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# Potentiometric Titration of Gold, Platinum, and Some Other Precious Metals

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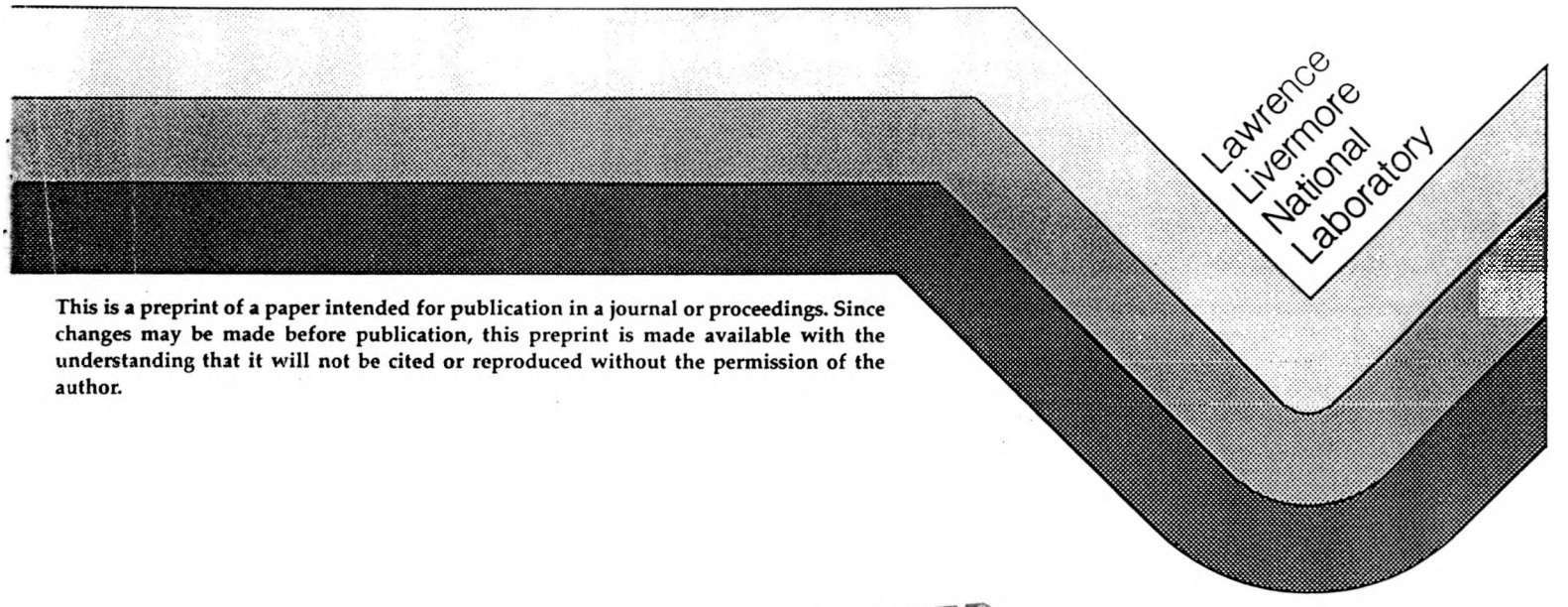

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# POTENTIOMETRIC TITRATION OF GOLD, PLATINUM, AND SOME OTHER PRECIOUS METALS

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## ABSTRACT

Gold, platinum, and several other platinum metals can be determined by titration with cetylpyridinium chloride (CPC). CPC forms a precipitate with $AuCl_4^-$ and $PtCl_6^{2-}$. Differentiation of $AuCl_4^-$ and $PtCl_6^{2-}$ with this titrant is not possible; however, their sum can be determined. Titration with tetraphenylarsonium chloride at pH 1 is selective for tetrachloroaurate, which thus can be determined in the presence of hexachloroplatinate. Hexachloroosmate(IV), tetrachloroplatinite(II), tetrachloropalladate(II), hexachloropalladate(IV), and hexachloroiridate(IV) can also be determined potentiometrically vs. CPC. The indicating electrode is prepared by coating a spectroscopic graphite rod with a solution of poly(vinyl chloride) (PVC) and dioctylphthalate (DOP) in tetrahydrofuran (THF).

