}Co, ^{65}Zn, ^{54}Mn, ^{59}Fe, and ^{51}Cr. The initial gamma-ray activity level of each isotope was sufficient to register $\geq 10^5$ counts/min for a 0.2 mL volume of solution.

Apparatus

The electrolysis cell designed for radiotracer monitoring of the depletion of impurities from various reagent solutions during electrolysis at the mercury cathode is shown in Fig. 1. A 454 g quantity (33.4 mL) of triply distilled mercury (Bethlehem Apparatus Co., Inc., Hellertown, Pa.) was routinely used with an initial 50 mL volume of the isotope-carrier doped reagent solution. The mercury pool was constantly stirred with a magnetic stirrer at the same speed during each experiment and the solution purged for at least 30 min with a purified nitrogen stream prior to the electrolysis. The nitrogen from a pressurized tank was metered through a flow controller, passed through a u-tube filled with copper wire mesh heated to 200°C, and then saturated by passage through a bubbler containing the solution undergoing purification. The

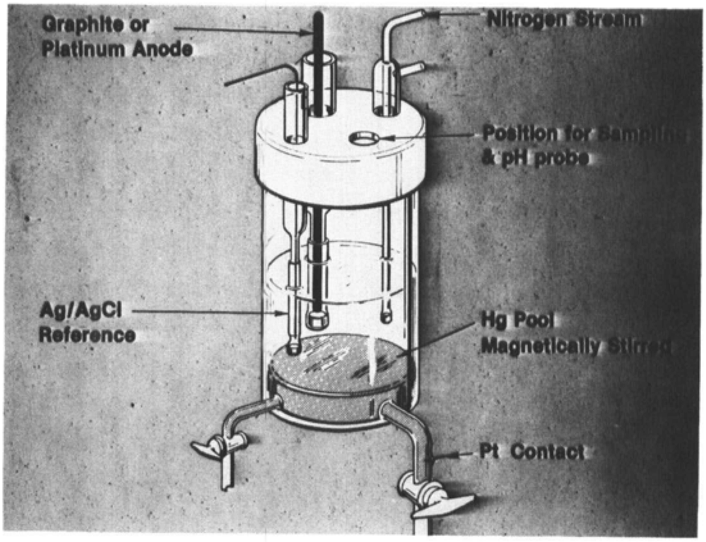

Fig. 1 Mercury cathode electrolysis cell for radiotracer monitoring

saturated gas was then admitted into the electrolytic cell through a tube capped with a porous frit which served to disperse the nitrogen in small bubbles. This prevented splashing of the reagent solutions onto the walls of the cell during electrolysis and also minimized evaporation.

Experimental conditions were optimized via electrolysis of a nonradiotracer doped reagent before the actual experiment was conducted with tracer doped solutions. In this way valuable time was saved by identifying possible preliminary malfunctions and eliminating them prior to the execution of the isotope experiment.

The cell consisted of a Pyrex vessel with a Teflon cap which contained ports through which the reference electrode, nitrogen purge tube, anode compartment, and either the pH probe or reagent sampling pipet were inserted during the course of the electrolysis. The electrode compartment for the reference electrode consisted of a porous Pyrex frit (0.63 cm dia.) wedged tightly into the end of

0.63 cm (O.D. dia.) heat-shrinkable Teflon tubing. The top end of the Teflon tube was shrunk around the outer circumference of a 1.27 cm bore quartz tube drawn to a 0.63 cm tip. The reference filling solution was contained in this compartment and was in constant contact with a freshly prepared Ag/AgCl wire produced by anodizing a bright Ag wire in 1M KCl solution. The anode was either a 0.36 cm dia. graphite rod or Pt wire housed inside a tube with a fritted glass end tube, which was constructed in a manner similar to that described previously for the reference electrode. The nitrogen purge tube contained an inlet through a porous glass frit and an outlet for gas to escape into the atmosphere after passing through the solution. The potential at the mercury cathode was controlled by a Princeton Applied Research Model 174A Potentiostat (Princeton, N. J.).

Procedures

Two tenths of a mL of reagent solution was withdrawn at various time intervals in order to measure the activity of the various isotopes. No more than twenty samples were withdrawn via plastic pipet during the course of a 48 hr electrolysis. Due to periodic problems caused by formation of bubbles or loss of the solution from the electrode compartments, experiments were observed closely throughout.

The gamma ray activities of aliquots withdrawn from the cell during the electrolysis were measured by counting for known periods using a lithium drifted germanium detector coupled to a 4096 multichannel computer based PHA system produced by Tennecomp Systems, Inc. Oak Ridge, Tenn. Background corrected photopeak areas for all isotopes were determined simultaneously.

Two cells were used during various experiments and were cleaned between experiments by rinsing successively with 0.5N HNO_3 acid, 0.1N HCl, 0.1N EDTA at pH 7.0 and finally with copious quantities of water. The cell and all component parts were then leached for 24 hours at 70°C in 1N HNO_3. This was followed by a thorough rinsing with water and a survey with GM tube counters to detect any residual radioactivity. Detectable radiation was usually found near and on the Pt wire which had been in contact with the mercury pool. However no contamination of fresh mercury was detected during subsequent preliminary experiments and cleaned cells were reused for various reagent experiments.

BASIC ASPECTS OF ELECTROCHEMICAL REDUCTIONS

For a free elemental cation undergoing a reversible reduction to the metallic state and then forming a soluble amalgam with mercury (M^o_{Hg}) the general cathode reaction

$$M^{n+} + ne^- \rightleftarrows M^o_{(Hg)} , \tag{1}$$

can be written. The single electrode potential, (E_c), for this reaction at 25°C at the mercury cathode is given by

$$E_c = E^o + \frac{0.059}{n}\log \frac{[M^{n+}][Hg]}{[M^o_{(Hg)}]} , \tag{2}$$

where E^o is the standard reduction potential for reaction (1). When the volume of the aqueous phase containing M^{n+} is different from the volume of the mercury pool (V_{Hg}) the potential at the cathode can be obtained from the expression

$$E_c = E^o + \frac{0.059}{n}\log \left[\frac{(1-X)/V_{aq}}{X/V_{Hg}}\right] , \tag{3}$$

where X is the mole fraction of total cation reduced and amalgamated with mercury.

Under polarographic conditions the potential at the dropping mercury electrode (dme) is given by the equation

$$E_{dme} = E_{1/2} + \frac{0.059}{n}\log \frac{i_d - i}{i} , \tag{4}$$

where

E_{dme} = potential of dropping mercury electrode

$E_{1/2}$ = half wave potential

i = current at the dme and

i_d = diffusion current.

The electrochemical reaction occurring in the polarographic cell can be duplicated in a larger electrolytic cell with a mercury pool cathode operated at controlled potential. Thus the current-voltage information obtained polarographically provides data needed for selecting the cathode potential required to achieve removal of a desired cation by reduction at the mercury pool. For the special case of removing groups of trace impurities from a nonelectroactive aqueous reagent electrolyte, tables of polarographic halfwave potentials can be consulted to estimate the negative potential below which a given impurity cation will undergo reduction at the mercury cathode.[4-6] The controlled cathode potential should be more negative than the $E_{1/2}$ value of the most difficultly reduced cation that is to be removed. $E_{1/2}$ values are sensitive to the chemical nature of the species undergoing reduction and a shift to more negative potentials generally occurs upon complexation of the metal cation. Thus the chemical nature of the reagent being purified and also its concentration must be considered when selecting the appropriate cathode potential. It is often necessary to directly determine polarographically the $E_{1/2}$ value of the contaminant species for the medium to be purified. This may be especially necessary in the case of the purification of strongly complexing reagents and certain buffer solutions.

At the anode the single electrode potential during electrolysis is determined by the primary anode reaction which depends largely upon the anode material and the composition of the reagent. At a platinum electrode the reaction

$$H_2O \rightleftarrows 1/2\ O_2 + 2H^+ + 2e^- \ , \qquad (5)$$

would predominate during mercury cathode electrolysis of an aqueous solution to remove metallic cations undergoing no anode reaction.

The voltage for the cell reaction,

$$2M^{n+} + nH_2O \rightleftarrows 2M^o_{(Hg)} + \frac{n}{2}O_2 + 2nH^+ \ , \qquad (6)$$

is given by the expression

$$\begin{aligned} E_{cell} &= E^o_{M^{n+},M^o_{(Hg)}} + E^o_{H_2O,O_2} \\ &+ \frac{0.059}{n}\log\frac{[M^{n+}]^2\ P^{n/2}_{O_2}[H^+]^{2n}}{[H_2O]^n[M^o_{Hg}]^2} \end{aligned} \qquad (7)$$

where P_{O_2} is the oxygen pressure in atmospheres.
It is clear from this equation that increasing the amounts of hydrogen ion in solution shifts the cell potential to a less negative value thereby potentially impeding the reduction of the cations at the cathode. Consequently anode materials are selected and in some cases electrolytes are added to induce an anode reaction that does not generate H^+.

