Spectrophotometric Determination of Copper and Iron Subsequent to the Simultaneous Extraction of Bis(2,9-dimethyl-1,10-phenanthroline)copper(I) and Bis[2,4,6-tri(2-pyridyl)-1,3,5-triazine]iron(II) into Propylene Carbonate

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Propylene carbonate (4-methyl-1,3-dioxolane-2-one) simultaneously extracts the 2,9-dimethyl-1,10-phenanthroline (neocuproine; NC) chelate of copper(I) and the tri(2-pyridyl)-1,3,5-triazine (TPTZ) chelate of iron(II) from acetate-buffered aqueous solutions. Molecular absorption spectrophotometric quantification is accomplished by measuring the absorbance of the iron(II)–TPTZ chelate at 596 nm and that of the copper(I)–NC chelate at 458 nm. The copper(I)–NC chelate does not absorb at 596 nm and consequently copper does not interfere with the determination of iron. The iron(II)–TPTZ chelate exhibits an absorbance at 458 nm that is 0.123 times its absorbance at 596 nm; therefore, correction for the effect of iron on the determination of copper is straightforward. The development of the method and the results of analyses of sea water, tap water, and aluminum alloy are reported.

It is widely accepted that the presence of copper and iron, alone or in combination, has beneficial or deleterious effects on the properties of many substances and the nature of various biological systems; consequently, the determination of the two metals is a matter of considerable interest. Several authors have pointed out the need for simple and reliable analytical methods for the determination of copper and iron (*1–3*).

Various ferroin-type chelating agents have been proposed for use in the simultaneous and/or stepwise spectrophotometric determination of copper and iron. Wilkins and Smith (*1*) chelated both metals with 1,10-phenanthroline and extracted the copper(I) chelate into *n*-octonal. Zak and Ressler (*2*) investigated three techniques: the determination of bis(2,9-dimethyl-1,10-phenanthroline)copper(I) and tris(1,10-phenanthroline)iron(II) in aqueous solutions by making use of simultaneous equations; a similar technique applied subsequent to the extraction of tris(4,7-diphenyl-1,10-phenanthroline)iron(II) and bis(2,9-dimethyl-1,10-phenanthroline)copper(II) into isopentyl alcohol; and the measurement of tris(1,10-phenanthroline)iron(II) in the aqueous phase and bis(2,9-dimethyl-1,10-phenahthroline)copper(I) in isopentyl alcohol. Fair accuracy was reported for the single-phase techniques and good accuracy for the two-phase system. Neither interference studies nor actual analyses were reported. Three-to-five-minute shaking times were required for the extractions, and centrifugation at 3500 rpm for 10 min was necessary for good phase separations. Even when equal masses of copper and iron were present, both tris(1,10-phenanthroline)iron(II) and tris(4,7-diphenyl-1,10-phenanthroline)iron(II) absorbed more at the wavelength of maximum absorbance of bis(2,9-dimethyl-1,10-phenanthroline)copper(I) than did the copper chelate itself. Banerjea and Tripathi (*4*) investigated the use of methyl-2-pyridyl ketoxime as a reagent for the simultaneous determination of copper and iron in alkaline aqueous solution. Each chelate absorbed at the wavelength of maximum absorbance of the other chelate; thus the solution of two equations simultaneously was required for application of the method. Nickel, cobalt, and manganese interfered seriously in the determination of both copper and iron. The method was studied very thoroughly; however, no actual analyses were reported. Zak *et al.* (*5*) used disodium 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonate and TPTZ for the determination of copper and iron, respectively, in aqueous solutions. Actually, the method developed was a stepwise rather than a simultaneous method since the absorbance of the analytical solution was measured after the addition of each chromogen. Neither interference studies nor actual analyses were reported. Schilt and Taylor (*3*) reported the use of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine as a chromogen for both copper and iron. Essentially the method involved complexing the metals, extracting the chelates into isoamyl alcohol, measuring the absorbance at 488 nm, adding cyanide, and finally measuring the absorbance at 488 nm and 555 nm. The final absorbance at 555 nm and the loss in absorbance at 488 nm were reported to be proportional to the iron and copper concentrations respectively.