Gold in gold cyanide plating baths and in potassium aurocyanide can be determined by potentiometric titration vs standard silver nitrate, using a silver ion-selective indicating electrode. The monovalent gold need not be converted to the trivalent state with aqua regia, resulting in a considerable saving of time and effort. Free cyanide and aurocyanide can be titrated sequentially by this method. Chloride does not interfere and can, in fact, also be sequentially determined.

## KEYWORDS

Precious metal analysis, gold, platinum, silver, titration, potentiometry, cetylpyridinium chloride, tetraphenylarsonium chloride.

## INTRODUCTION

A number of methods are available for the titrimetric determination of the precious metals. Willard and Smith (1) recommended tetraphenylarsonium chloride ($\Phi_4$AsCl) for the gravimetric determination of some large anions and complex halides. In 1968 Baczuk and DuBois (2) used $\Phi_4$AsCl for the potentiometric titration of perchlorate, using a perchlorate ion-selective electrode (ISE). We have found that quaternary ammonium halides (quats) can replace $\Phi_4$AsCl as the titrant in this and many other titrations (3). In earlier work we used cetyltrimethylammonium bromide (CETAB) as titrant (4). More recent work has shown that CPC is preferable because of its higher solubility in water, which makes it possible to use more concentrated titrant solutions, if desired (5). We have also replaced the commerial ISE's with inexpensive homemade plastic-coated graphite sensors (6). This work has previously been reviewed (7, 8).

## EXPERIMENTAL

The sensing electrodes were prepared from graphite rods (Spectroscopic graphite, EF-4S, Ultra Carbon Corp., Bay City, MI), 6" long and 1/4" in diameter. They were purchased in 12" length. Other grades of graphite will serve equally well, and the diameter is not critical.

The coating solution was prepared by dissolving 1 g of low molecular weight PVC and 1 g of DOP in 30 ml of THF in an Erlenmeyer flask, applying heat, and occasionally shaking to promote solution. The graphite rods were dipped for a few secs to a depth of about 1/2" into the cooled coating solution and air-dried. The coating process is repeated 3-5 times. The cost of the coating solution is less than 1 cent per electrode; one batch will coat many electrodes and will keep indefinitely in a stoppered glass vessel.

When the coating deteriorates, as indicated by decreasing and/or less steep endpoint breaks, it can be entirely removed with hot THF. The graphite rod can then be recoated and reused.

Any convenient reference electrode can be used in conjunction with the sensor. We have used a plastic, double-junction Ag/AgCl electrode with a 0.1 M sodium nitrate salt bridge. The electrodes are connected to the measuring instrument which can be any convenient pH/millivolt meter. The coated graphite sensor is connected to the meter my means of an alligator clip.

Because we like to work on the microscale, our titrants were 0.01 M CPC (prepared from the monohydrate) and silver nitrate. The primary standards were gold solutions prepared from Widberg gold wire of ≥99.995% purity and platinum solutions prepared from high-purity wire. For less exacting work atomic absorption standards (usually containing 1 mg/ml of the metal) are sufficient.

## RESULTS AND DISCUSSION: TITRATION OF TRIVALENT GOLD, PLATINUM, AND SOME OTHER PRECIOUS METALS

Simple titrimetric methods were required in our laboratory for the analysis of mg amounts of platinum or gold in highly acid solution. We routinely employ controlled-potential coulometry for the determination of gold and silver in this range (9, 10), but there is no comparable method for platinum. According to Beamish and Van Loon (11) there is a marked deficiency of acceptable volumetric methods for most of the platinum metals.

Quats were used by us previously to determine a large variety of inorganic and organic anions. This work has been summarized in reviews ( 7, 8). Although many different quats can be used as titrants, CPC is our reagent of choice.

The analytical reactions for Au(III) and Pt(IV) are shown in equations (1) and (2):

$$C_{21}H_{38}N^+ + AuCl_4^- \longrightarrow (C_{21}H_{38}N)AuCl_4\ (s) \qquad (1)$$

$$2C_{21}H_{38}N^+ + PtCl_6^{2-} \longrightarrow (C_{21}H_{38}N)_2PtCl_6\ (s) \qquad (2)$$

where $C_{21}H_{38}N^+$ is the cetylpyridinium cation.