By substituting the appropriate E^o values and data for $[M^{n+}]$, P_{O_2} and $[M^o_{Hg}]$ into Eq. (7) the cell voltage can be computed. For a nonspontaneous electrolytic reaction an external negative potential at least equivalent to the E_{cell} value must be applied to induce the reduction of the cation. Because of overpotential at the anode and at the cathode, and resistance of the cell to current flow, the negative potential required to induce electrolysis must be greater than the value computed from Eq. (7). Thus the applied potential for electrolysis is given by

$$E_{applied} = E_{cell} + E_{o.c.} + E_{o.a.} + IR \qquad (8)$$

where $E_{o.c.}$ and $E_{o.a.}$ are overvoltages of the cathode and anode and, IR is the ohmic voltage.

Application of a constant applied potential during electrolysis does not maintain a given potential at the cathode since changes in $E_{o.c.}$, $E_{o.a.}$, IR, temperature, and the concentrations of reactive species in Eq. (7) are occurring. Generally the cathode potential will become more negative as the electrolysis proceeds with a constant applied potential. This trend is favorable for a purification process since other cations would be reduced. Conversely undesired reactions of the electrolyte might also commence. Obviously control of the cathode potential rather than the applied voltage is more desirable.

SCOPE OF APPLICATION

Electrolysis of Cations

In principle any reagent forming an aqueous solution upon dissolution can be purified by electrolysis at the mercury cathode provided its dissociated component anion and cation are not electroactive at the applied cathode potential required for reduction of the impurity ion. Electrochemical inertness at the anode potential is also required. Additionally, the reagent solution must be chemically inert with respect to solubilization or reaction with mercury. Solutes consisting of any combinations of the cations and anions in Tables I and II can usually be purified.

Removal of electroreducible trace transition cations from solutions of the salts of alkali, alkaline earth, and many rare earths can be accomplished especially well. Effective depletion from aqueous solutions of the cations listed in Table III can generally be obtained by reduction to the metal and amalgamation at the mercury cathode.

In practice effective electrochemical purifications can often be precluded by chemical reactivity or excessive solubility of Hg in the reagent undergoing electrolysis, by simultaneous cyclic reactions of impurities at the cathode and anode, by nonamalgam

TABLE I. CATIONS CAPABLE OF BEING PURIFIED BY MERCURY CATHODE ELECTROLYSIS[a]

Half Reaction[b]	E^o(v)
$Al^{3+} + 3e^- \rightleftarrows Al^o$	-1.66
$Ba^{2+} + 2e^- \rightleftarrows Ba^o$	-2.90
$Be^{2+} + 2e^- \rightleftarrows Be^o$	-1.70
$Ca^{2+} + 2e^- \rightleftarrows Ca^o$	-2.87
$Cs^+ + e^- \rightleftarrows Cs^o$	-2.92
$K^+ + e^- \rightleftarrows K^o$	-2.925
$Li^+ + e^- \rightleftarrows Li^o$	-3.045
$Mg^{2+} + 2e^- \rightleftarrows Mg^o$	-2.37
$Na^+ + e^- \rightleftarrows Na^o$	-2.7141
$Rb^+ + e^- \rightleftarrows Rb^o$	-2.98
$Sc^{3+} + 3e^- \rightleftarrows Sc^o$	-2.08
$Sr^{2+} + 2e^- \rightleftarrows Sr^o$	-2.89
$Y^{3+} + 3e^- \rightleftarrows Y^o$	-2.37
$La^{3+} + 3e^- \rightleftarrows La^o$	-2.4

[a] Most $E_{1/2}$ values for these cations in NO_3^-, PO_4^{3-}, ClO_4^-, SO_4^{2-} are beyond the potential for decomposition of H_2O.

[b] Values taken from Refs. 7-12.

formation, and by complexation of impurities to form difficultly reduced species.

Electrolysis of Anions

The counter ion of a cation undergoing purification by mercury cathode electrolysis must also be nonelectroactive. Generally the anion must be more inert toward reduction than the corresponding

TABLE II ANIONS CAPABLE OF BEING PURIFIED BY MERCURY CATHODE ELECTROLYSIS

		$E_{1/2}$ in Various Media				
Half Reaction	E°(V)[a]	0.1F KNO_3	0.04F $LaCl_3$	0.1F NaOH	OAc^-,pH3.6	0.1F NH_4Cl
CH_3COO^-	---	---	---	---	---	---
NH_4^+	---	---	---	---	---	---
$HCOO^-$	---	---	---	---	---	---
Borate	---	---	---	---	---	---
$Br_2 + 2e^- \rightleftarrows 2Br^-$	+1.09	(1mM)+0.12	---	---	---	---
$Cl_2 + 2e^- \rightleftarrows 2Cl$	+1.36	(1mM)+0.25	---	---	---	---
Cl_3CCOO^-	---	---	---	---	---	---
ClO_4^-	NR	NR	NR	NR	NR	NR
Citrate	---	---	---	---	---	---
$F_2 + 2e^- \rightleftarrows 2F^-$	+2.85	NR	NR	NR	NR	NR
H_2CO	---	---	---	---	---	---
H_2O_2	---	---	---	---	---	---

$I_2(KI_3) + 2e^- \rightleftarrows 2I^-$	+0.5345	(1mM)+0.03	---	---	---	---
N_2H_4	---	---	---	(4F)-0.334	---	---
NH_2OH	---	---	---	(1F)-0.43	---	NR
NO_2^-	---	---	---	---	---	---
NO_3^-	---	---	-1.58	---	---	---
$O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$	+0.815	-0.05	---	-0.18	---	---
OH^-	---	(1mM)+0.08	---	---	---	---
Oxalate	---	---	---	---	---	---
PO_4^{-3}	---	---	---	---	---	---
SO_3^-	---	(1mM)+0.01	---	---	-0.54	---
$SO_4^{-2} + 4H^+ + 2e^- \rightleftarrows$	NR	NR	NR	NR	NR	NR
$H_2SO_3 + H_2O$	+0.17	---	---	---	---	---
Tartrate	---	---	---	---	---	---

[a] All $E_{1/2}$ values taken from Ref. 5.

TABLE III. CATIONS REDUCED AND AMALGAMATED AT THE MERCURY CATHODE

$Ev_{1/2}$ In Various Media Versus S.C.E.

Half Reaction	$E^o(v)$	Cl^-	NO_3^-	ClO_4^-	SO_4^{-2}
$Ag^+ + e^- \rightleftarrows Ag^o$	+0.7991	(8FHCl)>0	---	---	---
$Au^+ + e^- \rightleftarrows Au^o$	+1.7	---	---	---	---
$Au^{3+} + 3e^- \rightleftarrows Au^o$	+1.50	---	---	---	---
$BiO^+ + 2H + 3e^- \rightleftarrows Bi^o + H_2O$	+0.32	---	(-0.01) 1NHNO$_3$	---	---
$Cd^{2+} + 2e^- \rightleftarrows Cd^o$	-0.4019	(0.1MKCl)-0.600	(-0.59) 1MHNO$_3$	(1MNCLO)-0.62	---
$Ce^{3+} + 3e^- \rightleftarrows Ce^o$	-2.48	(0.1MCl$^-$)-2.0	---	---	---
$Co^{2+} + 2e^- \rightleftarrows Co^o$	-0.27	(5MCaCl$_2$)-0.82	(Co(NH$_3$)$_6$)-0.28(1MHNO)$_3$	(0.1MNaClO$_4$)-0.25(Co(NH$_3$)$_6$	(0.5MK$_2$SO$_4$)-1.43
$Cr^{3+} + 3e^- \rightleftarrows Cr^o$	-0.71	(0.1MCl$^-$)-0.61	---	---	---
$Cu^{2+} + 2e^- \rightleftarrows Cu^o$	0.521	(0.1MCl$^-$)+0.04	---	---	(0.5MH$_2$SO$_4$) 0.00
$Fe^{2+} + 2e^- \rightleftarrows Fe^o$	-0.440	(0.1MCl$^-$)-1.3	---	(1MNaClO$_4$)-1.43	
$Ga^{3+} + 3e^- \rightleftarrows Ga^o$	-0.52	(0.1MCl$^-$)-1.1	(0.1MKNO$_3$)-1.12	---	---
$H^+ + e^- \rightleftarrows 1/2\ H_2$ (Pure H_2O)	-0.414	(0.1MCl$^-$)-1.58	---	---	---
$Hg_2^{2+} + 2e^- \rightleftarrows 2Hg^o$	+0.789	(1FKCl)>0	---	---	---
$2Hg^{2+} + 2e^- \rightleftarrows Hg_2^{2+}$	+0.920	(0.1MCl$^-$)>0	---	---	---