Propylene carbonate (4-methyl-1,3-dioxolane-2-one) is gradually coming into use as an extractant in analytical chemistry. Stephens and Suddeth (*6*) originally proposed it as an extractant for the 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline, and 2,4,6-tri(2-pyridyl)1,3,5-triazine chelates of iron(II). Stephens *et al.* (*7*) used propylene carbonate to extract tris(pentan-2,4-dione)iron(III) from aqueous solutions in a method for the spectrophotometric determination of iron. Jakubiec and Boltz (*8*) examined propylene carbonate as an extractant for molybdophosphoric acid and the corresponding hereropoly blue.

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Murata and Ikeda (*9*) used the solvent to extract molybdenum(VI) from acidic solutions.

Propylene carbonate has very desirable characteristics as an extractant. It is colorless, nontoxic, practically odorless, and is not prone to form emulsions. Pertinent physical properties are: density, 1.2 g ml^{-1} at 25 °C; boiling point, 242 °C; freezing point, −49 °C; solubility in water at 25 °C, 0.25 g ml^{-1}; solubility in 2.7*M* sodium chloride at 25 °C, 0.12 g ml^{-1}. Interestingly, the solvent is not completely miscible with water at room temperature even though its dielectric constant is 69 esu at 23 °C (*10*).

This paper describes a further application of propylene carbonate to the field of analytical chemistry. The solvent extracts the TPTZ chelate of iron(II) simultaneously with the neocuproine chelate of copper(I). Collins *et al.* (*11*) reported that nitrobenzene was the only common solvent that would extract the iron(II)–TPTZ chelate from aqueous solutions; propylene carbonate therefore is unique in affording the opportunity to extract the yellow copper(I)–NC chelate and the violet iron(II)–TPTZ chelate simultaneously into an odorless, nontoxic solvent. A consequence of this particular yellow-violet color combination in the propylene carbonate extract is that spectrophotometric quantification is relatively simple since the yellow chelate does not interfere with absorption measurements of the violet chelate.

EXPERIMENTAL

Apparatus. Separatory funnels with Teflon plugs and plastic stoppers were used for the extractions. A Perkin-Elmer Model 202 recording spectrophotometer and a Corning Model 10 pH meter were the principal instruments used.

Reagents. Distilled water was passed through a monobed ion exchange column composed of Dowex 50W-X2 resin in the hydrogen form and Dowex 1-X1 resin in the hydroxide form. Propylene carbonate was vacuum distilled in all-glass apparatus. Hydroquinone was purified in the following manner: Hot water was saturated with hydroquinone; charcoal, Dowex 50W-X2 resin in the hydrogen form, and Dowex 1-X1 resin in the hydroxide form were added, and the mixture was stirred for a few minutes and filtered through Whatman No. 42 paper. The crystals from the cooled solution were filtered and sucked to near dryness with the aid of rubber sheeting placed over the filter funnel and air-dried overnight. Half-molar aqueous solutions of hydroquinone were prepared fresh daily. The pH 4.75 buffer solution was 2*M* in acetic acid and sodium acetate. It and 1*M* hydroxylammonium chloride were rendered copper- and iron-free by following the extraction technique described in the general procedure; extractions were continued until the extracts were perfectly colorless—this assured complete removal of copper, iron, and the unreacted neocuproine and TPTZ.

Stock 2.125 × $10^{-3}M$ iron solution was prepared by dissolving electrolytic iron in HCl; 5.31 × $10^{-5}M$ iron solution was prepared fresh daily from the stock solution. Stock 6.64 × $10^{-3}M$ copper solution was prepared by dissolving analyzed reagent grade copper wire in nitric acid and taking to fumes with sulfuric acid; 1.66 × $10^{-4}M$ copper solution was prepared fresh daily from the stock solution. Solutions of 0.02*M* neocuproine and 0.02*M* TPTZ were prepared in propylene carbonate.