The titrant was standardized vs the primary gold solution. The mean normality was 0.01022, with a standard deviation of 0.00002 for 9 replicates. A typical titration curve is shown in Fig. 1. Statistics for the recoveries of 1 to 10 mg of Pt(IV) are shown in Table 1. The mean recovery over the entire range was 100.16% with a pooled standard deviation of 0.34% for 36 replicates. While CPC does not differentiate between Au(III) and Pt(IV), experiments indicated that their sum can be accurately determined with a mean recovery of 99.9%.

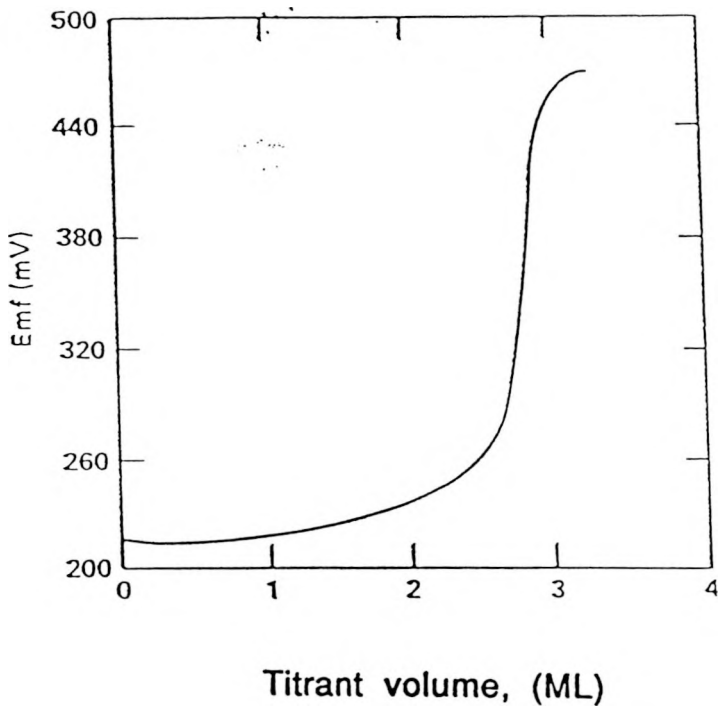


Fig. 1 Titration of 0.025 mmol of $AuCL_4^-$ vs. 0.01 M CPC at pH 0.5

Table 1

Statistics for the Recovery of Platinum as $K_2PtCl_6$ (99.9%)

| Taken, mg Pt | Recovered, mg Pt | Recovered, % | Number of replicates (standard deviation) |
|---|---|---|---|
| 0.969 | 0.985 (0.005) | 101.69 (0.52) | 7 |
| 2.422 | 2.422 (0.007) | 99.99 (0.29 | 7 |
| 3.875 | 3.846 (0.004) | 99.26 (0.10) | 5 |
| 4.843 | 4.855 (0.035) | 100.25 (0.74) | 6 |
| 7.265 | 7.273 (0.014) | 100.11 (0.19) | 6 |
| 9.687 | 9.602 (0.010) | 99.12 (0.11) | 5 |

Willard and Smith (1) have discussed the use of $\Phi_4AsCl$ for the gravimetric determination of various anions. The halide complexes of Au(III) and Pt(IV) are also precipitated by this reagent. Baczuk and DuBois (2) first used tetraphenylarsonium chloride as titrant for perchlorate, monitoring the titration with a perchlorate ISE. We found that with our electrode system at a pH near 1, $\Phi_4AsCl$ reacts stoichiometrically with Au(III) according to equation (3):

$$(C_6H_5)_4As^+ + AuCl_4^- \longrightarrow [(C_6H_5)_4As]AuCl_4\ (s) \qquad (3)$$

but it does not react with Pt(IV). In solutions containing both ions, only Au(III) is titrated. This makes the titration of Au(III) and Pt(IV) in the same solution feasible: The sum of the 2 ions is determined by titration vs CPC, while Au(III) alone is determined by titration vs tetraphenylarsonium chloride in another aliquot, and the amount of Pt(IV) is calculated by difference.