$In^{3+} + 3e^- \rightleftarrows In^o$	-0.34	$(0.1MCl^-)$-0.56	---	---	---
$Ir^{3+} + 3e^- \rightleftarrows Ir^o$	+1.0	---	---	---	---
$Mn^{2+} + 2e^- \rightleftarrows Mn^o$	-1.05	(1FKCl)-1.51	---	---	---
$Ni^{2+} + 2e^- \rightleftarrows Ni^o$	-0.250	$(0.1MCl^-)$-1.1	---	$(HClO_4)$-1.1	---
$Pb^{2+} + 2e^- \rightleftarrows Pb^o$	-0.1288	$(0.1MCl^-)$-0.40	$(0.1MNaNO_3)$-0.38	$(0.1MHClO_4)$-0.37	---
$Pd^{+2} + 2e^- \rightleftarrows Pd^o$	0.83	$(1MKCl/OHMen\ Pd(en)^{+2})$ -0.65	---	---	---
$Pb^{2+} + 2e^- \rightleftarrows Pb^o$	+1.2	(1FKCl)-0.1	---	---	---
$Rh^{2+} + 2e^- \rightleftarrows Rh^o$	+0.6	---	---	---	---
$Sn^{2+} + 2e^- \rightleftarrows Sn^o$	-0.136	$(1MHCl/4MNH_1Cl)$-0.25	---	$(1MHClO_4)$+0.13	$(1MH_2SO_4)$-0.46
$Tl^{+} + e^- \rightleftarrows Tl^o$	-0.3363	$(0.1MCl^-)$-0.46	---	---	---
$Ti^{2+} + 2e^- \rightleftarrows Ti^o$	-1.63	$(1MNaNO_3)$-0.46	---	---	$(0.1MNa_2SO_4)$-0.47
$UO^{2+} + 4H^+ + 6e^- \rightleftarrows U^o + 2H_2O$	-0.82	---	---	---	$(0.1MH_2SO_4)$-0.85
$Zn^{2+} + 2e^- \rightleftarrows Zn^o$	-0.762	(1FKCl)-1.00	$(1MKNO_3)$-1.12	---	---
$ZrO^2 + 2H^+ + 4e^- \rightleftarrows Zr^o + H_2O$	-1.5	(0.1MKCl)-1.65	---	---	---

cation and the trace impurities being reduced. Once the requirements of stability toward reduction are satisfied, a primary concern then becomes possible reactions at the anode. Optimally the anion should be less readily oxidized than OH^- and chemically inert toward mercury. Various polarographic investigations have shown perchlorate, sulfate, nitrate, acetate, phosphate, chloride, and fluoride to be suitable for use with the dropping mercury electrode. Thus solutions of these anions are candidates for purification by mercury cathode reduction. The basic electrochemistry of anions and other information for assessing the suitability of a given anion as the counter ion of a cation undergoing trace element removal by mercury cathode electrolysis are provided below. Table II can be consulted to obtain the estimated maximum cathode potentials operative without electrochemically modifying the anion.

Acetate. Reduction of acetate in neutral or alkaline solution does not appear to be significant at the mercury cathode. The acidic form, acetic acid, gives a wave at the dropping mercury electrode that is due to the discharge of hydrogen.[13] The $E_{1/2}$ in 0.1NLiCl or 0.1NLi_2SO_4 and 0.05 N TMAI solutions containing 0.1-10 millimoles/L of acetic acid has been reported as -1.76 and -1.86 respectively versus the S.C.E. Glacial acetic acid as a solvent shows hydrogen discharge as -1.7 V versus the S.C.E. Acetate solutions can be oxidized at the platinum anode at potentials $\geq$2.14 V versus the S.C.E.[14] Sodium acetate solutions (0.5 to 1.5M) undergo no appreciable oxidation until the potential at the platinum anode reaches $\geq$+2.0 V.[15] Kolbe[16] first showed acetic acid to be oxidized at the Pt anode via the reaction

$$2CH_3COOH + 1/2O_2 \rightleftarrows C_2H_6 + 2CO_2 + H_2O \ . \qquad (9)$$

Further investigations have revealed that acetates of K^+, Na^+, NH_4^+, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mg^{2+}, Zn^{2+}, and Ni^{2+} are probably first reduced to radicals which in turn generate the principle products ethane (or methane) and carbon dioxide as indicated by the reaction sequence

$$\left\{\begin{array}{l} 2CH_3COO^- \rightleftarrows 2CH_3COO^\bullet + 2e^- \\ \\ 2CH_3COO^\bullet \rightleftarrows C_2H_6 + 2CO_2 \ . \end{array}\right\} \qquad (10)$$

Since the oxidation products of this Kolbe type reaction are methane or ethane and CO_2, acetate can be conveniently used to prevent otherwise damaging anode reactions during reductions in a nondivided cell.

Carbonate. Saturated solutions of potassium carbonate at low temperature (-10°C) can be oxidized at a Pt anode to percarbonate. Solutions of Li^+, Na^+, NH_4^+, and Cs^+ when electrolyzed show no percarbonate precipitates but the formation of the soluble percarbonate is suspected. This interferring reaction is prevented completely by increasing temperature or by using a platinized platinum anode. The latter approach however reduces the magnitude of the anode overvoltage required for oxygen evolution.

Halides. Halides with the exception of fluoride are all readily oxidized to their respective free halogens; the order of ease of oxidation being I > Br > Cl > F. The halide overvoltages on Pt and graphite electrodes are given in Table IV. By carefully controlling the potential at a graphite anode below the potential for halide

TABLE IV. HALIDE OVER-VOLTAGES ON VARIOUS ANODES[17]

Halide	Current Density $A\text{-}cm^{-2}$	Overvoltage Platinized Pt	Smooth Pt	Graphite
$C\ell^-$	0.1	0.03	0.05	0.25
Br^-	0.1	0.01	0.01	0.27
I^-	0.1	0.03	0.03	0.10
$C\ell^-$	1.0	0.07	0.24	0.50
Br^-	1.0	0.20	0.40	0.33
I^-	1.0	0.20	0.22	0.70

oxidation, successful purifications of halide-containing solutions would be possible. However where other more electrolytically inert anions can be tolerated their selection would facilitate the mercury cathode purification process.

Nitrate and Nitrite. In neutral or alkaline solutions nitrate can undergo reduction to yield primarily hydroxylamine and ammonia via the reactions

$$NO_3^- + 7H^+ + 6e^- \rightleftarrows NH_2OH + 2H_2O \ , \tag{11}$$

$$NO_3^- + 9H^+ + 8e^- \rightleftarrows NH_3 + 3H_2O \ . \tag{12}$$

These final products and another intermediate, nitrite, have been formed at the mercury cathode. In concentrated sodium nitrate solutions the principle product for reduction is ammonia. Should the cathode potential be sufficient to reduce sodium the resulting Na-Hg amalgum causes reduction of nitrate to ammonia with simultaneous liberation of hydrogen.[18]

Certain cationic and anionic impurities seem to facilitate the reduction of nitrate. For example in lithium chloride containing acetic acid and acetate, nitrate produces a broad polarographic wave between -0.6 and -1.6 V.[19] Reduction occurs at the following voltages in 0.1N solutions of the electrolytes: $LaCl_3$, -1.22 V; $CeCl_3$, -1.23 V; $MgCl_2$, -1.74 V; $CaCl_2$, -1.78 V; $SrCl_2$, -1.79 V; $(CH_3)_4$ NCl, -2.15 V; and LiCl, -2.17 V versus the S.C.E. Nitrate and nitrite have similar reduction potentials and in concentrated supporting electrolytes the reduction potentials of both approach a limiting value of -1.5 V regardless of the cation charge.[20]

Perchlorate. Perchlorate is an extremely stable anion for which no tendency toward reaction has been recorded at the mercury cathode in any medium. At strongly anodic potentials at a platinum anode perchlorate may be oxidized to the perchlorate radical which subsequently reacts to ultimately generate chlorine oxides. The extremely high electrochemical stability of perchlorate toward reduction and oxidation in combination with high aqueous solubility of most salts affords an excellent anion choice for purification work. The poor complexing powers of perchlorate is another favorable characteristic.

Phosphate. Phosphate shows no detectable reduction at the mercury cathode in neutral or basic solution. The acid and 2N solutions of K_2HPO_4 or the corresponding salts of Cs^+, Pd^{2+}, and NH_4^+ are oxidized stubbornly at the platinum anode to perphosphoric acid, $H_4P_2O_8$, or to the $M_4P_2O_8$ salt.[21]

Sulfate and Sulfite. The sulfate ion is not reducible at the dropping mercury electrode.[21] Likewise sulfite does not reduce in neutral or alkaline solutions. However in 1NHCl the reduction of sulfurous acid is observed at -0.2 V versus the S.C.E. In contrast, at platinum anodes sodium sulphite is electrolyzed readily according to the reaction

$$2SO_3^{2-} \rightleftarrows S_2O_6^{2-} + 2e^- \ . \tag{13}$$

An alternative route for this oxidation includes

$$2OH^- \rightleftarrows H_2O_2 + 2e^- \ , \tag{14}$$

followed by

$$2SO_3^{-2} + H_2O_2 \rightleftarrows S_2O_6^{-2} + 2OH^- \ . \tag{15}$$

In acid solutions, i.e. sulfuric acid, at the platinum anode electrolysis proceeds to produce oxygen, ozone, $H_2S_2O_8$, and H_2SO_5. From acid solutions of ammonium sulfate the corresponding insoluble persulfate salts are precipitated during electrolysis.

Electrolysis of Carboxylic Acids

Aliphatic acids and the corresponding anions can be reduced at the dropping mercury electrode. In the acid form the specie is reduced via liberation of hydrogen. As the concentration of the acid increases the $E_{1/2}$ becomes more negative. Values reported previously by Kolthoff and Lingane[12] are provided in Table V.