General Procedure. Place an acid solution of the sample in an appropriate separatory funnel whose stem and stopcock bore have been rinsed with propylene carbonate. Add 5 ml of 1*M* hydroxylammonium chloride, 5 ml of 0.5*M* hydroquinone, 5 ml of pH 4.75 buffer and adjust the pH to 4.5–5.0 with sodium hydroxide solution. Add 2 ml of 0.02*M* neocuproine, 3 ml of 0.02*M* TPTZ, 1 ml of 1*M* sodium perchlorate, and 5 ml of saturated sodium chloride. Swirl the separatory funnel gently after each addition of reagent to ensure complete mixing. Add enough propylene carbonate to give about 5 ml of extractate. This can be accomplished by adding 15 ml of propylene carbonate for each 100 ml of aqueous solutions, shaking the funnel for a few seconds, adding 5-ml portions of the solvent followed by shaking until a second phase is noted, and adjusting the volume of extractate to about 5 ml. Shake the funnel vigorously for about 10 sec and allow the phases to separate while gently swirling the funnel intermittently. Drain the lower phase into a volumetric flask and rinse the stopcock bore and funnel stem with about 1 ml of propylene carbonate and rinse after each extraction. Make up to volume with propylene carbonate and measure the absorbance at 458 nm and 596 nm in 1.00-cm cells using water as reference. Subtract reagent blanks, multipy the absorbance at 596 nm by 0.123, and subtract the product from the absorbance at 458 nm; calculate the amount of copper and iron present by referring to calibration graphs or by performing appropriate calculations. A proper sample is one containing 40–200 μg of copper and 10–50 μg or iron. Larger amounts of the metals can be accommodated by increasing the volume of the extracts and/or decreasing the path length of the spectrophotometric cells. In such cases the amounts of reagents added should be doubled for each additional 200 μg of copper and 50 μg of iron. Smaller amounts of the metals can be accommodated by decreasing the volume of the extract and/or increasing the path length of the cells. The general procedure is suitable for up to 100 ml of aqueous solution. For volumes between 100 and 500 ml, double the amounts of all reagents except 1*M* sodium perchlorate which should be added at the rate of 2 ml for each 100 ml of aqueous solution.

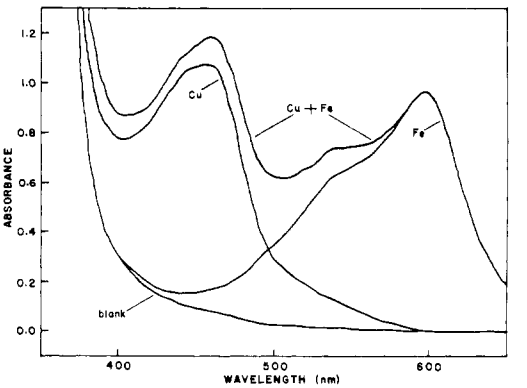

Figure 1. Molecular absorption spectra of the copper(I)–NC (2.60 × $10^{-5}M$) and iron(II)–TPTZ (8.36 × $10^{-6}M$) chelates in propylene carbonate extracts. Absorbance measured in 5.00-cm cells

RESULTS AND DISCUSSIONS

Absorption Spectra. The molecular absorption spectra of the copper(I)–NC and iron(II)–TPTZ chelates in propylene carbonate extracts are shown in Figure 1. Note that the copper(I)–NC chelate does not absorb at 596 nm, the wavelength of maximum absorbance of the iron(II)–TPTZ chelate; however the iron(II)–TPTZ chelate does absorb at 458 nm, the wavelength of maximum absorbance of the copper(I)–NC chelate. Fortunately, the absorbance due to the iron(II)–TPTZ chelate at 458 nm is always 0.123 times its absorbance at 596 nm. The effect of iron on the copper absorbance is therefore easily calculated and appropriate correction made.

Effect of Concentration. Using the general procedure (25.0-ml extracts, 1.00-cm cells), the sensitivity of the method for copper is 208 μg per absorbance unit; similarly the sensitivity of the method for ion is 60.4 μg per absorbance unit. Molar absorptivities are 7.64 × 10^3 for the copper(I)–NC chelate at 458 nm and 2.31 × 10^4 for the iron(II)–TPTZ chelate at 596 nm. Analyzing the spectrophotometric data according to the method of Ringbom (*12, 13*), the range of minimum analysis error is 40–200 μg for copper and 10–50 μg for iron.

