

Coulometric Titration with Electrogenerated Tin(II). Titration of Platinum(IV)

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ima in the diffusion currents interfered with the measurements. Similar difficulties with solid and amalgamated electrodes have been reported (4, 5).

Current-Time Method. The application of cathodic stripping polarography to the determination of microgram quantities of chloride in standard solutions by the current-time technique was investigated. Chloride was deposited on a mercury microelectrode by applying a potential of +0.4 volt *vs.* S.C.E. for 15 minutes with stirring as before. A reduction potential of +0.15 volt *vs.* S.C.E. was then applied and the cathodic process was allowed to proceed for 3 minutes. The area under the recorded current-

time was determined by weighing the paper after cutting out the curve and the microcoulombs involved were calculated and then correlated with the concentration of chloride initially present.

The microcoulometric method appeared to be equivalent in precision to that obtained by measuring chloride by the current-potential scan method. However, because the latter technique is more convenient and more easily adapted to the analysis of samples, it was preferred.

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Coulometric Titration with Electrogenerated Tin(II) Titration of Platinum(IV)

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► A method is described for the coulometric titration of platinum(IV) with electrogenerated tin(II) in an acidic bromide medium. The platinum(IV) is reduced only to the II state by the tin(II). Back-titration with electrogenerated bromine, oxidizing platinum(II) to (IV), is also possible. From 2 to 13 mg. of platinum are titratable with an average error of ca. $\pm 0.5\%$ using potentiometric end point detection. Spectrophotometric observation of the titration indicated that PtCl_6^{-2} was reduced to PtCl_4^{-2} . Upon reoxidation, $\text{PtCl}_4\text{Br}_2^{-2}$ was formed. Spectrophotometric end point detection may also be employed. Of the platinum metals, palladium(II), rhodium(III), and iridium(IV) slightly interfere under the conditions of the titration.

RECENT studies (2, 3) have shown that tin(II) can be generated with 100% current efficiency at a gold cathode in a concentrated (3 to 4M) bromide solution of stannic chloride. By employing this electrogenerated tin(II), the coulometric titrations of iodine, bromine, gold(III), vanadium(V), and copper(II) (10) were successfully performed.

The present study extends the use of electrogenerated tin(II) to the titration of platinum(IV). A recent review (5) indicates the paucity of successful titrimetric methods for the determination of

platinum. Methods have been devised for the reduction of platinum(IV) with chlorocuprous ion, hydrazine, and ferrous iron, but the reductions were generally slow and usually involved back-titration with oxidants. Recently, during a study of the interferences in the coulometric titration of gold(III), Lingane (9) showed that platinum(IV) could be titrated coulometrically (albeit slowly) with electrogenerated chlorocuprous ion. Generation of an excess of chlorocuprous ion and back-titration with electrogenerated AuCl_2^- gave large positive errors, ascribed to the partial reduction of PtCl_4^{-2} to metallic platinum.

The present study demonstrates that platinum(IV) is reduced only to the II state by equivalent amounts of tin(II), and a successful titration may be performed by generating a slight excess of tin(II) and back-titrating with electrogenerated bromine, using either potentiometric or spectrophotometric end point detection.

EXPERIMENTAL

The titration cell, apparatus, and conditions for 100% current efficiency have been described (2). Potentiometric end point detection followed the usual practice (11).

Absorption curves were recorded with a Beckman recording spectrophotometer, Model DK-1 (Beckman Instruments, Inc., Fullerton, Calif.). Spec-

trophotometric titrations were performed in an apparatus similar to that of Sweet and Zehner (14), but having a 10-cm. silica absorption cell, equipped with inlet and outlet arms. A Beckman DU spectrophotometer was used for measuring absorbance during the titration.

The supporting electrolyte is 2 to 4M sodium bromide, 0.2M stannic chloride, and 0.3M hydrochloric acid. The current efficiency for reduction of tin(IV) is 99.5 to 99.9% with generating current densities of 10 to 84 ma. per sq. cm. at a gold generator electrode (2). A 1 × 1 cm. platinum generator anode was used for the generation of bromine. As with other titrations with tin(II), dissolved oxygen must be eliminated from the test solutions by passing nitrogen through the titration and auxiliary electrode chambers.