TABLE V. POLAROGRAPHIC BEHAVIOR OF ALIPHATIC ACIDS

Acid	K_{diss}	Concn. mmoles/L	$E_{1/2}$ (S.C.E.)
Formic[a]	1.77×10^{-4}	1-10	-1.74 to -1.85
Acetic[a]	1.75×10^{-5}	2-15	-1.76 to -1.86
Oxalic[b]	5.90×10^{-2}	1.8	-1.66 to -1.80
Malonic[b]	1.49×10^{-3}	2-13	-1.69 to -1.74
Tartaric[b]	1.04×10^{-3}	1-8	-1.64 to -1.77
Citric[b]	8.40×10^{-4}	1-6	-1.64 to -1.77

[a] In either 0.1N LiCl, 0.1M Li_2SO_4 or 0.05N tetramethyl ammonium iodide (TMAI).

[b] Only one wave observed in neutral supporting electrolytes.

Polarography of benzoic acid shows reductions similar to those of the aliphatic acids in 0.05N TMAI, 0.1N LiCl or 0.1N Li_2SO_4. Its dissociation constant, concentration in mmoles and $E_{1/2}$ versus the S.C.E. are 6.3×10^{-5}, 0.9 - 8, and -1.56 to -1.72V respectively.

Formic Acid. In acid solution formaldehyde is oxidized to formic acid via the reaction

$$H_2CO + H_2O \rightleftarrows HCOOH + 2H^+ + 2e^- \quad (16)$$

Formic acid is also formed in basic solution via oxidation of acetaldehyde via the reaction

$$CH_3CHO + 4OH^- \rightleftarrows 2HCOOH + CH_3OH + 4e^- \quad (17)$$

At a platinum anode formate is oxidized according to the reaction

$$HCOO^- + 3OH^- \rightleftarrows CO_3^{2-} + H_2O + 2e^- \quad (18)$$

Detailed experimental investigations of the mechanism of formic acid and formate oxidation at smooth platinum have been conducted.[22,23] A 0.04M formic acid solution in 1.0M H_2SO_4 is oxidized beginning at a potential of 0 volts versus the S.C.E. Another specie is oxidized shortly before oxygen evolution at +1.2 volts. In acid solution three anodic oxidation reactions usually occur. The acidic H^+ atom is first split off and oxidized, chemisorption of O_2 and other intermediates on the surface of the electrode occurs and is then followed by oxidation of formic acid.[24] As the pH is increased the potential for the onset of oxidation shifts to -0.2V at pH 2.12, and to -0.6V at pH 10.0.

Oxalic Acid. Oxalic acid in 1M H_2SO_4 is oxidizable at the Pt anode via the overall reaction

$$HOOC{=}COOH \rightleftarrows 2CO_2 + 2H^+ + 2e^- \ . \qquad (19)$$

The corresponding dibasic anion hydrolyzes in neutral solution and undergoes oxidation according to the reaction

$$^-OOC{=}COO^- \rightleftarrows {}^\cdot OOC{=}COO^\cdot + 2e^- \ . \qquad (20)$$

The diradical subsequently decomposes into CO_2. The oxidation is inhibited if the Pt electrode is preoxidized by being briefly brought to a potential of +1.5 volts vs. S.C.E. in 1F H_2SO_4 and then used immediately.[25] The presence of cations forming oxalate complexes also inhibits the oxidation of the anions as well as increasing the pH above 6.

ELECTROLYTIC CELLS

Design Considerations

A review of the development of various cells for mercury cathode electrolysis up to 1950 has been reported previously by Maxwell and Graham.[2] Further developments and modifications during the next decade were reported in 1962.[3] Most of the cells described in these reports were designed primarily for electrochemical separations or electrogravimetric determinations. Those capable of being modified for general use in purification of large volumes ($\geq$1L) of solution are described in this section. Commercially available cells are also described.

Conceptually there are no limits to the size of the electrolysis cell. However optimization of the electrolysis time and efficiency does impose some practical limitations, since the mercury pool and solution must be agitated adequately, the solution continuously purged, cell resistance minimized to reduce heating, and appropriate solution-to-mercury volume ratios maintained. Essential features for electrolytic cells include large cathode surface areas, provisions for easy removal of spent mercury and purified solutions, nitrogen purging, and stirring by means of mechanical, magnetic, or gaseous agitation of the solution. When large current densities are used a provision for water-jacket cooling is desirable for controlling the temperature during electrolysis.

The cell first designed by Melaven possessed the necessary features for use as a purification apparatus.[26] This apparatus shown in Fig. 2, is a modified separatory funnel with a conical

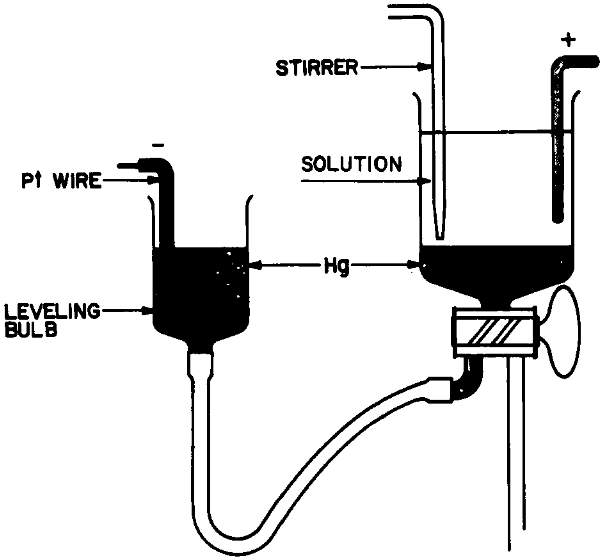

Fig. 2 The Melaven cell

base and a two-way stopcock. The mercury level in the cell is controlled via a leveling bulb through the stopcock. At the end of an electrolysis the spent mercury is easily separated by lowering the bulb and draining out the mercury. The schematic diagram of a 4000 mL cell shown in Fig. 3 was used previously by Steinmetz for analytical purposes.[27] With appropriate modifications it can be easily adopted for purifications as well. Rabbits devised an even larger volume Melaven-type cell which used 4 Kg of mercury.[28] Lingane further improved the Melaven-type cell by adding the S.C.E. reference electrode, the silver-wire anode, and a propeller shaft to keep the mercury-solution interface in rapid motion.[29] Either of these cells can be upgraded for use as a purification apparatus.

Cells optimized for treatment of several liters of reagent solutions are now available commercially. The ESA Model 2014P Reagent Cleaning System introduced by Environmental Sciences Associates is diagrammed schematically in Fig. 4. The apparatus consists of a 4L reagent flask which is usually a borosilicate glass vessel, a separate electronic console used to set the poten-

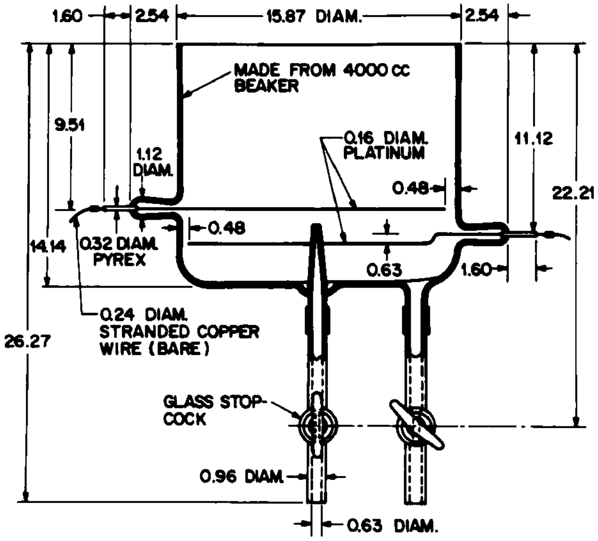

Fig. 3 Schematic diagram of a large volume cell

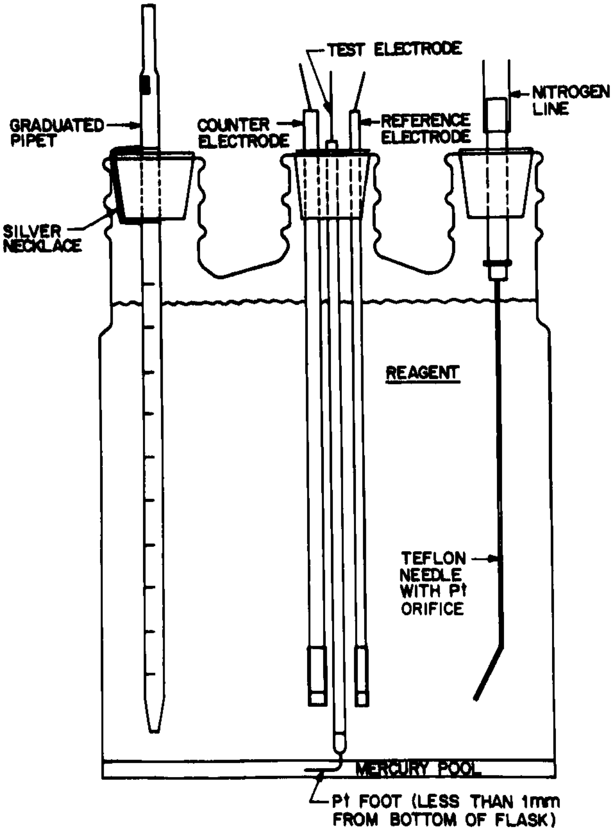

Fig. 4 Model 2014P reagent cleaning system

tial to values down to -1.5 V versus the Ag/AgCl electrode, a reference electrode, and a counter electrode. The nitrogen inlet supplies a constant flow of gas bubbling through the solution to displace oxygen and to serve as a high purity mixing vehicle.