Table 2 lists the optimum pH, feasible pH ranges, and quality of the titration curves (as judged from their magnitude and steepness) for $AuCl_4^-$ and $PtCl_6^{2-}$ as well as of some other precious metal chlorides.

Some comments on the results follow:

(1) Precious metal bromides yield compounds less soluble than the chlorides and thus the endpoint breaks will probably be larger and sharper.

(2) Aqueous solutions of divalent platinum, $PtCl_4^{2-}$, were unstable; the volumes of CPC required for consecutive aliquots of the same solution decreased continuously. In 10% HCl, however, reproducible recoveries were obtained.

(3) No analytically useful results were obtained for $IrCl_6^{3-}$ and tetrachlororuthenate. The titration curves were small and quite shallow. Hexachlororhodate(III) solutions were unstable both in aqueous solution and dilute HCl and could not be analyzed by our method.

(4) $OsCl_6^{2-}$, $PtCl_6^{2-}$, $IrCl_6^{2-}$, and $PdCl_6^{2-}$ yielded good titration curves.

(5) While $PdCl_6^{2-}$ could be satisfactorily titrated vs CPC, the resulting precipitate was of the same elemental composition as that for $PdCl_4^{2-}$. This was confirmed by X-ray diffraction patterns for the precipitate. It seems that

Table 2

Summary of Conditions and Results for Various Precious Metal Chlorides vs CPC

| Ion determined | Optimum pH-range | Feasible pH-range | Quality of titration curve | Remarks |
|---|---|---|---|---|
| $AuCl_4^-$ | 0.5 – 1 | <0 – 5 | very good | at pH <2 curve has 2 inflections |
| $PtCl_6^{2-}$ | 0.5 | <0 – 2 | very good | at pH <2 curve has 2 inflections |
| $PtCl_4^{2-}$ | 1.15 | | very good | at pH <2 curve has 2 inflections |
| $PdCl_4^{2-}$ | 1 – 2 | 0.65 – 4.1 | very good | |
| $PdCl_6^{2-}$ | 0.5 – 1 | 0.15 – 4.1 | good | ppt. reduced to $Pd^{2+}$ |
| $OsCl_6^{2-}$ | 0.5 – 1 | 0 – 6.3 | very good | |
| $IrCl_6^{3-}$ | 5.5 – 8 | 1.8 – 10 | very good | not analytically useful, breaks too shallow |
| $IrCl_6^{2-}$ | 3 – 7 | 0.8 – 7 | very good | |
| $Ru_2Cl_{10}^{4-}$ | 1.7 – 2.4 | | poor | not analytically useful, breaks too shallow |
| $Ru_2Cl_6^{3-}$ | 1.8 – 2.1 | | fair | not analytically useful, breaks too shallow |

during the titration the tetravalent Pd is reduced to the more stable divalent state.

Some of the cetylpyridinium salts, as well as the tetraphenylarsonium salt of $AuCl_4^-$, were isolated by filtration, washing with water, and air-drying. The Ir salts could not be isolated by filtration. C, H, and N analysis for the recovered precipitates agreed well with the calculated values, confirming our postulated stoichiometry.

$PdCl_4^{2-}$ and $PtCl_4^{2-}$ at their optimum pH-values for titration vs CPC did not form precipitates with tetraphenylarsonium chloride. It is, therefore, likely that $AuCl_4^-$ can be determined in their presence.

Attempts to determine $KAu(CN)_2$ by titration vs CPC failed: very poor titration curves were obtained even in the presence of excess of cyanide. The titration of this material vs silver nitrate is discussed below. If titration of gold vs CPC is desired, it must first be converted to the trivalent state by heating with aqua regia. Platinum cyanide, however, could be titrated vs CPC in the presence of excess of cyanide according to the following equations:

$$Pt(CN)_2 + 2CN^- \longrightarrow Pt(CN)_4^{2-} \qquad (4)$$

$$Pt(CN)_4^{2-} + 2C_{21}H_{38}N^+ \longrightarrow (C_{21}H_{38}N)_2Pt(CN)_4\ (s) \qquad (5)$$

A 150-fold excess of cyanide yielded the best titration curves.