A standard platinum solution was prepared by dissolving pure platinum wire in aqua regia and evaporating several times with hydrochloric acid to remove oxides of nitrogen.

PERFORMANCE DATA

The general characteristics of a potentiometric titration curve for the reduction of platinum(IV) with tin(II), and the back-titration, oxidation of platinum(II) with bromine, are shown in Figure 1. Reduction of platinum(IV) proceeds only to the II state upon titration with tin(II), even upon addition of a four or fivefold excess of stannous ion.

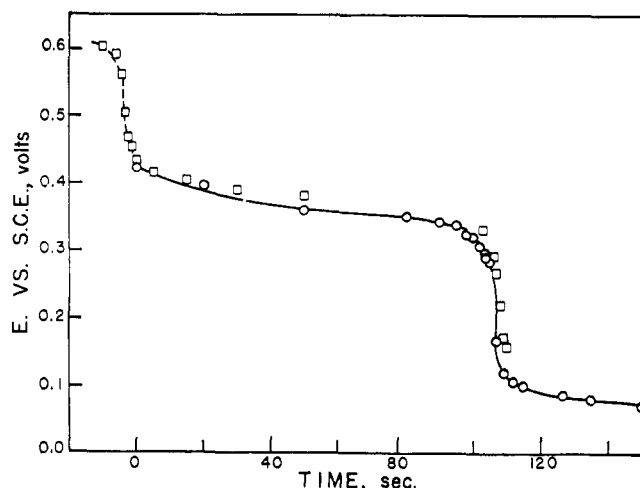


Figure 1. Titration of 5.256 mg. of platinum(IV) in 90 ml. of 4M sodium bromide, 0.2M stannic chloride, and 0.3M hydrochloric acid, with a generating current of 48.32 ma.

Potential of platinum indicator electrode measured vs. S.C.E. with pH meter

- Titration of platinum(IV) with tin(II)
- Back-titration of platinum(II) with bromine

Table I. Coulometric Titration of Platinum(IV)

No. of Trials	Current, Ma.	Platinum, Mg.		Av. Dev., Mg.
		Taken	Found (av.)	
5	19.32	2.624	2.638	0.010
3	19.32	2.624	2.614	0.002
3	48.32	5.256	5.302	0.020
2	96.70	13.14	13.14	0.01
2	9.660	2.624 ^a	2.610	0.002
2	19.32	2.624 ^a	2.647	0.002
2	19.71	2.624 ^b	2.657	0.006
2	20.10	2.624 ^c	2.675	0.002
1	20.03	2.624 ^d	2.694	
1	37.56	5.256 ^d	5.341	
1	68.84	10.52 ^d	10.67	

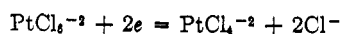
^a 2.01 mg. palladium(II) added.

^b 1.38 mg. rhodium(III) added.

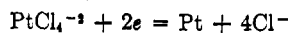
^c 1.91 mg. iridium(IV) added, solution boiled 15 minutes before titration.

^d 1.00 mg. palladium(II), 2.06 mg. rhodium(III), and 1.91 iridium(IV) added, solution boiled 15 minutes before titration.

Because the potentials of the platinum couples involved are (8):



$$E^\circ = +0.44 \text{ volt vs. S.C.E.}$$



$$E^\circ = +0.51 \text{ volt vs. S.C.E.}$$

reduction of platinum(II) to the zero oxidation state should take place as completely as reduction to the II state. That it does not probably reflects a very slow reaction between platinum(II) and stannous ion. Lingane (9) noticed similar behavior in the reduction of platinum with chlorocuprous ion in a chloride medium. In the well-known spectrophotometric method for the determination of platinum, involving the formation of a platinum-tin-chloride

complex (1), platinum appears to be reduced to the zero oxidation state by tin(II) (12). This reduction might be due to the chloride medium, which thermodynamically favors reduction of platinum(II) and makes tin(II) a stronger reductant, and the very large excess of stannous chloride (50- to 300-fold) employed.