An improved apparatus shown in Fig. 5 is provided by Princeton Applied Research, Princeton, New Jersey. This apparatus has the added conveniences of a leveling bulb for adjustment of the mercury volume, and stopcocks for removal of either mercury or pure reagent without opening the apparatus to the atmosphere or shutting-off the

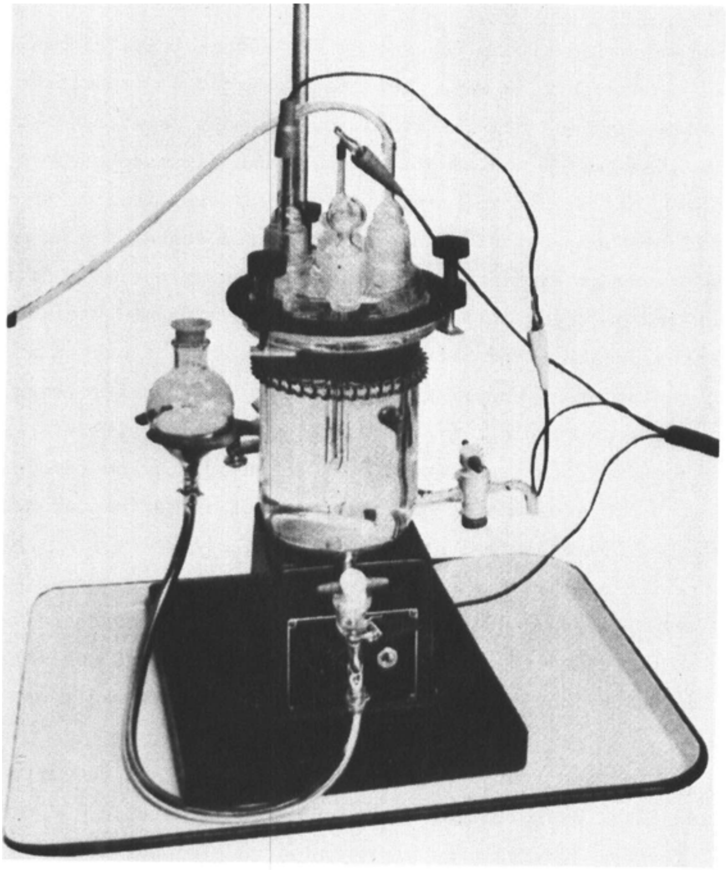

Fig. 5 Model 9500 electrolyte purification apparatus

applied potential. When the desired degree of purification has been obtained, the leveling bulb can be lowered so that no mercury exists in the side arm of the solution drain. The solution can then be dispensed through the drain tube with the potentiostat still on and the electrolysis maintained. In this way amalgamated impurities are prevented from being spontaneously released from the mercury pool to recontaminate the solution.

Sources of Contamination

Contamination of the reagent during electrolysis can be introduced through many ways, but these sources of impurities can be minimized and essentially eliminated in most cases. Contamination from the vessel container, which is usually made of borosilicate glass, has been found minimal. However substitution of a Vitreosil or vapor deposited synthetic quartz vessel can be made to obtain even greater protection against contamination. Stirring via bubbling nitrogen through Teflon needle valves is a contamination-free approach. The nitrogen should be free of oxygen and prefiltered prior to entering the apparatus. High efficiency, micron sized, particulate free, Teflon or cellulose filters in plastic housings are recommended. Nitrogen purging to remove oxygen also provides mixing but this mode of agitation may need to be augmented by mechanical stirring where large volumes of solutions (>1.9L) are being electrolyzed. Magnetic bars encased in quartz have been used successfully, but smooth Teflon coated magnetic stirrers are more abrasion resistant and are the mechanical stirring devices of choice. A Teflon blade and shaft may also be used.

Contamination from the electrodes and electrode compartment is minimized first by selecting quartz and Teflon materials and porous Vycor frits for construction of the electrode compartment. Appropriate preliminary leaching of these materials must be executed prior to use. A preliminary operation of the entire electrolytic cell can of course serve as a prepurification of the apparatus and components. Replenishing the electrolyte solution in the reference electrode compartment can be a limiting factor to purification due to the presence of metallic impurities in the saturated electrolyte. This source of contamination is minimized by pre-electrolyzing a solution of the electrolyte to be used in the reference-bridge tube or compartment. Alternatively, after adjusting the initial potential to sufficiently negative values the electrode compartment can be replenished with the solution undergoing purification. This approach has the disadvantage that the cathode potential can no longer be accurately determined during the electrolysis.

Contamination from the reference electrode material is insignificant in comparison to that potentially introduced by dissolution of the anode. Anode dissolution is usually retarded by using a material such as high purity platinum and maintaining conditions during the electrolysis so that a harmless anode reaction occurs in solution more readily than the oxidation of the anode material. Platinum contamination of halide solutions or other complexing media can be expected since dissolution has been documented experimentally.[30]

Electrodes

Mercury is the cathode material of choice for electrochemical purification by reduction of cationic impurities. This general use results from the high negative reduction potential for hydrogen due to a larger overvoltage on mercury as compared to other metals. The order of increasing hydrogen overvoltage for the most common cathode metals is Pt $\underline{\sim}$ Pd, Ir, Au, Ag, Pb, Zn, and Hg. A table of hydrogen overvoltages on various cathodes has been reported by Lingane.[31]

The relative ease of purification and large surface area of a fluid electrode are additional advantages offered by mercury. Limitations to its use can be imposed by limits of solubility of metallic impurities and by the solubility or complexation of the reagent solution. Solubilities of some metals in mercury are reported in Table VI. Fortunately, even when the solubility of certain elements in mercury is low, considerable quantities may deposit within the electrode as a separate phase without interfering with the function of the electrode.[32] Metals with potentials too high to be deposited from aqueous solutions, alkali and alkaline earths for example, can often be removed by amalgamation with mercury.

Anode materials for electrolytic purification have essentially been restricted to the use of either platinum, 10% Ir-Pt, and

TABLE VI. SOLUBILITIES OF METALS IN MERCURY AT 18°C, Wt%

Co	$< 1\times10^{-6}$	Pb	1.30	Na	0.68	Ca	0.30
Fe	1.5×10^{-6}	Sn	0.62	Li	0.09	Ba	0.33
Ni	$< 2\times10^{-6}$	Zn	2.15	K	0.80		
Cr	$< 4\times10^{-7}$	Cd	4.92	Sn	1.00		
Cu	2×10^{-3}	Tl	42.8				
Mn	1.7×10^{-3}	Bi	1.4				

graphite. Sometimes silver, lead and gold, in rare cases, have also been used. Comparison of the oxygen overvoltage on smooth platinum, gold, and graphite show similar values at current densities below 0.05 A/cm^2. Significant differences are observed above 0.1 A/cm^2 as shown in Table VII. When halide-containing solutions are to be electrolyzed graphite would seem to be the anode material of choice over platinum since its overvoltage for halides is a factor of 3 to 4 greater than platinum. Graphite anodes however show extensive evolution of bubbles during electrolysis which is often accompanied by disintegration or erosion of the graphite electrode with the production of carbon particulates in the anode compartment.