Any cation capable of forming a chloride complex is expected to interfere in the titration of precious metal halides vs CPC, but for single-component solutions, the titrant is quite useful.

## TITRATION OF MONOVALENT GOLD

The assay of gold in so-called gold cyanide, actually aurocyanide, $Au(CN)_2^-$, is usually required in plating baths as well as in the salt prior to the preparation of solutions. The methods given for aurocyanide in gold plating solutions in the Electroplaters Process Control Handbook (12) are based either on the reduction of trivalent gold with iodide or on a similar reduction with sulfur dioxide. Both methods require conversion of monovalent to trivalent gold by means of aqua regia. This is a time-consuming process requiring handling of

corrosive acids and operations in a hood. Another technique, controlled-potential coulometry , has been used in our Laboratory for many years as the primary assay technique for plating solutions (9, 10). This technique also requires conversion of gold to the trivalent state.

The sparingly soluble silver salt of the aurocyanide cation, prepared according to equation (6),

$$Ag^+ + Au(CN)_2^- \longrightarrow Ag[Au(CN)_2]\,(s) \qquad (6)$$

has been known since 1925 (13). The reaction forming this salt has been first recommended by Frant (14) for the determination of aurocyanide. We have described the titration in detail (15). A typical titration curve for the titration of 0.025 mmol of aurocyanide with 0.01 M of silver nitrate is shown in Fig. 2. An aqueous solution of potassium aurocyanide has an approximate pH of 6.6. The titration is also feasible in nitric acid solutions down to a pH of 1.25. The aurocyanide complex is quite stable in acid solution; the log of the stability constant is 38.3 (16).

Cyanide can also be determined by titration with silver nitrate (17). The reactions are as follows:

$$Ag^+ + 2CN^- \longrightarrow Ag(CN)_2^- \qquad (7)$$

$$Ag^+ + Ag(CN)_2^- \longrightarrow Ag[Ag(CN)_2] = 2AgCN\,(s) \qquad (8)$$

Reaction (7) yields a soluble complex and a steep titration break while reaction (8) yields a fairly shallow endpoint break and a precipitate. A typical titration curve is shown in the original publication (17). When both free cyanide and aurocyanide are present in solution, the first break upon titration with silver nitrate is due to reaction (7), while the second endpoint break is due to the sum of reactions (6) plus (8).

When both free cyanide and aurocyanide are present, the results for aurocyanide are less accurate than when aurocyanide alone is present, probably because of coprecipitation of AgCN and $Ag[Au(CN)_2]$. The results for the assay of solid potassium aurocyanide as well as for some gold cyanide plating baths are shown in Table 3. The previously used controlled-potential coulometric method (9, 10) was compared with the new titrimetric method. In general, the standard deviations for the new method were lower than those for the controlled-potential coulometry, which is not surprising because the