Precision. The relative standard deviation over the range of minimum analysis error is 0.48% for copper and 0.63% for iron. The relative standard deviations over the

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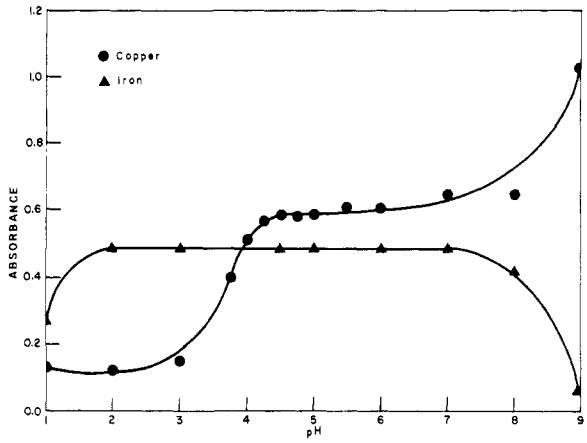

Figure 2. Effect of pH on the extraction of the perchlorate-associated copper(I)-NC ($7.85 \times 10^{-5}M$) and iron(II)-TPTZ ($2.08 \times 10^{-5}M$) chelates into propylene carbonate. Absorbance measured in 1.00-cm cells

ranges 21.1-211 μg copper and 5.93-59.3 μg iron for six determinations of each element simultaneously are 1.16% and 2.58%, respectively.

Distribution Coefficients. The distribution coefficients for the distribution of the copper(I)-NC chelate and the iron(II)-TPTZ chelate between aqueous and propylene carbonate layers were determined by using the conditions of the general procedure. In one experiment, 106 μg of copper was extracted: the separatory funnel was shaken vigorously for 1 min and allowed to stand at 23 °C until the aqueous layer was completely clear (10 min). The absorbance of the propylene carbonate layer was measured in 1.00-cm cells and that of the aqueous layer was measured in 10.00-cm cells. The distribution coefficient was ~800. In another experiment, 30 μg of iron was extracted and in another 106 μg of copper and 30 μg of iron were extracted simultaneously. The distribution coefficient for iron alone was ~230; when copper and iron were extracted together the distribution coefficients were ~240 and ~140, respectively. It is doubtful that the conditions under which these experiments were conducted presented equilibrium conditions; however, they approximated actual analysis conditions.

Effect of pH. The conditions of the general procedure were followed and the pH was varied using dilute HCl and NaOH solutions. The amounts of copper and iron used at each pH were 106 μg and 30 μg, respectively. The results depicted in Figure 2 show that the iron complex is extracted over a rather wide pH range. The copper complex is satisfactorily extracted over the pH range 4.5-8.0; however, hydroquinone begins to yield yellow extractable substances at about pH 6 and this tendency is intensified at higher pH values. When hydroxylammonium chloride alone is used as reducing agent, these colored substances are not in evidence even at pH 10. Good results are obtained for copper and iron over the pH range 4.5-6.0; the pH range recommended for routine analysis is 4.5-5.0. As it turns out, this is a convenient pH range since the pH of equimolar buffer solutions of acetic acid and sodium acetate have a pH of ~4.75. When highly acidic or basic solutions or large volumes of even moderately acidic or basic solutions are to be analyzed for copper and iron, it is convenient to add 5-10 ml of the pH 4.75 buffer and complete the adjustment of the pH to 4.5-5.0 by the dropwise addition of 6*M* sodium hydroxide or 6*M* hydrochloric acid. For example, in one analysis of 200 grams of acidified sea water to which 10 ml of the pH 4.75 buffer had been added, 50 drops of 6*M* NaOH were required to raise the pH to 4.7 and 10 more drops to raise the pH to 4.8. Therefore, in the routine analysis of the acidified sea water, 55 drops of 6*M* NaOH were added after the addition of the buffer to ensure the appropriate pH for extraction; no verification of the pH was necessary.

Table I. Effect of Diverse Species on the Method (106 μg of Copper; 30 μg of Iron)