Purification of Mercury

The mercury used as the cathode pool must be of reasonably high purity with respect to trace elements and should not become saturated with any amalgamated impurity during the electrolysis. Several methods have been used for purification of mercury. A classic manuscript on the purification of mercury has previously described the state of the art prior to 1955.[33]

Badly contaminated mercury should first be filtered, degreased by washing with acetone and then with distilled water. Several

TABLE VII. OXYGEN OVERVOLTAGE AT VARIOUS ANODES

Current Density A/cm^2	Smooth Platinum	Gold	Graphite
0.001	0.72	0.67	0.53
0.01	0.85	0.96	0.90
0.05	1.16	1.06	--
0.1	1.28	1.24	1.09
0.5	1.43	1.53	1.19
1.0	1.49	1.63	1.24
1.5	1.38	1.68	1.28

additional purification steps can then be made. Concentrated mercury amalgams (few % of impurities) can be prepurified simply by rapid air oxidation of the impurity metal. Air rapidly drawn through the mercury amalgam for several hours converts the impurity into an easily removed oxide scum.[34] Oxidation of amalgamated impurities by leaching with nitric acid has been found effective for removing Cd, Cu, Pb, Tl, Zn, and Ga.[35] Many heavy metals, Co and Ni for example, are particularly resistant to acid leaching alone. Vigorous shaking with cold saturated $KMnO_4$ solutions followed by washing with dilute HNO_3 and water has been recommended.[36] Na, K, Ca, Al, Pb, and Sb were removed at pH 7, and Ba, Mn, Zn, Fe, Cd, Co, Ni, Sn, Bi, Cu, and Ag were removed under basic conditions. Microgram/mL amounts of Cu, Tl and Zn in mercury have been redissolved easily by shaking with 1N H_2SO_4, but under the same conditions Fe, Ni and Co could not be removed without oxidation of the mercury.[37] A simple method for agitating mercury in contact with acid in a suction flask is shown in Fig. 6. This apparatus recommended by Gordon and Wichers[33] is simply two 4-liter heavy

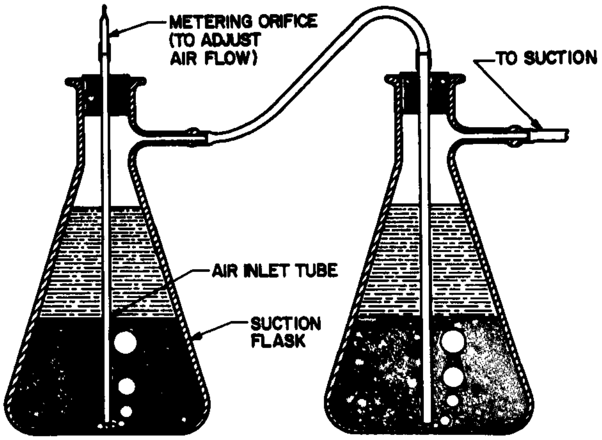

Fig. 6 Apparatus for washing mercury with air agitation

walled suction flasks connected in series to a water aspirator or other vacuum source. Attachment of a suitable filter to the air inlet is essential. After a twelve to sixteen hr acid wash with 1:9 concentrated HNO_3-H_2O, the acid layer is drawn-off and the operation is repeated with fresh acid. Following the acid leach the mercury is rinsed several times in the same manner with distilled water.

Several procedures and apparatus have been suggested for atomization or dispersion of mercury into fine droplets prior to chemical leaching. A reaction of Hg spray with HCl solutions to dissolve impurities has been reported.[38] Atomization of Hg with compressed air before falling into the acid wash solution has been accomplished commercially in an apparatus with a yield of up to 130 kg/hr.[39] Counter current extraction techniques have provided extremely efficient leaching of impurities by $2\underline{M}$ HNO_3 - $0.1\underline{M}$ $HgNO_3$.[40]

Electrolytic oxidation of impurities to remove them from a mercury pool anode can be an effective method for purification of contaminated mercury. A product comparable in purity with triply distilled mercury has been prepared by electrolysis for 90 min. at

50-60 A/cm^2 in the presence of a slightly acidic $HgNO_3$ solution.[41] Electrolysis at 0.25 - 0.50 A/sq cm using Pt electrodes, has been performed in the presence of 2$\underline{N}$ H_2SO_4.[42] The anode potential can be determined by measuring the difference between the Hg anode and an auxiliary Hg sulfate half cell and controlled below the voltage required for Hg oxidation. Alternatively, the completion of the oxidation of impurities can be visually determined by the appearance of a cloudy solution which signals the beginning of the anodic oxidation of Hg. Impurities with amalgam-metal ion potentials above the positive value of the $Hg\text{-}Hg^+$ system can not be removed from the mercury. For example, many of the transition metals, Co, Fe and Ni are not removed without oxidation of Hg. Nitric acid-hydrogen peroxide electrolyte shows high efficiency for removal of Cu, Mn and Ni during anodic stripping. Generally where only a single or several impurities are to be removed electrolytic oxidation is practical. However in most cases this approach has limited utility where a broad range of impurities are to be removed simultaneously.

Following acid leaching, chemical or electrolytic oxidation, mercury is usually dried and distilled. The best drying method appears to be heating via an infrared lamp or on a hot plate in a fused quartz tray. An evacuated glove box with an efficient cold trap is a proper closed system for drying the sample. The apparatus described by Carlson and Borchardt[43] can still be used conveniently to produce 454 g/hr of leached, dried and distilled Hg. Several conveniently designed laboratory stills for mercury distillation have been reported.[33] Where possible distillation with air agitation should be used due to greater efficiency than corresponding vacuum distillations. Reference (33) can be consulted for design details. Although distillations of Hg provide a better method than leaching for removing a broader range of impurities, both methods are complementary and should be used in tandum.

The order of preferential removal of various impurities from mercury by different chemical purification methods according to

Gordon and Wichers[33] is related to the oxidation-reduction potentials of the impurity. Their table of impurities in descending order of ease of removal is included below (Table VIII).

Interferences

The reduction of oxygen at the Hg cathode via the reactions

$$O_2 + 2H^+ + 2e^- \rightleftarrows H_2O_2 \text{(acid medium)} \qquad (21)$$

$$O_2 + 2H_2O + 2e^- \rightleftarrows H_2O_2 + 2OH^- \text{(neutral or } OH^-\text{)} \qquad (22)$$

$$H_2O_2 + 2H^+ + 2e^- \rightleftarrows 2H_2O \qquad (23)$$

$$H_2O_2 + 2e^- \rightleftarrows 2OH^- \text{(alkaline)} \qquad (24)$$

proceeds at low negative potentials and thus would prevent the reduction of cationic impurities with more negative reduction potentials. The first oxygen wave [reactions (21) and (22)] is essentially independent of pH in the range 1 to 10 and commences at -0.05 V versus the S.C.E. The second wave [reactions (23) or (24)] is very broad and occurs between -0.5 and -1.3 V versus the S.C.E. As is well known this interference is easily eliminated by nitrogen purging of the solutions prior to and during electrolysis.

The anodic dissolution of mercury via the reaction

$$Hg^o \rightleftarrows Hg^{2+} + 2e^- , \qquad (25)$$

into a solution with anions showing no appreciable complexation of the mercurous ion starts at a potential of 0.4 to 0.45 versus the S.C.E. In the presence of complexing anions capable of forming soluble complexes at appropriate concentrations, thiosulfate, sulfite, hydroxide, thiocyanate, cyanide, chloride, bromide, iodide, and sulfide, the anodic wave occurs at more negative potentials than for reaction (25).

TABLE VIII. REMOVAL OF METALS FROM MERCURY BY DIFFERENT METHODS

Order of Absorption of Oxygen by Amalgams (a)	Metals Removed by KOH (b)	Order of Removal by HNO_3 (b)	Order in Vacuum Distillation (b)	Order in 1N H_2SO_4 (c)	Order in Acid $KMnO_4$ (d)	Order in Potential Series (e)
Na	Sn	Mg	Au	Zn	Zn	Na
Mg	Zn	Al	Pt	Cd	Cd	Mg
Zn	Pb	Cr	Ag	Tl	Mn	Al
Cd		Mn	Cu	Cu	Tl	Mn
Pb		Cd	Sn	Fe	Sn	Zn
Sn		Ni	Pb	Co	Pb	Cr
Tl		Sn	Zn	Ni	Bi	Fe
		Pb	Cd		Cu	Cd
		Cu			Cr	Tl
					Fe	Co
					Mo	Ni
					Co	Sn
					Hg	Pb
					Ni	H
					W	Cu
						Hg
						Ag
						Pt
						Au

Reactions of mercury with some interfering anions (0.001m) and the corresponding $E_{1/2}$ values versus the normal calomel electrode have been reported by Conway and are provided below.[6]

$$2Hg + 2Cl^- \rightleftarrows Hg_2Cl_2 + 2e^- \quad , +0.17\ V \qquad (26)$$

$$Hg + CNS^- \rightleftarrows HgCNS + e^- \quad , +0.10 \qquad (27)$$

$$2Hg + 2Br^- \rightleftarrows Hg_2Br_2 + 2e^- \quad , +0.04 \qquad (28)$$

$$Hg + 2OH^- \rightleftarrows HgO + H_2O + 2e^-, +0.00 \qquad (29)$$

$$2Hg + 2I^- \rightleftarrows Hg_2I_2 + 2e^- \quad , -0.42 \qquad (30)$$

$$Hg + 2CN^- \rightleftarrows Hg(CN)_2 + 2e^- \quad , -0.42 \qquad (31)$$

$$Hg + S^{2-} \rightleftarrows HgS + 2e^- \quad , -0.70 \qquad (32)$$

Obviously solutions containing these anions are not candidates for purification by the mercury cathode process.

The oxidation of water at the Pt anode via the reaction

$$H_2O \rightleftarrows 1/2O_2 + 2H^+ + 2e^- , \qquad (33)$$

constitutes an interference only if it is extensive enough to generate considerable amounts of H^+ and O_2. The influence of the latter is reduced by nitrogen purging during electrolysis. The corresponding cathode reaction,

$$2H_2O + 2e^- \rightleftarrows H_2 + 2OH^- , \qquad (34)$$

also occurs at the mercury pool. Often the Hg cathode electrolysis is conducted under conditions of simultaneous evolution of hydrogen. The potential of the cathode is thus regulated by hydrogen evolution making it possible to reduce those elements whose reduction potentials are less negative than that required for the hydrogen ion.