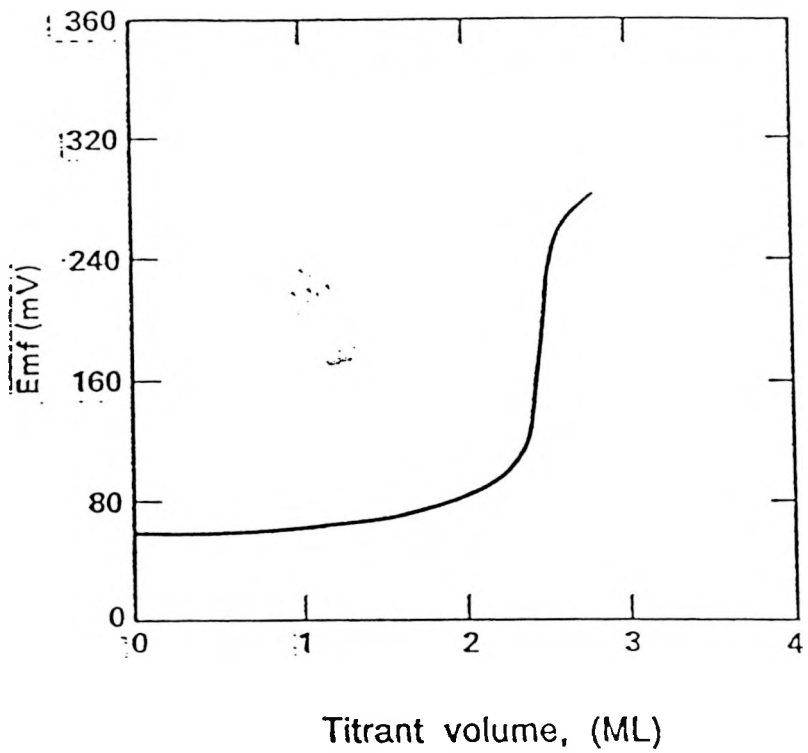


Fig. 2 Titration curve of approximately 5 mg of gold as $Au(CN)_2^-$ with 0.01 M silver nitrate

Table 3

Comparison of Analytical Results for Gold Salt and Plating Baths

| Sample | Units | Analysis by Coulometry Mean | n | % s | Analysis by Titration Mean | n | % s | means % relative | Analysis by Gravimetry Mean | n | % s |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Gold salt 5/84 | Percent. | 68.07 | 3 | 0.66 | 68.44 | 3 | 0.25 | +0.54 | | | |
| Gold salt 7/84 | Percent. | 67.76 | 3 | 0.47 | 68.15 | 1 | | +0.57 | | | |
| Gold salt 8/84 | Percent. | 67.25 | 3 | 0.36 | | | | | | | |
| Gold salt 9/84 | Percent. | 67.40 | 3 | 0.24 | 68.46 | 3 | 0.12 | +1.56 | 67.91 | 3 | 0.02 |
| Gold strike 7/84 | g/L | 1.386 | 3 | 0.07 | 1.44 | 6 | 0.7 | +3.9 | | | |
| Gold strike 8/84 | g/L | 2.396 | 3 | 0.13 | 2.45 | 4 | 0.9 | +2.3 | | | |
| Gold strike 9/84 | g/L | 2.369 | 3 | 0.29 | 2.36 | 5 | 1.5 | -0.4 | | | |
| Gold strike 10/84 | g/L | 2.328 | 3 | 0.30 | 2.28 | 6 | 0.4 | -1.2 | | | |
| Gold Plating 7/84 | g/L | 15.33 | 3 | 0.85 | 15.73 | 8 | 0.45 | +2.1 | | | |
| Gold Plating 9/84 | g/L | 14.23 | 3 | 0.15 | 14.54 | 7 | 0.14 | +2.1 | | | |
| Pinex plating | g/L | 11.20 | 3 | 0.10 | 11.33 | 6 | 0.51 | +1.2 | | | |

Note: n is number of discrete samples of original material taken. Each mean is the result of multiple measurements on that sample.

latter method requires an acid boil-down and treatment with aqua regia prior to measurement of the gold. This is probably the step that introduces most errors because of possible loss of gold. The coulometric measurement step itself is much more precise (9). Three samples of the salt were also assayed by a gravimetric method in which the gold was precipitated and weighed as the metal. Not surprisingly, the results were about midway between those obtained by controlled-potential coulometry and direct titration.

If desired, free cyanide can be masked or complexed by formaldehyde solution according to

$$HCN + HCNO \longrightarrow CNCH_2OH \qquad (9)$$

forming cyanohydrin. This reaction proceeds to completion at room temperature within 15 min and can be used to remove the effect of free cyanide in the titration of the cyanide complexes. Chloride, as well as other halides, are also determined commonly by titration with silver nitrate according to

$$Ag^+ + X^- \longrightarrow AgX(s) \qquad (10)$$

where X may be chloride, bromide, or iodide. Only chloride is of concern in cyanide plating baths. Aurocyanide and chloride in the same solution yield 2 endpoint breaks with silver nitrate, the first due to the aurocyanide, and the second due to the sum of aurocyanide plus chloride. Finally, aurocyanide, cyanide, and chloride can be estimated in the same solution, yielding 3 distinct endpoint breaks:

The first break is the cyanide break (equation 7), the second is the sum of cyanide plus aurocyanide (equations 6 plus 8), and the third is the total of all the ingredients titratable with silver nitrate. When the three anionic species are present together, the second break was found to be rather poor, not yielding accurate results.

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