Diverse species	μg Added	Cu, % error	Fe, % error
Aluminum(III)	13,500	−1.74	+1.39
Arsenic(III)	74,000	+2.95	+3.95
Arsenic(V)	74,000	−2.14	+0.99
Barium(II)	69,000	+1.36	+0.19
Bismuth(III)	500	−3.72	+2.01
Cadmium(II)	10,000	+2.42	0.0
Cerium(IV)	10,000	−1.36	+4.97
Cobalt(II)	29,400	+84.2	−81.2
Cobalt(II)	1,000	+59.7	+11.4
Cobalt(II)	100	+4.4	0.0
Chromium(III)	10,000	−1.64	−5.5
Gold(III)	1,600	+1.67	+0.6
Lanthanum(III)	70,000	0.0	−1.19
Lead(II)	104,000	+1.93	−1.19
Magnesium(II)	12,200	+0.19	−0.59
Manganese(II)	27,000	+5.98	+4.73
Manganese(II)	1,700	+3.20	+3.90
Mercury(II)	20,000	+1.68	+3.10
Nickel(II)	300	+5.30	+1.10
Nickel(II)	180	0.0	0.0
Strontium(II)	44,000	0.0	−1.19
Thorium(IV)	116,000	−0.19	+0.79
Tin(II)	22,500	+32.2	+13.6
Tin(II)	5,600	+6.35	−3.8
Tin(II)	2,200	−0.84	−2.8
Uranium(VI)	135,000	+0.97	0.0
Zinc(II)	6,500	−4.17	−2.15
Zinc(II)	650	+2.52	+1.19
Borate	20,300	+3.40	+1.89
Bromide	50,000	+0.34	0.0
Citrate	900,000	+6.88	−94.8
Cyanide	10,000	+5.10	−8.9
Cyanide	1,000	+1.67	0.0
Dichromate	29,000	+88.3	+79.5
Dichromate	9,000	+23.2	+13.2
EDTA	500,000	−100	−100
Fluoride	9,000	−0.98	0.0
Iodide	50,000	+3.40	+1.89
Nitrite	8,500	+82.3	+54.1
Nitrite	850	+5.14	+2.00
Phosphate	48,000	+1.75	−9.50
Phosphate	24,000	+0.38	−1.37
Tungstate	300	−1.67	−3.44
Vanadate	1,200	+3.00	0.0

Color Stability. When hydroquinone is incorporated into the method as a reducing agent, the color of the extracts remains unchanged for at least 48 hours. When hydroxylammonium chloride alone is used as reducing agent, the color due to the copper(I)-NC chelate begins to fade slowly after extraction. Apparently enough hydroquinone is extracted into the propylene carbonate layer to inhibit any reoxidation of copper(I). It would seem that hydroquinone alone would suffice as the reducing agent. However, when hydroquinone alone is used as reducing agent, the quinone produced extracts somewhat into the propylene carbonate layer and absorbs at 458 nm, causing high results for copper. The ideal reducing agent combination seems to be hydroxylammonium chloride-hydroquinone. The former reduces copper and iron to the +1 and +2 oxidation states, respectively, without producing colored products; the latter extracts into the propylene layer and prevents any reoxidation of the metal complexes. Care should therefore be taken that the hydroxylammonium chloride is always added prior to the addition of the hydroquinone.

Table II. Determination of Copper and Iron in NBS Standard Sample (85B Wrought Aluminum Alloy)

Run	% Cu	% Fe
1	4.00	0.250
2	4.02	0.244
3	4.03	0.251
4	3.99	0.248
5	3.99	0.247
6	4.02	0.244
Average	4.01	0.247
NBS reported	3.99	0.24
NBS range	3.97–4.03	0.23–0.24

Table III. Copper in Beach Water Which Contains a Relatively Large Amount of Iron (42.7 μg)[a]

μg Cu added	μg Cu found	μg Cu present
None	6.54	
None	5.58	6.47 av
None	7.28	
5.28	13.3	11.8
10.6	18.4	17.1
10.6	15.8	17.1
15.8	22.6	22.3
21.1	27.8	27.6
21.1	28.1	27.6

[a] 200 grams beach water; 25 ml of extract; 5-cm cells; iron absorbance at 596 nm: 3.53.

Reagent Concentration. The amounts of neocuproine and TPTZ were optimized by using the general procedure. Amounts of copper and iron appropriate to the use of 25.0-ml extracts and 1.00-cm cells were used. Reagent amounts used are not critical so long as the minimum amounts recommended are used. The neocuproine must be added before the TPTZ or the analytical results will be scattered.

Effect of Diverse Species. The general procedure was used incorporating 106 μg of copper and 30 μg of iron. Cations were added as solutions of their nitrate, chloride, or sulfate salts and anions as solutions of their sodium, potassium, or ammonium salts; the volume of the aqueous solutions were made to 60 ml. Gram quantities of chloride, nitrate, sulfate, ammonium, and alkali-metal ions do not interfere. The results shown in Table I are grouped as cations and anions in alphabetical order. Any error less than 3.0% can reasonably be considered to be within the precision of the method itself. Positive errors shown are in some cases undoubtedly due to the presence of copper and/or iron in the solutions of the diverse ions.