Oxidation of the platinum anode via the reaction

$$Pt^{o} \rightleftarrows Pt^{2+} + 2e^{-} \quad (35)$$

or the graphite anode according to a possible series of reactions

$$C + H_2O \rightleftarrows CO + 2H^{+} + 2e^{-} \quad (36)$$

$$C + 2H_2O \rightleftarrows CO_3^{2-} + 6H^{+} + 4e^{-} \quad (37)$$

$$C + 3H_2O \rightleftarrows HCO_3^{-} + 5H^{+} + 4e^{-} \quad (38)$$

$$C + 3H_2O \rightleftarrows H_2CO_3 + 4H^{+} + 4e^{-} \quad (39)$$

produces the obvious interferences previously described under Sources of Contamination. The reduction potentials at which these reactions become significant are 1.188 for Pt in a noncomplexing medium and for carbon between 0.2 to 0.5 vs. the hydrogen electrode.

Efficiency of Electrochemical Purifications

Current-Time Monitoring. The monitoring of the mercury cathode electrolysis to determine the efficiency of the removal of impurities can be done most conveniently by measuring the current flow. The current reading versus time has been reported to be a reliable criterion of the progress of the deposition of impurities into the mercury pool.[1] The initial current usually is at the 100 to 500 milliampere level depending on the total initial concentration of impurities present in the solution. Upon completion of the electrolysis the current decreases to 10 milliamperes or less. A typical current-time curve is shown in Fig. 7. This curve, obtained by Lingane[1] during the separation of Cu from Bi, Pb and Cd via mercury cathode electrolysis at a potential maintained between -0.13 and -0.16 volt, is a typical representation of those obtained

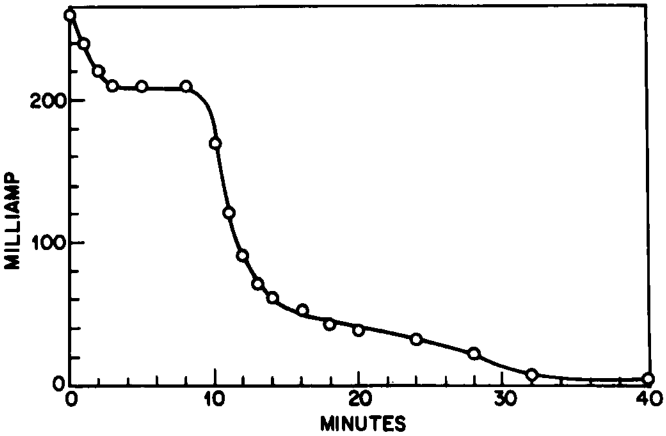

Fig. 7 Typical electrolysis current-time curve. Obtained during electrolysis of an acidic tartrate solution pH 4.5 containing 20 millimolar copper, 0.50 millimolar bismuth, 0.40 millimolar lead, and 0.465 millimolar cadmium. Potential of mercury cathode between -0.13 and -0.16 volts versus S.C.E.

in cases where the potential is sufficiently negative to cause depletion of most electroreducible cations from the solution being purified.

Polarography and Stripping Voltammetry. Traditionally D.C. polarography has been the method of choice for analyzing reagents purified by mercury cathode electrolysis. In fact it was the quest for pure electroanalytical reagents for polarography that provided the impetus for the perfection of the mercury cathode purification technique. Since the full utilization of the sensitivity of polarography had been precluded by the limits of purity of electrolytes and other concentrated analytical reagents, methods for producing extremely pure reagents were paramountly important. For example during the development of a polarographic method for the determination of zinc in lead and its compounds, the zinc wave in the blank resulting from sodium hydroxide reagent was approximately equal in height to the wave which would have been obtained from the sample.[44] This would have seriously affected the accuracy and precision of the determination of zinc in the sample. A comparison of the polarograms of the 2M sodium hydroxide reagent and of a portion of this solution purified for 30 min. by mercury cathode electrolysis at -1.8 volts versus S.C.E. is made in Fig. 8. Curve (a) was recorded at 1/10 the maximum sensitivity of the polarograph while (b) was obtained using the maximum sensitivity. It was estimated from the diffusion currents of known amounts of zinc in 2MNaOH that the purified solution was less than 0.0002 millimolar in zinc.

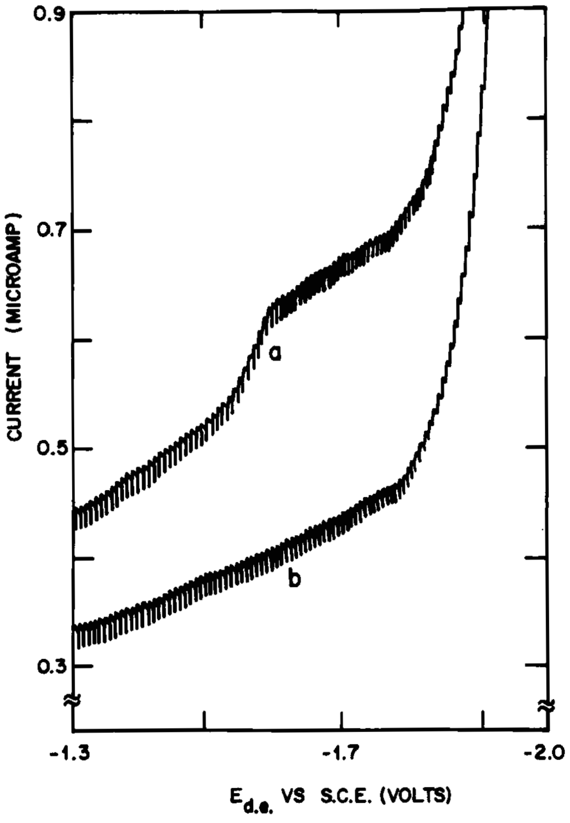

Fig. 8 Polarograms of 2M sodium hydroxide. (a) Before and (b) after controlled potential electrolysis at -1.80 volts versus S.C.E.

Differential pulsed anodic stripping voltammetry (DPASV) has been applied for determining the degree of purification of sodium acetate with respect to Cd and Pb during a 110 hour deposition at the mercury cathode.[44] The voltammograms in Fig. 9 show the concentration in the purified samples to be of the order of 0.2 ppb or less. DPASV is a more sensitive and reliable technique than dc polarography for assessing the efficiency of the Hg cathode purification.

Radioisotopes and Gamma-Ray Spectroscopy. Radioisotopes can be used to conveniently establish the conditions for optimum mercury cathode purification of a given reagent with respect to trace impurities having a suitable radioactive isotope. Elements with gamma ray emitting isotopes of sufficiently long half lines to be useful for monitoring the deposition of impurities are given in Fig. 10. Gamma ray spectroscopy has been used at this laboratory to simultaneously monitor the removal of five impurities, reduced over a broad potential range, from various buffer reagents. The The small cell shown in Fig. 1 was used to experimentally examine

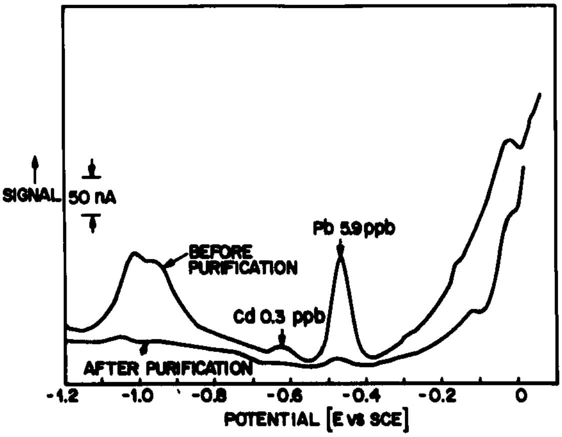

Fig. 9 Differential pulse anodic stripping analysis of 2M sodium acetate. Before and after 110 hrs electrolysis at -1.8 V versus S.C.E.