Figure 1 also illustrates the titration of platinum(II) with bromine. This reaction is somewhat slower than the

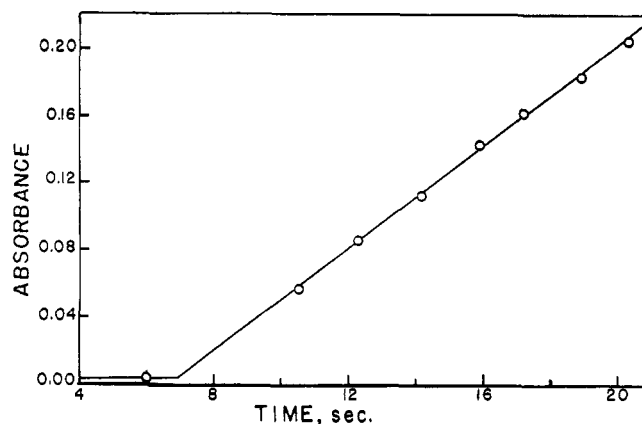


Figure 3. Spectrophotometric titration of 2.624 mg. of platinum(IV) in 135 ml. of 4M sodium bromide, 0.2M stannic chloride, and 0.3M hydrochloric acid with generating current of 19.32 ma.

Curve shows generation of bromine after generation of 150.4 seconds of tin(II). Absorbance measured against platinum-free supporting electrolyte at 400 m μ . Silica absorption cell with 10-cm. light path and 0.51-mm. slit width employed

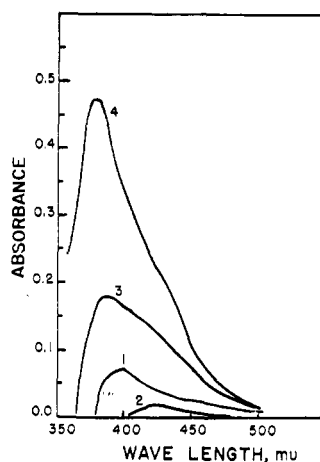


Figure 2. Absorption spectra during titration of 5.256 mg. of platinum(IV) in 105 ml. of 4M sodium bromide, 0.2M stannic chloride, and 0.3M hydrochloric acid

1. Original solution
 2. Equivalence point
 - 3, 4. During back-titration with electrogenerated bromine, 30 and 60 seconds of bromine generated, respectively
- Generating current 37.39 ma. Silica absorption cell with a 1-cm. light path used. Absorption measured against supporting electrolyte alone

reduction reaction, especially towards the equivalence point, and is not as useful analytically.

The titration is most conveniently performed by generating a slight (5 to 10%) excess of tin(II), waiting 4 to 5 minutes, and back-titrating to the equivalence point, taken at 0.24 volt vs. S.C.E., with electrogenerated bromine.

During the titration of platinum(IV), the solution, initially pale yellow, changes to almost colorless upon reduction to platinum(II). During the back-titration, it becomes deep yellow. These color changes suggested the possibility of following the titration spectrophotometrically.

Figure 2 shows spectrophotometric absorption curves taken during a titration of platinum(IV) with tin(II), and the back-titration of platinum(II) with bromine. The absorption is much larger during the reoxidation, because the species being reduced by the tin(II) is different from the one being formed on reoxidation. The platinum species added to the solution, and the one which undergoes reduction, is PtCl_6^{-2} , which shows a weak absorption maximum at 400 m μ . This species is not rapidly converted to the more stable bromide complex in the supporting electrolyte medium, because the rate of exchange of the hexachloroplatinat(IV) complex with bromide ions is very slow (13). This species is reduced by the tin(II) to tetrachloroplatinite(II). Although the bromo-complexes of platinum(II) are more stable than the chloro-complexes, the rate of exchange of ligands in PtCl_4^{-2} is slow, and it is likely that little exchange of bromide for chloride takes place in the short time between the reduction of PtCl_6^{-2} and the reoxidation of PtCl_4^{-2} (4). Upon reoxidation the

species formed is probably $\text{PtCl}_4\text{Br}_2^{-2}$, which has a much stronger absorption maximum at 380 $\text{m}\mu$.

A typical spectrophotometric curve for the back-titration is shown in Figure 3. The initial absorbance of the solution used in this titration—i.e., of PtCl_6^{-2} —was only 0.104.