Analyses. *Aluminum Alloy.* The copper and iron in National Bureau of Standards Standard Sample 85B wrought aluminum alloy was determined. Approximate 0.2-gram portions were weighed into Erlenmeyer flasks, dissolved in 10 ml of aqua regia, taken to fumes with 5 ml of sulfuric acid, and made to a volume of 1.00 liter. Twenty-five-milliliter aliquots were transferred to separatory funnels, diluted to about 50 ml, and the copper and iron extracted according to the general procedure. Absorbances were measured in 1.00-cm cells at 458 nm and 596 nm. The amount of copper and iron was calculated using the details outlined in the general procedure. It should be noted that the alloy contained 0.61% manganese, 0.211% chromium, and 0.084% nickel. The results are shown in Table II.

Sea Water. Two samples of South Carolina beach water were analyzed for copper and iron. One sample contained a high concentration of iron (0.21 ppm) relative to the copper concentration (0.032 ppm) and was analyzed to demonstrate that even though the iron(II)–TPTZ chelate absorbs at the wavelength of maximum absorption of the copper(I)–NC chelate, judicious selection of cell-path lengths will permit the determination of copper in the presence of relatively large amounts of iron. Two-hundred-gram portions were analyzed according to the details of the general procedure. The absorbances of the 25-ml extracts were measured at 458 nm in 5.00-cm cells and at 596 nm in 1.00-cm cells. Interestingly, the iron absorbance in the 1.00-cm cells was such that its value would have been 3.53 could it have been measured in 5.00-cm cells. The correction for the iron absorbance was made by subtracting 0.123 × 3.53 from the absorbance measured at 458 nm. The results are shown in Table III. The other sample of beach water contained nominal amounts of copper and iron. One-hundred-gram portions were analyzed according to the general procedure. The absorbances of the 25-ml extracts were measured at 458 nm and 596 nm in 1.00-cm cells. The results are shown in Table IV.

Table IV. Copper and Iron in Beach Water[a]

μg Cu			μg Fe		
Added	Found	Present	Added	Found	Present
None	2.50	2.50	None	15.4	15.4
31.7	35.6	34.2	8.90	24.6	24.3
52.8	55.1	55.3	14.8	29.8	30.2
52.8	57.8	55.3	14.8	30.3	30.2
63.4	68.0	65.9	17.8	33.5	33.2
95.0	96.7	97.5	26.7	41.0	42.1

[a] 100 grams beach water; 25 ml of extract; 1-cm cells.

Table V. Copper and Iron in Tap Water[a]

μg Cu			μg Fe		
Added	Found	Present	Added	Found	Present
None	17.3	17.3	None	6.10	6.10
52.8	66.8	70.1	14.8	20.2	20.9
106	123	123	26.7	34.4	32.8
137	153	155	44.5	49.9	50.6

[a] 500 grams tap water; 25 ml of extract; 1-cm cells.

Tap Water. Five-hundred-gram portions of a sample of Spartanburg, S.C., tap water were analyzed for copper and iron according to the general procedure (25-ml extracts; 1.00-cm cells). This experiment was conducted to demonstrate the applicability of the method to the analysis of large volumes of aqueous solutions. The results are shown in Table V.

CONCLUSIONS

The proposed method is safe and pleasant to use because of the odorless and nontoxic nature of propylene carbonate. Propylene carbonate extraction of the two chelates from aqueous solutions is rapid; only a few seconds of shaking is required for effective separation. Even vigorous shaking does not result in the formation of emulsions or indistinct interfaces. Propylene carbonate extracts are typically clear and free of water droplets. One side advantage of using the solvent is that, because of the fair solubility of propylene carbonate in water, clean, water-wet separatory funnels and volumetric flasks can be rinsed free of water by small amounts of propylene carbonate, thereby removing the necessity of drying such glassware. The only disadvantage in using propylene carbonate as an

extractant is that it is somewhat soluble in water; however, aqueous solutions can be rapidly and predictably saturated with the solvent.

Solutions of all the reagents except hydroquinone are stable for at least a month; hydroquinone solutions should be prepared fresh daily. All the diverse metal ions studied except cobalt(II) can be tolerated at levels above 100 μg. Dichromate interferes and should be converted to chromium(III) prior to application of the general procedure. The effectiveness of the proposed method in extracting the two chelates from large aqueous volumes should make the method particularly useful to oceanographers and limnologists. Judicious selection of sample size, extract volume, and cell-path length provides for the analysis of substances with wide and divergent ranges of copper and iron concentrations.