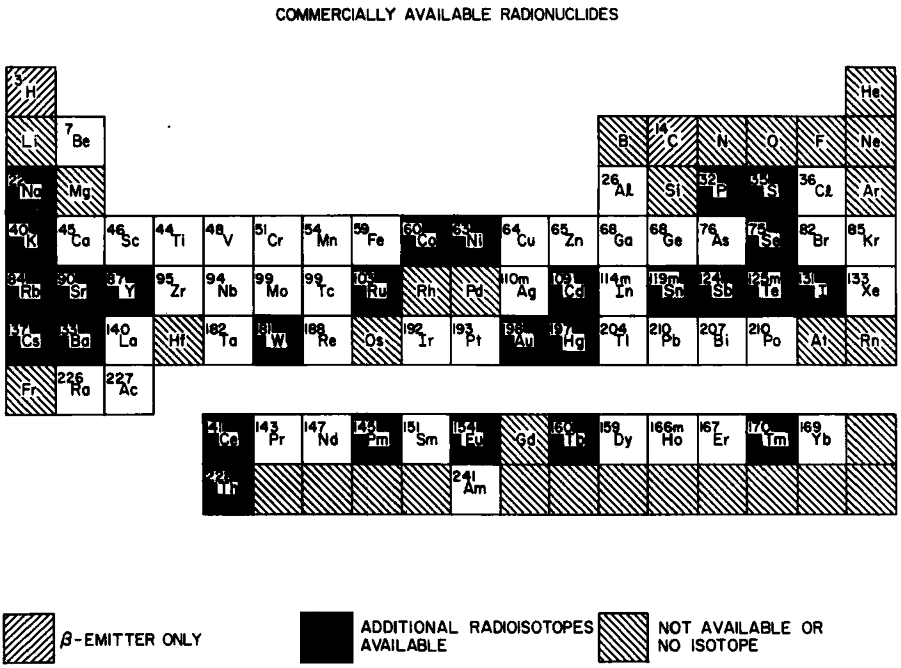

Fig. 10 Available isotopes of the elements

the depletion of Zn, Cr, Co, Mn, and Fe. A fifty mL solution of the reagent being examined was doped at the 100 ng/mL level with the above carrier elements which have $E_{1/2}$ values covering the range +0.52 to −1.05 V, a region in which the most common electroreducible transition elements are deposited at the mercury cathode. The percentage electrolysis curves for impurities in sodium acetate (Fig. 11) show rapid removal of Co and Zn, sluggish, but essentially complete removal of Fe and Mn, and incomplete removal of Cr after 46 hours. All of the impurities monitored were removed effectively from a 1.0M sodium carbonate solution during a 40 hr. electrolysis (Fig. 12).

Phosphate buffered reagents are widely used and in many biochemical experiments buffers of high purity are required. Examina-

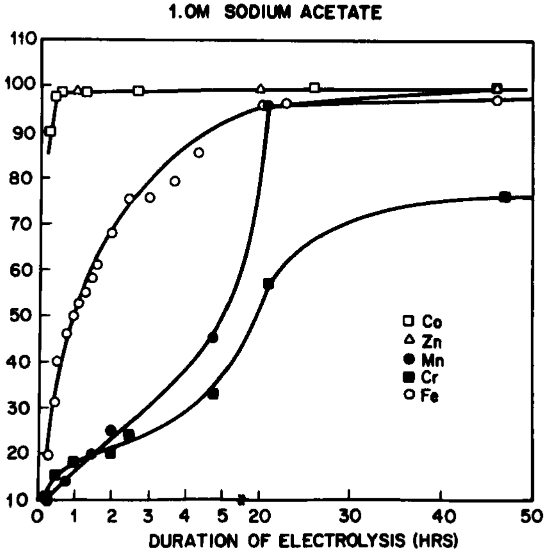

Fig. 11 Electrolysis of 1.0$\underline{M}$ sodium acetate monitored by gamma ray spectroscopy

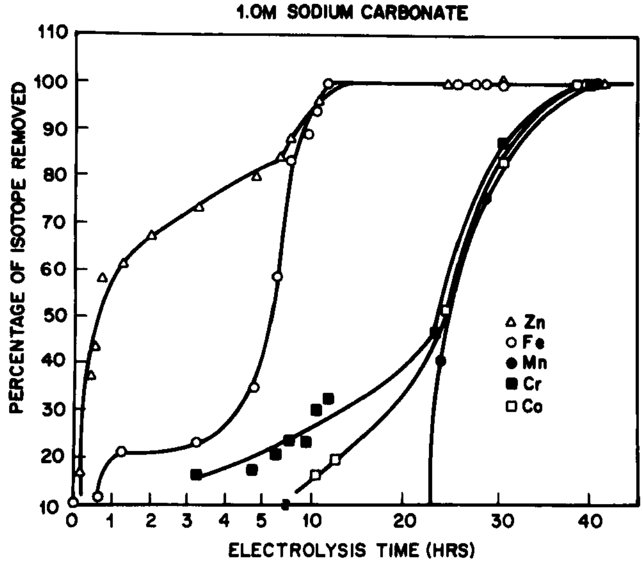

Fig. 12 Electrolysis of 1.0$\underline{M}$ sodium carbonate monitored by gamma ray spectroscopy

tions of the electrolysis of 0.1M KH_2PO_4 (Fig. 13), one of the components used to prepare phosphate buffers, indicated the reduction of Zn, but nonremoval of the other impurities during a relatively short electrolysis conducted over a 13 hr period. Phosphate complexation and the relatively low pH of the solution, are causative factors for the observed behavior. A high purity phosphate medium can be obtained as shown by the electrolysis curves in Fig. 14. Mn, Zn and Co are reduced well during the first 4 hours of electrolysis. Cr and Fe, metals capable of forming phosphate complexes, are not reduced fully during a short electrolysis of <10 hrs but would be further depleted during prolonged electrolysis periods.

The pH representative of solutions throughout the electrolysis and the final concentration of impurities in the solution are

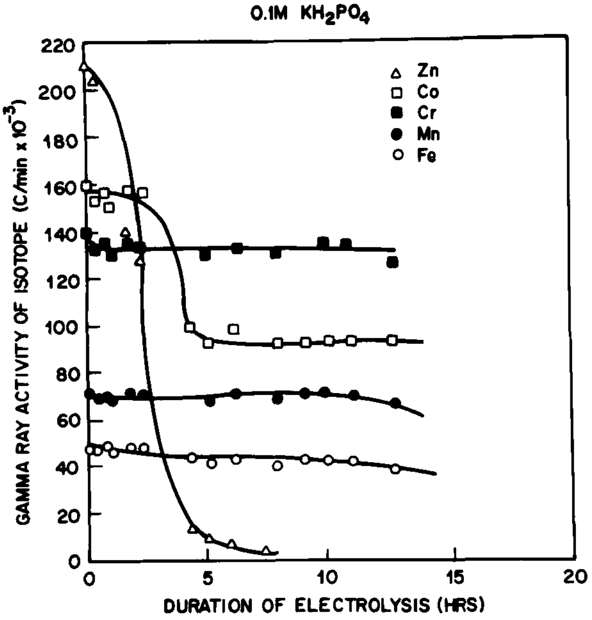

Fig. 13 Electrolysis of 0.1M KH_2PO_4 monitored by gamma ray spectroscopy

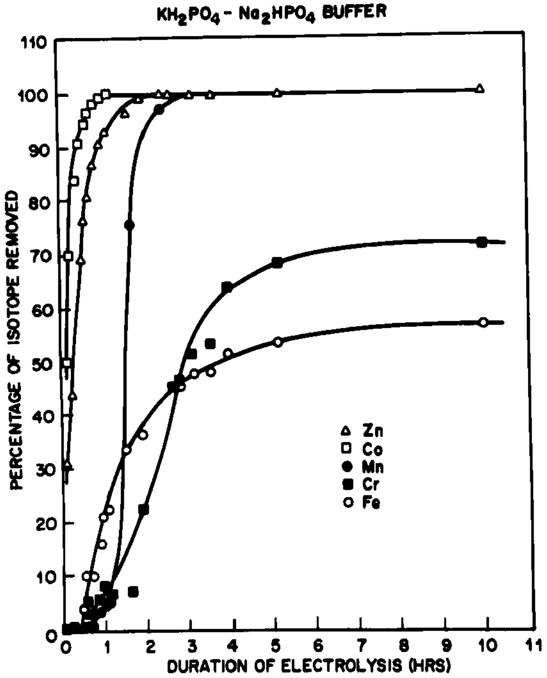

Fig. 14 Electrolysis of phosphate buffer monitored by gamma ray spectroscopy

reported in Table IX. As indicated by these data extremely pure carbonate solutions can be prepared by electrolysis.

Conditions shown to be effective for impurity removal during small scale radiotracer studies have been duplicated on a larger scale to effect purifications. Three liters of 1.0M sodium acetate solution were purified using the apparatus shown previously in Fig. 5. The results reported in Table IX demonstrate that the already high purity reagent was further purified during a reasonably short electrolysis period of 40 hrs. It has also been possible to prepare Kg quantities of ultrapure sodium and calcium carbonate by mercury cathode electrolysis of solutions from which respective carbonates were precipitated by high purity ammonium carbonate.

TABLE IX. PURIFICATION EFFICIENCY OF Hg CATHODE ELECTROLYSIS

			Final Concn. of Cation in Solution, ng/mL				
Reagent	pH	Electrolysis Period, hrs.	Cr	Mn	Fe	Zn	Co
1.0M NaAc	6.9	47	20	0.8	3.0	0.2	7×10^{-2}
1.0M NaAc[a]		40	(7,<2)	(1,1)	(30,<2)	(11,4)	(<2,<2)
1.0M KH_2PO_4[b]	3.3	15	940	1000	817	58	591
$\left\{\begin{array}{l}0.025M\ KH_2PO_4^-\\0.025M\ Na_2HPO_4\end{array}\right\}$[b]	6.3	10	284	6	434	1	0.7
1.0M Sodium Carbonate	11.1	40	8	(7,<2)	(1,1)	(30,<2)	(<2,<2)

[a] Solution analyzed by flameless AA before and after 40 hr electrolysis at -1.7 V (before,after)

[b] Initial $[M^{n+}]$ = 1000 ng/mL, for others 100 ng/mL

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