Table I summarizes data obtained in 24 titrations of 2.6 to 13.1 mg. of platinum using potentiometric end point detection. The average error for titrations of platinum alone was ca. $\pm 0.5\%$.

Interference of the other platinum metals was investigated. Neither palladium(II) nor rhodium(III) is reduced to any significant extent by tin(II) under the conditions of the titration. The potentials of the appropriate palladium and rhodium couples are such (δ) that reduction by tin(II) would be expected, and again failure of this reduction must be ascribed to a slow rate of reaction. At higher current densities the gold generator electrode gets slightly plated with palladium metal, owing to some direct electrode reduction of palladium(II), and slight positive errors result. This error can be minimized by low current densities, or regeneration

of the tin(II) before addition of the deaerated sample.

The bromide of the supporting electrolyte was oxidized by iridium(IV) to bromine, in agreement with the findings of Dwyer, McKenzie, and Nyholm (7). This bromine may be removed by boiling the acidified bromide solution containing the sample for about 15 minutes, before addition of stannic chloride. The solution is then cooled, stannic chloride is added, and the solution is titrated. This treatment was partially satisfactory, but still yielded high (1 to 2%) results, probably due to incompleteness of the iridium(IV)-bromide reaction.

Table I gives data for the titration of platinum in the presence of various amounts of palladium(II), rhodium(III), and iridium(IV).

Osmium and ruthenium in the higher oxidation states interfere, but are usually easily removed by volatilization.

Among the other metals commonly found associated with platinum, copper, iron, and gold interfere. Lead, mercury, and silver probably do not. In the presence of interfering metals the usual methods for the separation of the platinum metals (δ) must be employed.

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Polarographic Determination of Manganese in Gasoline Triethanolamine Complexes of Manganese(II) and (III) and Lead(II)

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► The triethanolamine complexes of manganese(II) and (III) and lead(II) have been studied polarographically, and their nature has been determined. A polarographic method for determining (methylcyclopentadienyl)manganese tricarbonyl and related compounds in gasoline has been developed. The organomanganese compounds are decomposed and the manganese is determined by measuring the diffusion current of the manganese(III)-triethanolamine complex in alkaline solution. The feasibility of determining tetraethyllead simultaneously has been investigated.

THE introduction of (methylcyclopentadienyl)manganese tricarbonyl as an antiknock compound for internal combustion engines (2) has necessitated the development in these laboratories of methods for the assay of organomanganese compounds and the determina-

tion of manganese in gasoline. This paper reports a procedure for the determination of manganese in gasoline which employs the equipment used for the polarographic determination of tetraethyllead. The manganese compound is decomposed by ultraviolet light and the manganese is extracted by refluxing with hydrochloric acid. The manganese is determined polarographically as the manganese(III)-triethanolamine complex. Tetraethyllead is decomposed and lead is extracted simultaneously with the manganese, and may be determined polarographically in an aliquot of the acid extract. The manganese(II) and (III) and lead(II) complexes with triethanolamine are characterized, and the formation of a manganese(III)-peroxide complex is confirmed (6).

REAGENTS AND APPARATUS

C. P. chemicals and distilled water were used to prepare all of the reagent

solutions. Triethanolamine (TEA) 98% (Matheson Coleman & Bell No. 2885) was used to develop the analytical procedure, although "regular" (80% minimum) triethanolamine is satisfactory for routine analyses. The triethanolamine can be dispensed conveniently from a 5-ml. hypodermic syringe fitted with a 13-gage needle.

Current-potential curves were recorded at $25.0^\circ \pm 0.1^\circ \text{C}$. using a Sargent Model XX Polarograph. A Hume-Harris saturated calomel reference electrode (S.C.E.) was used throughout, and all potentials are referred to the S.C.E.

PROCEDURE

Pipet a 50-ml. sample of gasoline containing 0.1 to 0.7 gram of manganese per gallon into an ASTM tetraethyllead extraction apparatus (1). Add 50 ml. of heavy petroleum distillate and 50 ml. of concentrated hydrochloric acid. Extract the gasoline as described in ASTM procedure D 526-56 (1). During the first stage of the extraction, irradiate