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Determination of Palladium by Controlled-Potential Coulometry

New Platinum-Working-Electrode Cell for Controlled-Potential Coulometry

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Palladium can be determined by oxidizing Pd(II) to Pd(IV) at +0.85 V *vs.* SCE in a supporting electrolyte of 0.2*M* NaN_3 and 0.2*M* Na_2HPO_4 at pH 7, then reducing the Pd(IV) to Pd(II) at +0.125 V. Samples containing 1–10 mg of Pd were analyzed with an accuracy and precision of 0.1%. The electrolysis reaction of the Pd(IV)/Pd(II) couple in this medium is totally irreversible. Five mg of Pd can be determined accurately in the presence of 0.5 mg Ag, 0.1 mg Au or Os, 0.2 mg Ir, 10 mg Pt, or >10 mg Rh. Small amounts of Ru, Co, Hg, CN^-, and I^- interfere. The procedure was developed using a new platinum-working-electrode cell assembly designed for ease of and moderate cost of construction, as well as good electroanalytical characteristics.

Because of its high accuracy and precision with small quantities of sample, controlled-potential coulometry is ideally suited as an assay technique for the precious metals in alloys and electroplating solutions. Good controlled-potential coulometric assay methods are available for gold, silver, rhodium, iridium, and ruthenium (*1*); but no viable procedures have thus far been developed for palladium.

Most previous investigations of the determination of palladium by controlled-potential coulometry have been limited to reactions involving the electrodeposition of the metal. Takata and Muto (*2,3*) found that Pd(II) could be reduced with nearly 100% current efficiency using either an ammoniacal chloride supporting electrolyte and a mercury-working-electrode, or an acid phosphate electrolyte and a gold electrode. Hydrochloric acid was also tested as a supporting electrolyte; but with the acid media and a solid electrode, errors were caused by the absorption of hydrogen in the palladium deposit (*2*). Phillips (*4*) has also estimated palladium coulometrically by electrodeposition on a platinum electrode with sulfuric and hydrochloric acids as supporting electrolytes.

Clem and coworkers (*5,6*) found that azide ion strongly complexes with Pd(IV), lowering the formal potential of the Pd(IV)/Pd(II) couple to a region where this reaction could be utilized for the controlled-potential coulometric determination of palladium (*6*). For coulometric determinations at solid electrodes, reactions involving soluble products are usually preferred over electrodepositions, which present the possibility of interference by codeposition and problems in the removal of the deposit. Thus, since none of the proposed coulometric procedures suggested for palladium have been subjected to a thorough analytical characterization, and because the Pd(IV)/Pd(II) couple in azide medium appeared to be the most promising for further investigation, this reaction has been examined with the goal of developing a useful method.

This study was carried out using a new platinum-working-electrode cell assembly that was designed especially for ease of construction, moderate cost, uniformity of electrode potential, and a capability of solution deoxygenation by the gas overflow technique.

EXPERIMENTAL

Instrumentation. Circuit details and techniques of the operation of the instrumentation for controlled-potential coulometry have been described previously (*7*). The integrator was calibrated electrically (*7*) and its readout voltages were measured with a Non-Linear Systems Model 484-A digital voltmeter. Current-time curves were obtained by the use of a Pacific Measurements Model 1002 logarithmic converter and an Electro Instruments Model 400 X-Y recorder. Current signals to the logarithmic converter were filtered with a 1-Hz active filter.

Electrolysis Cell. The cell used in this work was designed for general application in coulometry with metal-gauze working electrodes, and is shown in Figure 1. The glass container is a Kontes Glass Co. No. K-333000-241, 50-mm-tall weighing bottle. A cylindrical cavity 3–4 mm deep was formed in the bottom of the cell by pressing a glassblower's $\frac{3}{8}$-in.-diam. graphite rod into the molten glass, and then carefully annealing the glass. This depression holds a $\frac{1}{2} \times \frac{3}{8}$-in.-diam. Bel-Art Cat No. F-37125, Teflon Spinfin.

The platinum working electrode was made from a 10.5- × 6.5-cm piece of 45-mesh gauze which was folded over in quarters,

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